SupraMOFs: Supramolecular porous materials assembled from metal—nucleobase discrete entities
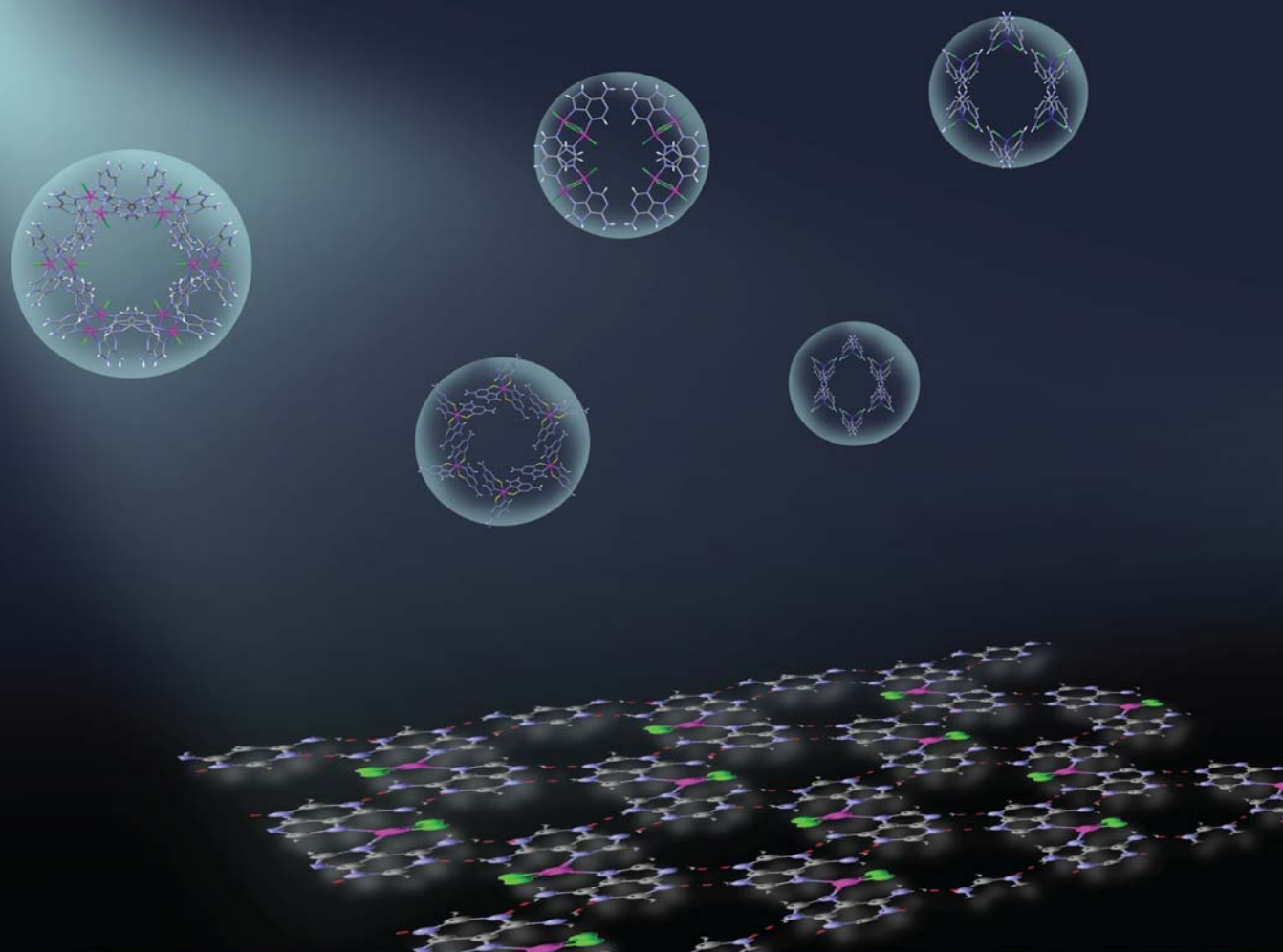

Jintha Thomas
July 2015

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SupraMOFs: Supramolecular porous materials assembled from metal–nucleobase discrete entities

A thesis submitted to the University of the Basque Country

in partial fulfilment of the requirements for the degree of

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Chemistry

by

JINTHA THOMAS

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Words of Gratitude.....

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To,

    My parents and brother

    My husband

    My children

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Chapter 1

Introduction

1.1   OVERVIEW OF CRYSTAL ENGINEERING

Historically, materials with appealing properties like mechanical, electrical, magnetic, thermal, optical, etc were discovered by serendipity and not because of a planned synthetic approach to achieve those properties. The development of crystal structure elucidation techniques at early 20th century arouse the interest of the scientific community in the correlation between the structural features and the properties of the materials, which, later on, sowed the seed of the pursuit for the general synthetic strategies to design materials with tuned functionalities, i.e. crystal engineering. Systematic crystal engineering was launched with Schmidt with his notable contributions in the 1950's and 1960's on solid state photochemical reactivity. [1] Although there is an earlier report by Pepinsky[2] wherein the term is actually mentioned for the first time, Schmidt[3] is usually credited with having introduced the term crystal engineering into the chemical literature with his works on topochemistry.

In spite of the large trail of time, crystal engineering did not reach its current importance until a handful of referential works were published in 1990´s, by outstanding authors such as Dunitz,[4] Desiraju,[5] Anthony,[6] etc. Dunitz in 1991, identified an organic crystal as a supramolecule par excellence.[4] The works of Desiraju focused on the transformation from a molecule to crystal as the key issue in crystal engineering.[5] He further defines crystal engineering as *'the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties'.*[7] In line with this, the modern crystal engineering follows the three principles as follows, (i) the study of intermolecular interactions; (ii) the study of packing modes in the context of these interactions with the aim of designing a strategy for crystal construction and (iii) the study of crystal properties.[8]

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[1] Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.
[2] Pepinsky, R. *Phys. Rev.* **1955**, *100*, 971.
[3] Schmidt, G. M. J.; Gerdhard, M. J. et al. *Solid State Photochemistry*, D. Ginsburg(ed), Verlag Chemie, Weinheim, 1976.
[4] Dunitz, J. D. *Pure Appl. Chem.* **1991**, *63*, 177.
[5] Desiraju, G. R. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311.
[6] Anthony, A. et al. *Cryst. Eng.* **1998**, *1*, 1.
[7] Desiraju, G. R. *Crystal Engineering: The design of organic solids*, Amsterdam: Elsevier, 1989.
[8] Desiraju, G. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 8342.

In crystal engineering, for the construction of solids with predetermined properties, not only the building blocks are important, but the way in which they are assembled too.[9] So crystal engineering is concerned with the construction of crystal structures or organic and metal–organic species, using design principles that are derived from an understanding of the intermolecular interactions that prevail in molecular solids.[7] Hence, the aims of crystal engineering are the understanding of intermolecular interactions and their application in the design of crystal structures with specific architectures and properties. Within a crystal, there exists medium range isotropic interactions, which are responsible for gross shapes and close packing effects while long range, isotropic interactions and those of electrostatic origin like hydrogen bonds account for all the fine effects and intermolecular orientations. In the case of metal organic systems, the metal–metal bonds and metal–ligand coordination bonds are to be considered.[10] So the understanding of the intermolecular interactions and coordination bonds has become very important in the control of molecular and ionic organization in the solid state.

Crystal engineering has grown to a very wide scope and the concepts of crystal engineering are applicable to any kind of intermolecular assembly, like a protein ligand recognition, system for drug delivery or the design of supramolecular polymers including MOFs.[11] In fact, one of the most active objective of crystal engineering is the design of new host systems in order to obtain nanoporous solids and this could be achieved by preventing the close packing, creating voids and thereby promoting inclusion of guest molecules.[6] These materials have become very important in the field of chemistry and material science due to their promising applications in catalysis,[12] energy storage,[13] sensing,[14] and separation.[15]

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[9] Rowsell, J. L. C. et al. *Micropor. Mesopor. Mat.* **2004**, *73*, 3.

[10] Desiraju, G. R. *J. Mol. Struct.* **2003**, *656*, 5.

[11] Desiraju, G. R. *J. Chem. Sci.* **2010**, *122*, 667.

[12] (a) Phann, A. et al. *Inorg. Chem.* **2011**, *50*, 7388. (b) Dhakshinamoorthy, A. et al. *Dalton Trans.* **2011**, *40*, 6344. (c) Corma, A. et al. *Chem. Rev.* **2010**, *110*, 4606. (d) Farrusseng, D. et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 7502. (e) Dhakshinamoorthy, A.; Garcia, H. *Chem. Soc. Rev.* **2014**, *43*, 5750. (f) Liu, J. et al. *Chem. Soc. Rev.* **2014**, *43*, 6011.

[13] (a) Zhao, D. et al. *Acc. Chem. Res.* **2011**, *44*, 123. (b) Murray, L. J. et al. *Chem. Soc. Rev.* **2009**, *38*, 1294. (c) Czaja, A. U. et al. *Chem. Soc. Rev.* **2009**, *38*, 1284. (d) Muller, U. et al. *J. Mater. Chem.* **2006**, *38*, 626. (e) He, Y. et al. *Chem. Soc. Rev.* **2014**, *43*, 5657.

1.2 POROUS MATERIALS BASED ON COORDINATION BONDS (METAL–ORGANIC FRAMEWORKS, MOFs)

Over the past few decades a vast number of solids that contain metal ions linked by molecular species have been indistinctly termed as coordination polymers, hybrid organic–inorganic materials and metal–organic frameworks. At this point, it is relevant to point out the difference between Coordination Polymers (CPs) and Metal–Organic Frameworks (MOFs). In 2013, the IUPAC published a series of recommendations to face the controversial use of terms in this area.[16] The term coordination polymers means an extended system of metal centers and ligands connected through coordination bonds, while for a solid to be named as metal–organic framework, it should be a coordination polymer with an open framework containing potential voids.[17]

The concept of crystal engineering based on coordination bonds, especially the case of metal–organic frameworks has aroused the interest of the scientific world for the last few decades because they are facile to prepare, aesthetically appealing and because of their inherent modularity, prototypal for a diverse range of structures that are amenable to crystal engineering design strategies.[18] In the new era of crystal engineering, the design and synthesis of coordination compounds has become apparently easy. The proper selection of the metal ions and ligands allow a rational design of the compounds with required or predetermined physical and chemical properties. For this purpose, it is important to have knowledge about the coordination geometries of the central metal ion and the coordination modes of the ligands.[19] The ligands may provide different modes of connectivity like, linear, angular, triangular, tetrahedral, etc (Figure 1.1).

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[14] (a) Chen, B. et al. *Acc. Chem. Res.* **2010**, *43*, 1115. (b) Liu, S. et al. *Inorg. Chem. Commun.* **2010**, *13*, 870. (c) Green, M. A. *Nat. Mater.* **2010**, *9*, 539. (d) Lan, A. et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 2334. (e) Hu, Z. et al. *Chem. Soc. Rev.* **2014**, *43*, 5815. (f) Falcaro, P. *Chem. Soc. Rev.* **2014**, *43*, 5513.

[15] (a) Basu, S. et. al. *J. Sep. Purif. Technol.* **2011**, *81*, 31.(b) Qiu, S.; Zhu, G. *Coord. Chem. Rev.* **2009**, *253*, 2891. (c) Manos, M. J. et al. *Angew. Chem. Intl. Ed.* **2005**, *44*, 3552. (d) Lee, H. et al. *Nature* **2003**, *425*, 385. (e) Czaja, A. U. et al. *Chem. Soc. Rev.* **2009**, *38*, 1284. (f) Barea, E. et al. *Chem. Soc. Rev.* **2014**, *43*, 5419. (g) Van de Voorde, B. et al. *Chem. Soc. Rev.* **2014**, *43*, 5766. (h) Qiu, S. et al. *Chem. Soc. Rev.* **2014**, *43*, 6116.

[16] Batten, S. R. et al. *Pure Appl. Chem.* **2013**, *85*, 1715.

[17] (a) Rowsell, J. L. C.; Yaghi, O. M. *Micropor. Mesopor. Mater.* **2004**, *73*, 3. (b) Corma, A. et al. *Chem. Rev.* **2010**, *110*, 4606. (c) Zhou, H.–C.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5415.

[18] Perry IV, J. J. *Chem. Soc. Rev.* **2009**, *38*, 1400.

[19] Pérez–Yáñez, S. *Doctoral Thesis*; Universidad del País Vasco/Euskal Herriko Unibertsitatea, 2012.
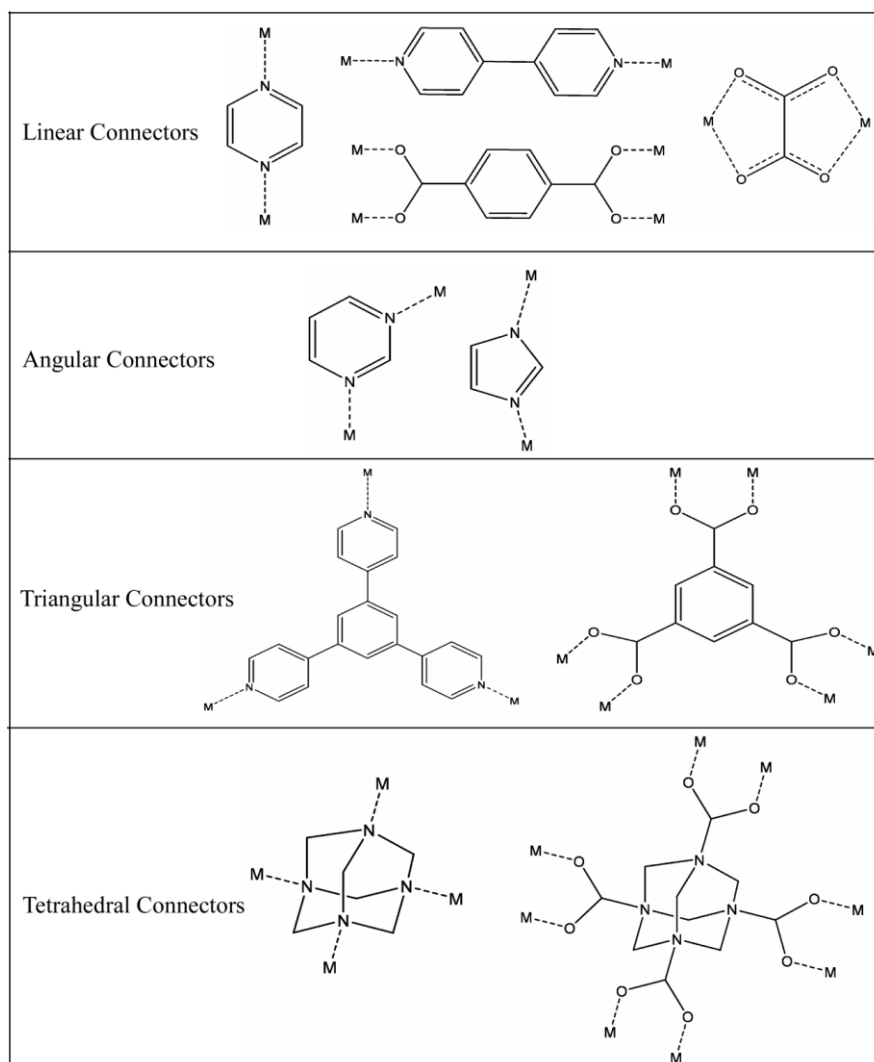
Figure 1.1: Examples of bridging ligands used as linkers in crystal engineering.

To make a coordination polymer, it is only necessary that a potentially bridging ligand reacts with a metal ion which has more than one vacant or labile site. Depending on the systems used, either infinite extended systems (polymers) or discrete closed structures can arise (Figure 1.2). For example, if divergent metal sites like mutually '*trans*' positions or all four sites of a tetrahedron are coordinated, extended polymers are formed.[20] The assembly between the metal centres and the ligands is mediated mainly through coordination bonds which determine the geometry, giving rise to a large variety of structurally diverse complexes ranging from discrete units to 1D, 2D and 3D extended systems.

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[20] James, S. L. *Chem. Soc. Rev*. **2003**, *32*, 276.
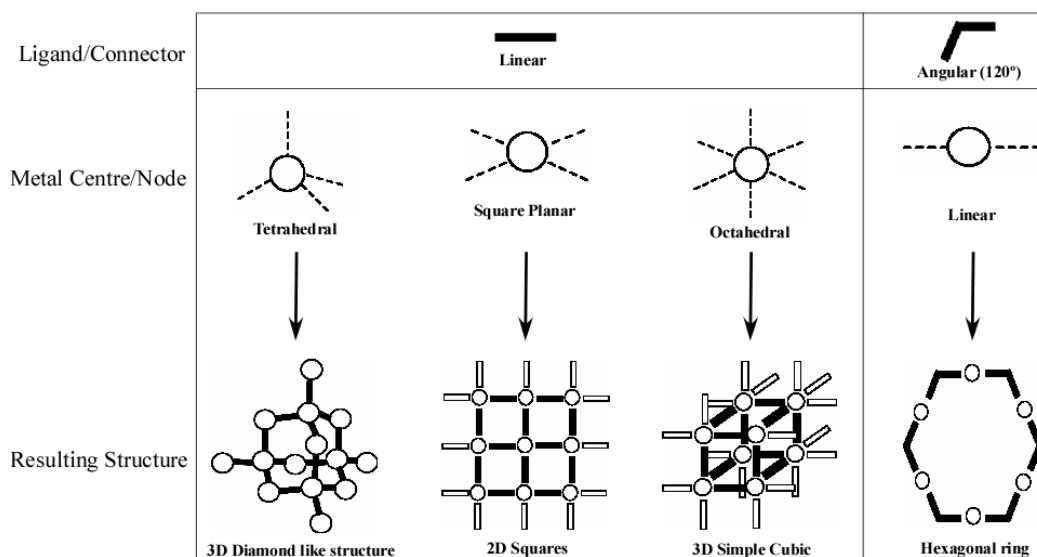
Figure 1.2: Different structural patterns determined by the combination of metal centres (nodes) and ligands (connectors).

In addition to this, the metal centres can be used as nodes with "exotic" geometries that differ from the usual coordination geometries, in cases where some coordination positions of the metal centre have been blocked (Figure 1.3).
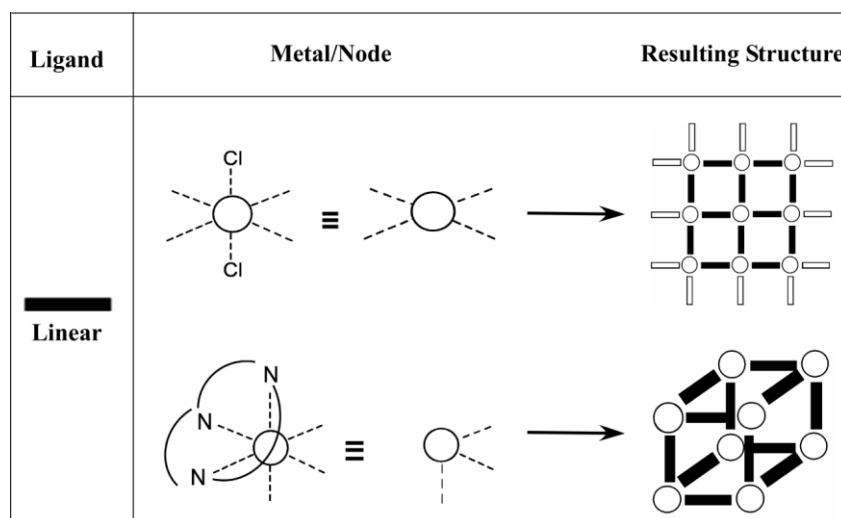
Figure 1.3: Different structures obtained using blocking ligands to create nodes with new geometries.

Yaghi and O'Keeffe expanded the node/connector design concept to exploit the concept of secondary building units (SBUs)[21] as molecular polygonal or polyhedral

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[21] Eddaoudi, M. et al. *Acc. Chem. Res.* **2001**, *34*, 319.

nodes, for the construction of the MOFs. They called this strategy reticular chemistry.[22] The SBUs are formed not only by the metal centers but also by the functional (coordinating) groups of the ligands.
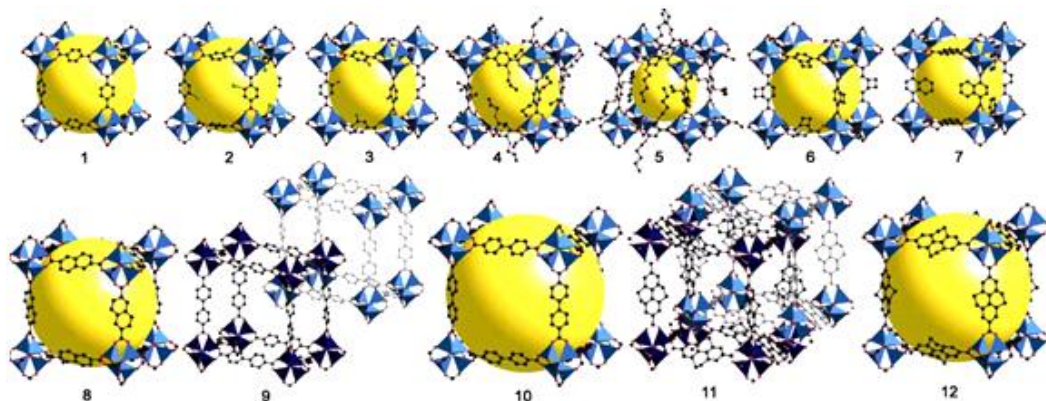
Figure 1.4: Examples of isoreticular MOFs based on Zn_4O clusters and ditopic linkers.[23]

The authors demonstrate how the topology of the framework can be rationalized and foretold by the geometrical features of the SBU and of the polytopic linker. Following this concept, a wide variety of diverse architectures with high structural stability have been prepared by connecting the SBUs with rigid organic linkers mediated through strong covalent bonds.[24] Figure 1.5 illustrates the structure of the compound $[Zn_4O(bdc)_3]_n$,[25] commonly known as IRMOF–1 or MOF–5, wherein the SBU is formed by four atoms of Zn with tetrahedral geometry, connected in the centre with the oxide O^{2-}, and six carboxylate bridging groups giving rise to an octahedral geometry. The connector here is benzene–1,4–diyl, which is a linear connector that connects the SBUs into a 3D cubic structure. The potential of this approach is better depicted in Figure 1.4, where maintaining $[Zn_4O(O_2C)_6]$ as the SBU and varying the length of the ditopic linker, a family of isoreticular MOFs (IRMOFs) can be designed, tuning easily the pore size, surface area and chemical functions. Some other examples of common SBUs are depicted in Figure 1.6.[18]

Another factor which affects the final product, to be considered is the synthesis conditions. The choice of solvents, their mixtures or synthesis without solvents,

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[22] Yaghi, O. M. et al. *Nature* **2003**, *423*, 705.
[23] Eddaoudi, M. et al. *Science* **2002**, *295*, 469.
[24] Reger, D. L. et al. *Inorg. Chem*. **2012**, *51*, 1068.
[25] Malik, M. A. et al. *Inorg. Chem.* **1995**, *34*, 6223.

controlling the pH, temperature, pressure, etc. are crucial in obtaining a specific end product from the same kind of building blocks.
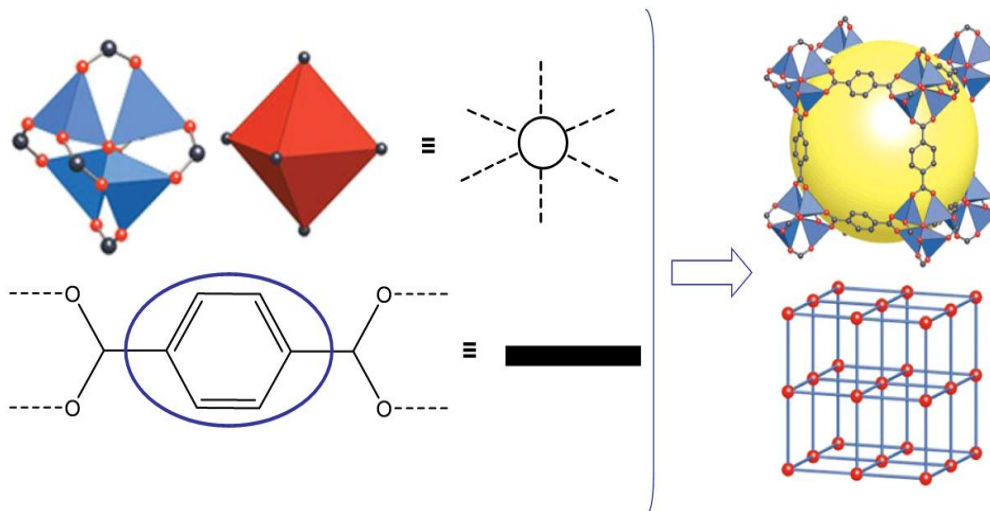
Figure 1.5: Structural breakdown of the compound $[Zn_4O(bdc)_3]_n$ (MOF–5, bdc: benzene–1,4–dicarboxylate).

Zn

Zn, Co, Be

Ru, Cu, Rh, Mo, Fe, Ni, Co, Re, Cr, Zn, Mn, W, Tc, Os, Cd, Bi, Rh/Bi, Pt, Al, Mg, In, Pd/Co, Pd/Mn, Pd/Zn

Fe, Cr, Ru, Mn, V, Ni, Sc, Co, Cr/Co, Ir, Al, Fe/Co, Fe/Zn, Cr/Fe/Ni, Zn, Ga, Fe/Ca

Cd, Zr, Hf, Nb
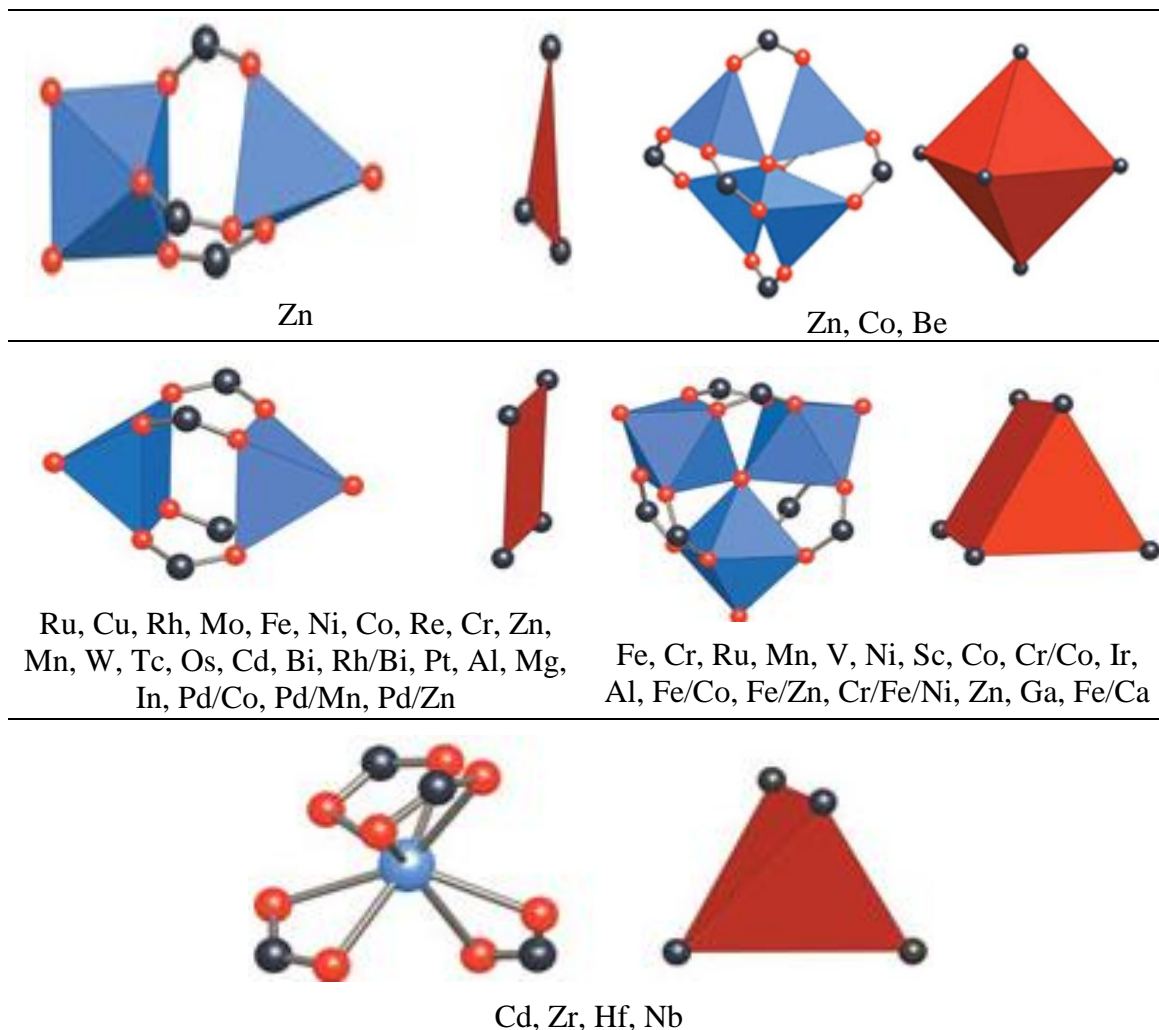
Figure 1.6: Examples of common SBUs.

Porosity is considered as the hallmark physical property of the metal–organic frameworks.[26] Nowadays, MOFs possess the highest surface areas ever reported.[27] The recently reported MOFs named as NU–109E and NU–110E exhibit the highest surface area ever reported, 7110 and 7140 m^2/g, respectively.[28] NU–110E consists of dicopper paddle–wheel SBUs connected by the BTTEI (BTTEI = 5,5′,5″–(((benzene–1,3,5–triyl–tris(ethyne–2,1–diyl))tris(benzene–4,1–diyl)tris(ethyne–2,1–diyl))triisophthalate) ligand with a solvent accessible volume of 93.0%.[29]

MOFs are well studied because of their structural beauty, diversity of properties, structural and functional tunability, and large number of applications.[30–31] Keeping this in mind, currently, researchers are focusing on developing MOFs with high surface areas,[32] high hydrogen storage capacity,[33] selective heterogeneous catalysis,[34] magnetic sorting,[35] channels capable of conducting polymerization,[36] selective capture of carbon dioxide,[37] host dependent luminescence,[38] proton conduction[39] and artificial photosynthesis and photo–catalysis.[40] Their crystalline nature, high and permanent porosity, uniform pore sizes, extraordinary surface areas, and finely tunable pore–surface properties have made these materials an attractive target for further study.[41]

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[26] An, J. et al. *Nat. Commun.* **2012**, *3*, 604.

[27] (a) Férey, G. et al. *Science* **2005**, *309*, 2040. (b) Koh, A. et al. *J. Am. Chem. Soc.* **2009**, *131*, 4184. (c) Farha, O. K. et al. *J. Am. Chem. Soc.* **2012**, *134*, 15016.

[28] Farha, O. K. et al. *J. Am. Chem. Soc.* **2012**, *134*, 15016.

[29] Zhang, M. et al. *CrystEngComm.* **2014**, *16*, 4069.

[30] Zhou, H.–C.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5415.

[31] (a) Chen, C.–T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293. (b) Janiak, C. *Dalton Trans.* **2003**, 2781. (c) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.

[32] (a) Murray, L. J. et al. *Chem. Soc. Rev.* **2009**, *38*, 1294. (b) Farha, O. K. et al. *J. Am. Chem. Soc.* **2012**, *134*, 15016. (c) Martin, R. L.; Haranczyk, M. *Chem. Sci.* **2013**, *4*, 1781.

[33] (a) Han, S. S. et al. *Chem. Soc. Rev.* **2009**, *38*, 1460. (b) Yang, J. et al. *Chem. Soc. Rev.* **2010**, 39, 656. (c) Goldsmith, J. et al. *Chem. Mater.* **2013**, *25*, 3373.

[34] (a) Lee, J. et al. *Chem. Soc. Rev.* **2009**, *38*, 1450. (b) Ma, L. et al. *Chem. Soc. Rev.* **2009**, *38*, 1248. (c) Dakshinamoorthy, A.; Garcia, H. *Chem. Soc. Rev.* **2014**, *43*, 5750. (d) Liu, J. et al. *Chem. Soc. Rev.* **2014**, *43*, 6011.

[35] Kurmoo, M. *Chem. Soc. Rev.* **2009**, *38*, 1353.

[36] Uemura, T. et al. *Chem. Soc. Rev.* **2009**, *38*, 1228.

[37] (a) Li, J.–R. et al. *Chem. Soc. Rev.* **2009**, *38*, 1477. (b) Düren, T. et al. *Chem. Soc. Rev.* **2009**, *38*, 1237. (c) Zhang, Z. J. et al. *Chem. Comm.* **2013**, *49*, 653.

[38] (a) Allendorf, M. D. et al. *Chem. Soc. Rev.* **2009**, *38*, 1330. (b) Hu, Z. et al. *Chem. Soc. Rev.* **2014**, *43*, 5815.

[39] (a) Yamada, T. et al. *Chem. Soc. Rev.* **2013**, *42*, 6655. (b) Yoon, M. et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 2688. (c) Ramaswamy, P. et al. *Chem. Soc. Rev.* **2014**, *43*, 5913. (d) Taylor, J. M. et al. *J. Am. Chem. Soc.* **2013**, *13*5, 1193.

[40] Zhang, T.; Lin, W. *Chem. Soc. Rev.* **2014**, *43*, 5982.

[41] Furukawa, H. et al. *Science* **2013**, *341*, 1230444.

Moreover, these easily modifiable materials were well studied and new methods has been developed to create novel porous flexible materials (breathing),[42] and MOF nanoparticles[43]. Likewise, simple synthetic strategies have been developed to produce these materials in industrial scale and thus boosting their potential impact in the market.[44,45,46,47]

1.3   SUPRAMOLECULAR CRYSTAL ENGINEERING

A crystal may be comprised of certain repetitive structural units with specific molecular functionalities responsible for the molecular recognition that defines specific interaction patterns between functional groups. These molecular functional groups could be associated with particular packing characteristics, being therefore the basic building units of a crystal structure and so are called as the *supramolecular synthons*. Supramolecular synthons are structural units within crystals that can be formed by known or conceivable synthetic operations.[5] The identification of synthons is crucial in the designing and analysis of a crystal. The Figure 1.7 lists some common examples of supramolecular synthons.

Supramolecular synthons are kinetically defined structural units that express the core features of the crystal structure and that encapsulate the essence of crystals in terms of molecular recognition. Synthons consist of molecular fragments and the supramolecular association between them is mediated through hydrogen bonds and other directional interactions. In effect, following the synthon theory, a supramolecular synthon can be considered as a reasonable approximation of the entire crystal and the synthon is the device through which information content passes from molecular structure to crystal structure.[11]

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[42] Zacher, D. et al. *Chem. Soc. Rev.* **2009**, *38*, 1418.
[43] Spokoyny, A. M. et al. *Chem. Soc. Rev.* **2009**, *38*, 1218.
[44] Czaja, A. U. et al. *Chem. Soc. Rev.* **2009**, *38*, 1284.
[45] Lanchas, M. et al. *Chem. Commun.* **2012**, *48*, 9930.
[46] Lanchas, M. et al. *RSC Adv*. **2014**, *4*, 60409.
[47] Lanchas, M. et al. *Inorg. Chem. Front.* **2015**, *2*, 425.
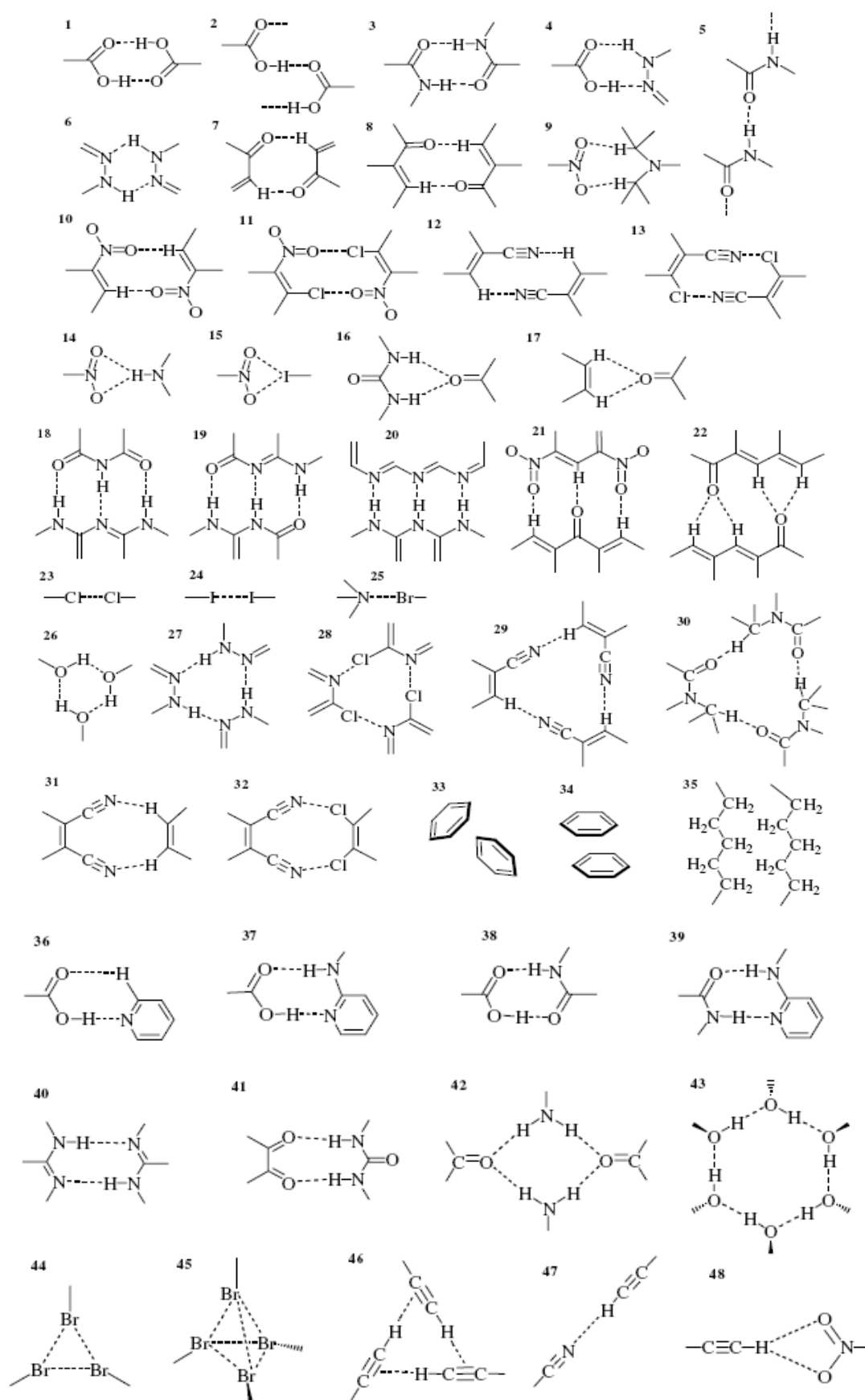
Figure 1.7: Examples of some common representative supramolecular synthons (taken from reference 5).

A detailed analysis of the intermolecular interactions in crystals permits the definition of supramolecular synthons as structural units that more realistically display the recognition process between molecules.[5] In simple examples like benzoic and terephthalic acids, structural patterns can be represented as networks with the molecules as nodes and the supramolecular synthons as node connections. Figure 1.8[10] depicts the structural rationalization from the molecular recognition of functional groups to the formation of supramolecular synthon and of the crystal structure using the examples of benzoic acid and terephthalic acid.
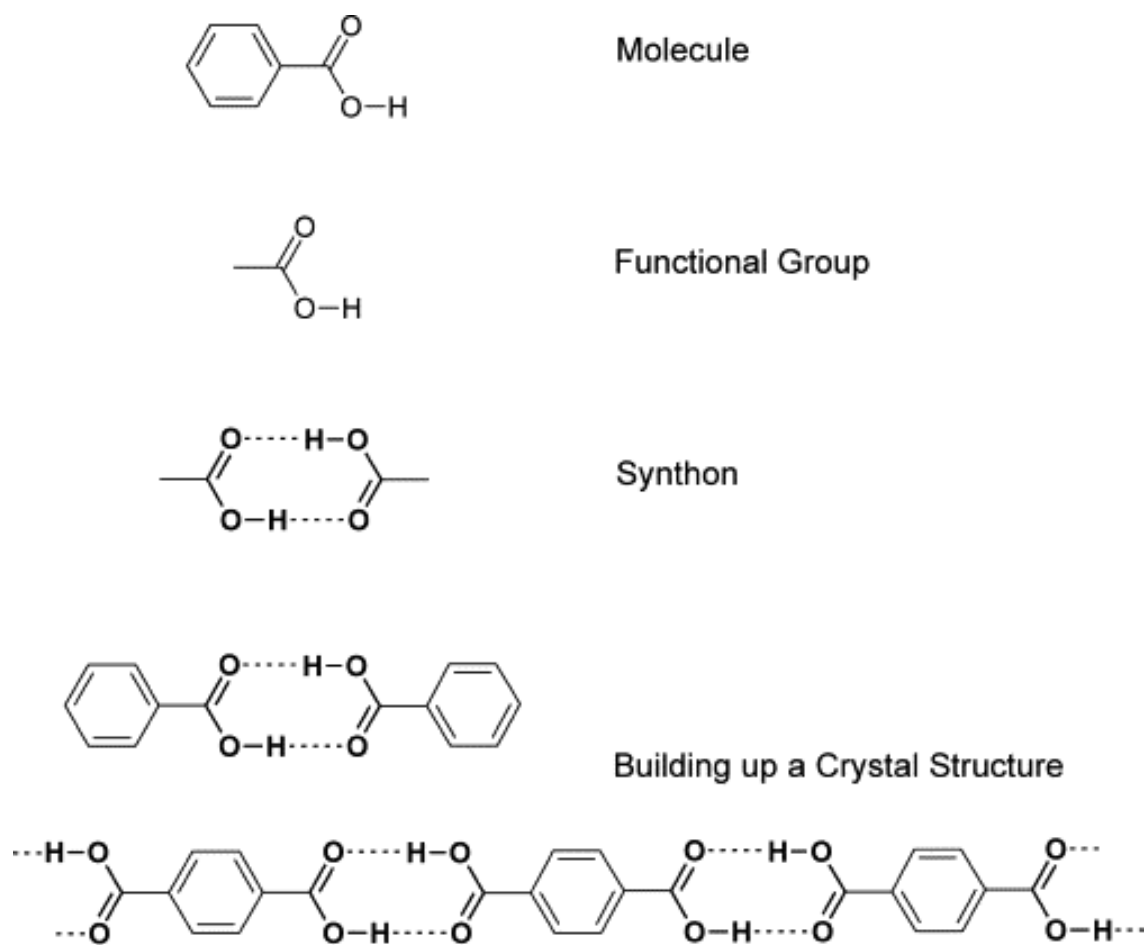
Figure 1.8: The self–assembly from molecule to crystal through supramolecular synthons.

The pioneering works of Etter and his group on the ability of hydrogen bonds to help control molecular crystalisation also revealed that, these hydrogen bonding motifs

are formed by many elementary functional groups frequently found in many simple molecules. [48] Wuest and coworkers named these special molecules, with multiple peripheral sites of strong directional interactions, that are set apart from molecules by their properties and their inherent suitability for engineering crystals[49] as '*tectons*',[50] which means '*builder*', that are active building units bearing recognition information and thus capable of recognizing each other. Figure 1.9 shows a schematic representation of the tecton–synthons concept together with an example of the supramolecular net of trimesic acid showing the hydrogen bonded synthons.
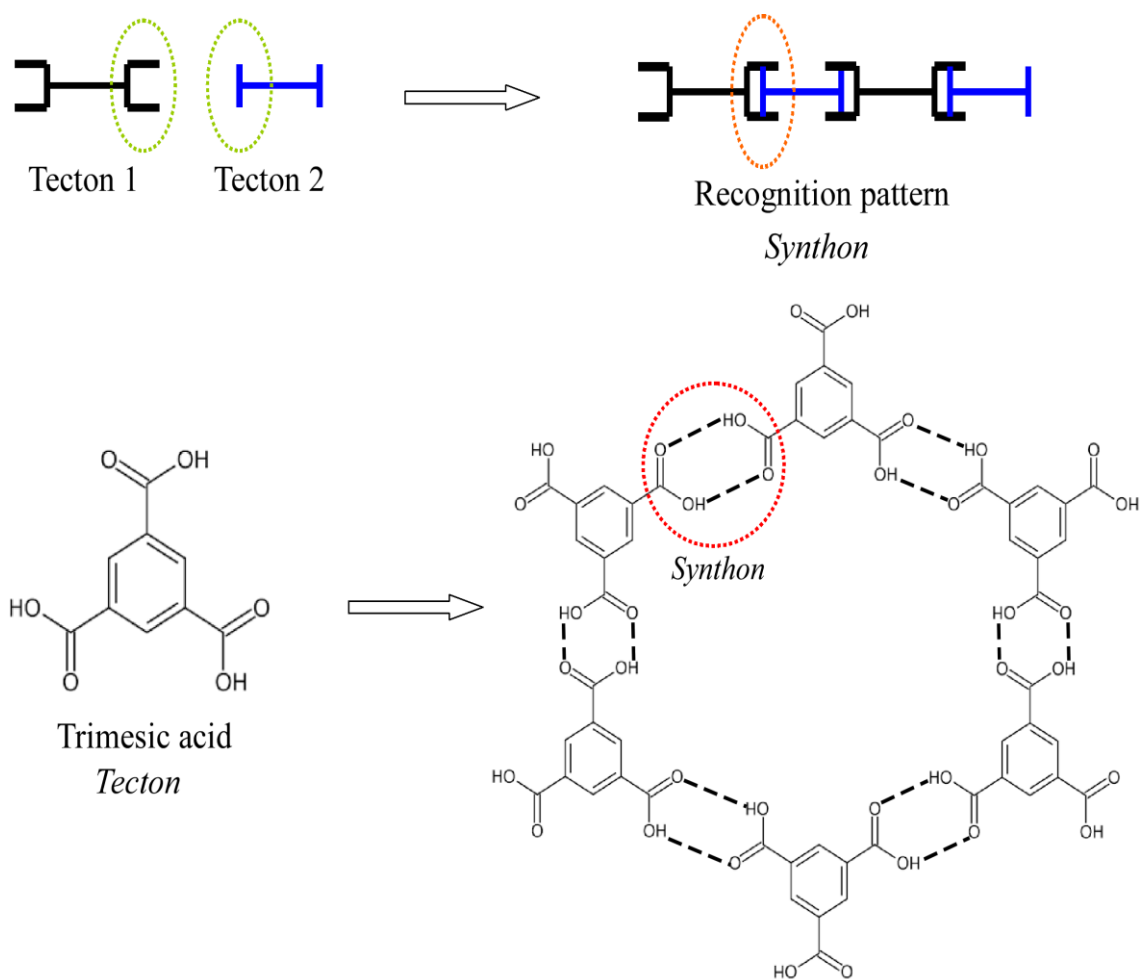
Figure 1.9: Scheme showing the "tecton–synthon" concept using trimesic acid as example.

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[48] (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (b) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

[49] Wuest, J. D. *Chem. Commun.* **2005**, 5830.

[50] Simard, M. et al. *J. Am. Chem. Soc.* **1991**, *113*, 4696.

In line with the principles of crystal engineering, the process of molecular recognition and the so formed repeating units of supramolecular synthons lead to the formation of supramolecular networks. Since supramolecular synthons are the basic building units of any supramolecular architecture, the suitable selection of the synthon with desirable properties permits the desirable tuning of the supramolecular array. So the designing of a crystal structure effectively becomes synthon design and it is possible only with the knowledge of the intermolecular interactions.[10] So crystal engineering can be well defined as the rational design of the functional molecular solids.[11]

Robustness is one of the important properties of the synthons and their identification facilitates the synthetic aspects of crystal engineering, resulting in high yield supramolecular synthesis.[51] For example, the robust carboxylic dimer synthons are normally used in crystal engineering.

A variety of noncovalent interactions like intermolecular interactions, van der Waals forces, π–π interactions, and other weak interactions were applied to molecular components to construct large entities called supramolecules. So, supramolecular chemistry is a broad field, owing to the myriad of diverse structures that can be formed using a variety of noncovalent intermolecular interactions. The examples include biologically relevant enzyme mimics, molecular devices including light harvesters, sensors, wires, rectifiers, liquid crystals, molecular flasks and many more.[52] Among these supramolecular interactions, hydrogen bonding is the most predominant organisational synthon in the design of supramolecular arrays due to its clearly defined, reproducible and transferable directional properties[53] and predictability.

Figure 1.10 gathers together some examples of supramolecular arrays held together through hydrogen bonded synthons between organic molecules. They include (a) the linear supramolecular chain formed from the self assembly of terephthalic acid, (b) the self–assembled supramolecular hexagonal ring of trimesic acid, (c) the hexagonal 2D network formed between cyanuric acid and melamine[54] and (d) a

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[51] Aakeroy, C. B. et al. *J. Am. Chem. Soc.* **2002**, *124*, 14425.
[52] Cook, T. R. et al. *Chem. Rev.* **2013**, *113*, 734.
[53] (a) Braga, D. et al. *Coord. Chem. Rev.* **2003**, *53*, 246. (b) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565.
[54] Ranganathan, A. et al. *J. Am. Chem. Soc.* **1999**, *121*, 1752.

supramolecular honeycomb grid of trimesate anions and secondary ammonium cations.[55]

(a) Supramolecular chain of terephthalic acid

(b) Supramolecular hexagonal ring of trimesic acid

(c) Supramolecular 2D network of melamine-cyanuric acid

TMA^{3-}: trimesate anion
(excess hydrogen bond acceptors)

secondary ammonium cation
(excess hydrogen bond donors)

(d) Supramolecular honeycomb grid of TMA^{3-} and secondary ammonium cations
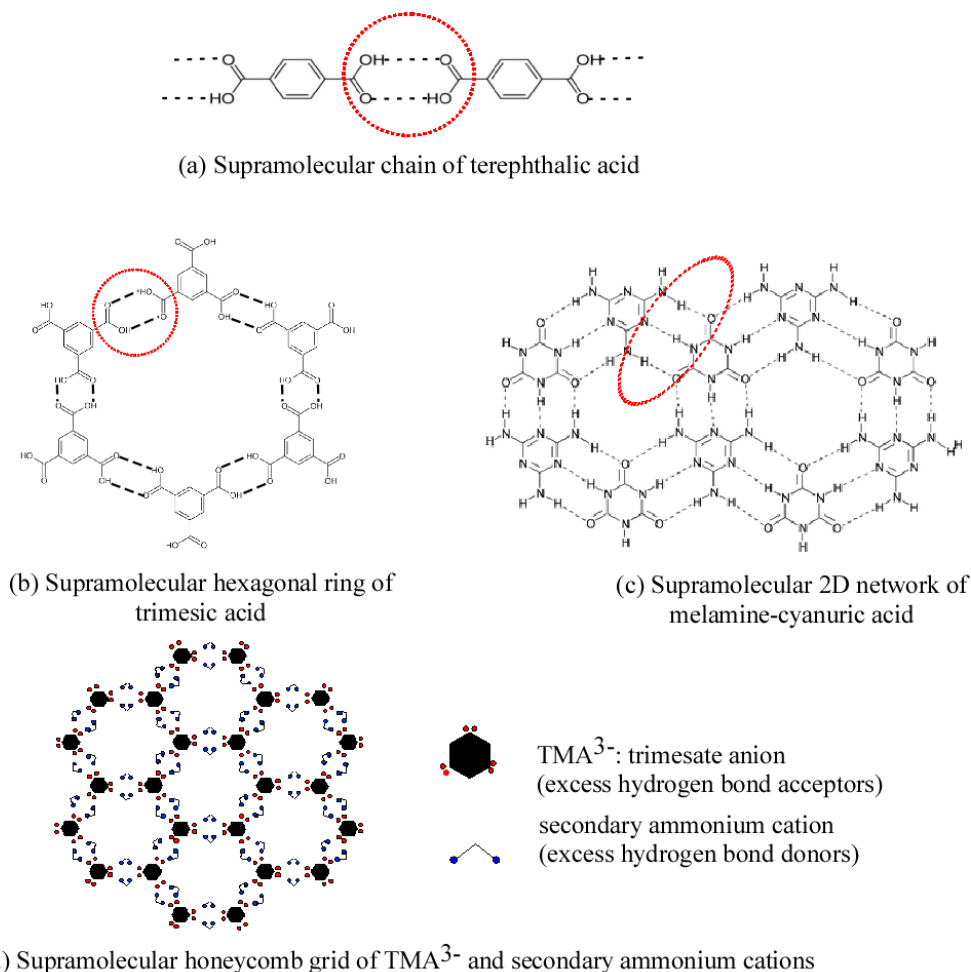
Figure 1.10: Examples of organic synthons formed through hydrogen bonding interaction. Hydrogen bonded synthons are highlighted within the circles.

In similarity to MOFs, Reger et al.[56] called a three dimensional structure of metal–organic discrete entities sustained by non–covalent interactions, as '*Supramolecular Metal–Organic Frameworks*' (*SMOFs*), where the building blocks are organized partially or completely by robust supramolecular interactions. They reported some examples of this type of compounds mainly based on the π–π stacking between π deficient 1,8–naphthalimide rings (Figure 1.11) which is not as directional as hydrogen

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[55] Melendez, R. E. et al. *Angew. Chem. Int. Engl.* **1996**, *35*, 2213.
[56] Reger, D. L. et al. *Inorg. Chem.* **2011**, *50*, 10225.

bonding. These compounds although presenting potential voids in their crystal structure, still do not have proved to present a permanent porosity.

<div align="center">(a)   (b)</div>
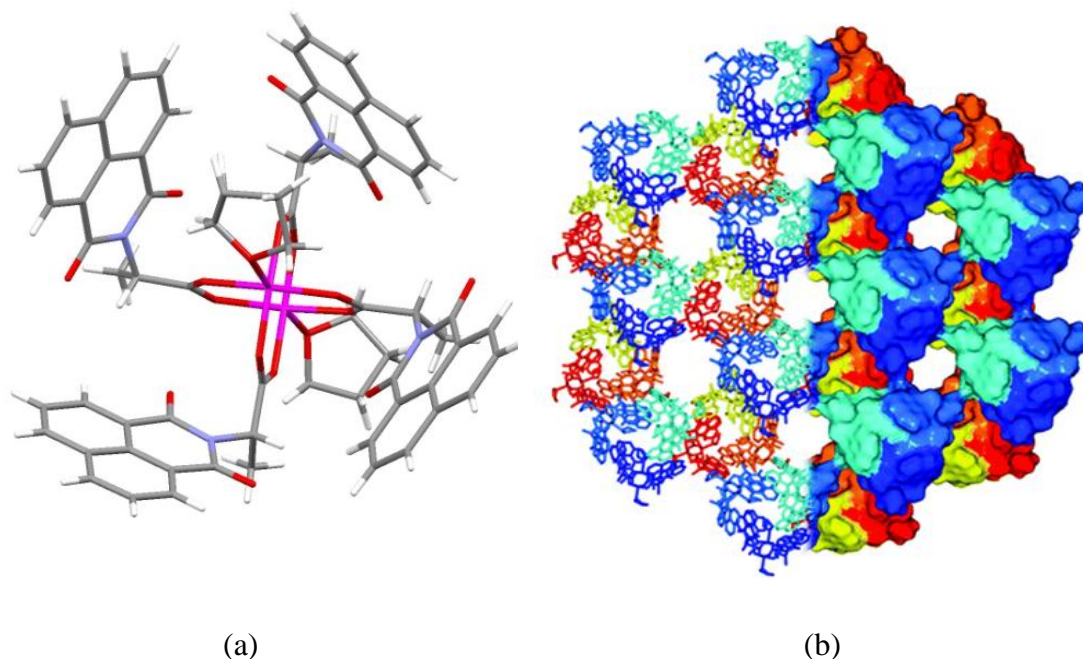
Figure 1.11: (a) The building unit of compound $[Cu_2((S)–2–(1,8–naphthalimido)$ propanoate$)_4(THF)_2]$; (b) The right section of the image represent the van der Waals surface of the structure sustained through $\pi–\pi$ interactions.

1.4 NUCLEOBASES AS COORDINATION BONDING LINKERS

Rosi et al. put forth many potential applications of MOFs like biological applications including drug delivery, intracellular imaging and many proposed applications may require them to be built from non–toxic building materials and that are biologically and environmentally compatible. [57] This can be achieved by using biomolecules as the building blocks to construct Metal–Biomolecule Frameworks (MBioFs), which are defined as MOFs constructed from at least one biomolecule which serves as an organic linker.

There are many advantages and applications that arise from the use of biomolecules as building blocks and some of them are mentioned below. Simple biomolecules, including amino acids, nucleobases, sugars and others are readily and naturally available in quantities and prices amenable to preparing bulk quantities of

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[57] Imaz, I. et al. *Chem. Commun.* **2011**, *47*, 7287.

materials. Another advantage is that biomolecules can lead to biologically compatible MOFs. Biomolecules are structurally diverse, they can be rigid or flexible and depending on that the functional nature of the MBioFs varies. Biomolecules can have different metal–binding sites and they can exhibit multiple possible coordination modes increasing the potential structural diversity of the MBioFs. Moreover, many biomolecules have intrinsic self–assembly properties which can be used to direct the structure and function of MBioFs. Finally, many chiral biomolecules can be used to construct chiral MBioFs, which may have interesting recognition, separation and catalytic properties. All these characteristics renders biomolecules particularly attractive building blocks for constructing MOFs with new properties and applications that cannot be accessed using the simple organic linkers traditionally used in MOF construction.

Among the bridging biomolecules, nucleobases appear as appealing alternatives since they provide a rigid molecular linker outfitted with many positions able to coordinate to metal centers and additionally are able to establish complementary hydrogen bonding–interactions.[58] Nucleobases or nitrogenous bases are biological molecules and are key constituents of the nucleic acids, DNA and RNA. The primary nucleobases are, adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U). In Figure 1.12, the nucleobases are classified into two groups, the purine bases (adenine and guanine) and the pyrimidine bases (thymine, cytosine and uracil). While adenine, guanine, cytosine and thymine are found in the DNA, uracil replaces thymine to form the RNA.

The greater heteroatom number of the purine nucleobases makes them better bridging ligands than the pyrimidinic ones, as it can be derived from the results for bridging puric (adenine: 63 hits, and guanine: 5 hits) and pyrimidinic (thymine: 2 hits, uracil: 17 hits, and cytosine: 15 hits) nucleobases found in the CSD database.[59] The low number of guanine bridged complexes is not due to an inappropriate geometry disposition of the coordination donor atoms but due to its great insolubility in common solvents.

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[58] Beobide, G. et al. *Coord. Chem. Rev.* **2013**, *257*, 2716.
[59] Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

PYRIMIDINES

Cytosine   Thymine   Uracil

PURINES

Adenine   Guanine
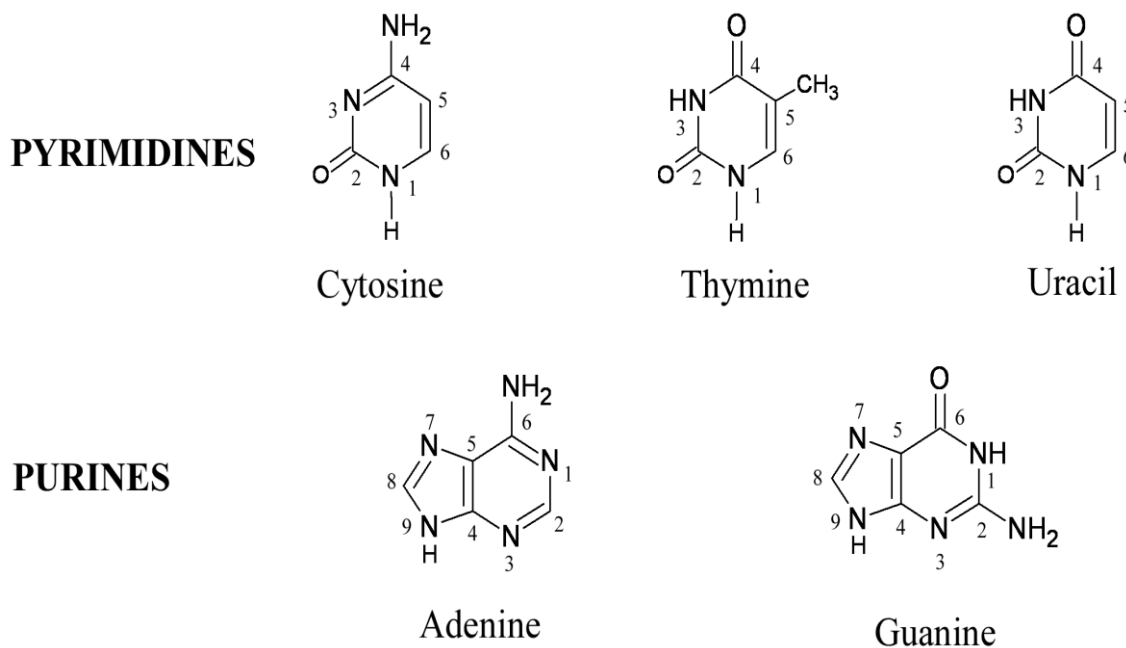
Figure 1.12: Structure and numbering pattern of the nucleobases.

For a long time, nucleobases were evaluated as suitable ligands for the construction of biomimetic compounds,[60] but recently there has been a substantial increase in their use as pillars for the building up of porous materials.[58] The first porous polymeric compound of this type was reported by our research group in 2004.[61] It consists of a 3D coordination polymer with formula $[Cu_4(\mu_3\text{–adeninato–}\kappa N3{:}\kappa N7{:}\kappa N9)_4(ox)_2(H_2O)_4]_n$ containing the adenine nucleobase as an anionic *N3,N7,N9*–bridging ligand. The deprotonation of the adenine in the reaction media promotes the polymerization of the framework by sequentially bridging $[Cu_2(\mu\text{–}adeninato)_4(H_2O)_2]$ paddle–wheel entities through $[Cu(ox)(H_2O)]$ units (Figure 1.13) The resulting structure contains one–dimensional (1D) tubular channels with a diameter of about 1.3 nm, that represent around a 40% of the total volume.

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[60] (a) Lippert, B. *Coord. Chem. Rev.* **2000**, *200–202*, 487. (b) Verma, S. et al. *Acc. Chem. Res.* **2010**, *43*, 79.
[61] García–Terán, J. P. et al. *Inorg. Chem.* **2004**, *43*, 4549.
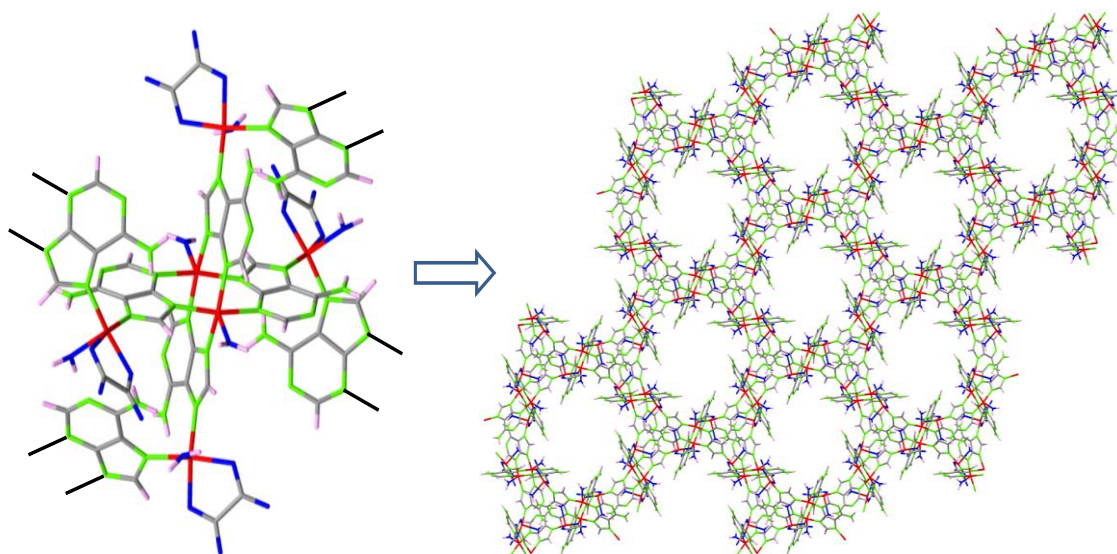
Figure 1.13: Crystal structure of $\{[Cu_2(\mu-adeninato)_4(H_2O)_2][Cu(ox)(H_2O)]_2\}_n$.

In 2009, Rosi et al. reported a compound with porous network of formula $(Me_2NH_2)_2[Zn_8(\mu_4-adeninato-\kappa N1:\kappa N3:\kappa N7:\kappa N9)_4(\mu-BPDC-\kappa O:\kappa O\prime)_4(\mu-BPDC-\kappa^2 O,O\prime:\kappa^2 O\prime\prime,O\prime\prime\prime)_2(\mu_4-O)]\cdot 8DMF\cdot 11H_2O$ (BPDC: biphenyldicarboxylate) obtained under solvothermal conditions at 130 ℃.[62] It consists of infinite zinc–adeninate columnar secondary building units (SBUs) composed of vertex–sharing zinc–adeninate octahedral cages (Figure 1.14a). The zinc–adeninate columns are interconnected via multiple BPDC linkers giving rise to an anionic network that allows the exchange of the cationic counterions. The authors proved that this compound was able to store and release cationic drug molecules. Later, in 2012, they published $(Me_2NH_2)_4[Zn_8(\mu_4-adeninato-\kappa N1:\kappa N3:\kappa N7:\kappa N9)_4(\mu-BPDC-\kappa O:\kappa O\prime)_6(\mu-O)]\cdot 49DMF\cdot 31H_2O$ compound with the same building blocks but lowering the solvothermal reaction temperature to 85 ℃ (Figure 1.14b). The same components are arranged in such a way that they could build up a mesoporous material with a high surface area ($4300 \ m^2 g^{-1}$) and one of the largest metal–organic framework pore volume reported till date ($4.3 \ cm^3 g^{-1}$).[26]

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[62] An, J. et al. *J. Am. Chem. Soc.* **2009**, *131*, 8376.

(a)

(b)
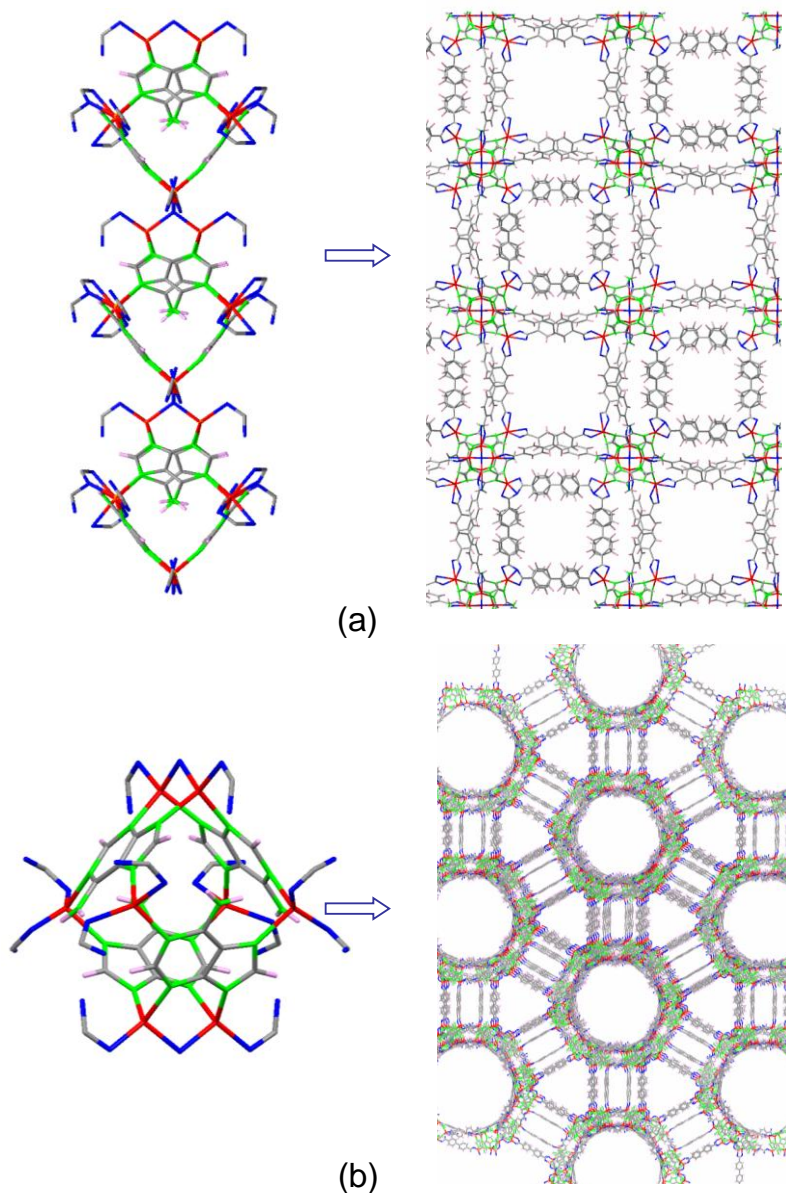
Figure 1.14: SBUs and the resulting crystal structures of compounds (a) $(Me_2NH_2)_2[Zn_8(\mu_4-adeninato)_4(\mu-BPDC)_6(\mu_4-O)]\cdot 8DMF\cdot 11H_2O$, and (b) $(Me_2NH_2)_4[Zn_8(\mu_4-adeninato)_4(\mu-BPDC)_6(\mu-O)]\cdot 49DMF\cdot 31H_2O$.

Another family of metal–adenine–carboxylate compounds that have attracted great interest is that of the formula $[M_2(\mu_3-adeninato-\kappa N3:\kappa N7:\kappa N9)_2(\mu-OOC(CH_2)_xCH_3-\kappa O:\kappa O')_2]_n$.[63] The crystal structure consists of paddle–wheel shaped centrosymmetric dimeric units in which two metal(II) atoms are bridged by two adenine ligands coordinated through their N3 and N9 nitrogen atoms and two carboxylic ligands with a μ–

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[63] (a) An, J. et al. *J. Am. Chem. Soc.* **2010**, *132*, 38. (b) Pérez–Yáñez, S. et al. *Inorg. Chem.* **2011**, *50*, 5330. (c) Lanchas, M. et al. *Inorg. Chem. Front.* **2015**, *2*, 425.

O,O´ coordination mode. These units are cross–linked through the apical coordination of the imidazole N7 atom of the adeninato ligands in such a way that each paddle–wheel shaped unit is linked to four adjacent entities (Figure 1.15). This self–assembling process generates a 4–connected uninodal net that exhibits a three–dimensional system of intersecting cavities. The accessible effective volume is directly related to the length of the aliphatic chain, which is pointing toward the inner portion of the channels. The free–volume ranges from ca. 40% for the acetate analogues and is negligible for pentanoate and longer carboxylates. It is worthy to mention that the synthetic conditions play a relevant role in obtaining the different members of this last family of compounds. In fact, cobalt(II) analogues are obtained under solvothermal conditions,[64] the copper(II) ones using room condition aqueous synthesis,[65] and the nickel(II) and zinc(II) ones employing a less common solvent free approach under conventional oven or microwave assisted heating.[47]

The presence of the highly polar amino groups of the adenines in the pore walls makes these compounds to present a great adsorption selectivity towards CO_2, especially for those with narrower pores.[66] Related to this great adsorption selectivity and taking advantage of the invariability of the crystal structure even when the carboxylic ligand is changed, core–shell frameworks comprising a porous mixed core (acetato/pentanoato) and a less porous shell (pentanoato) were prepared. Thus, the resulting material exhibited 30% higher CO_2 uptake than the pentanoato analogue and low N_2 uptake in comparison to the core.[67] These compounds also showed an enhancement of their adsorptive properties by making use of the template effect exerted by butyric acid microemulsions, to define a simple synthetic route that doubled the adsorption capacity of the butanoate analogue.[68] Moreover, this last 3D crystal structure seems to be so robust that it is obtained even when using long chain aliphatic dicarboxylic acids: $HOOC(CH_2)_nCOOH$ [n from 3 to 5].[69] Surprisingly, only one of the two carboxylic groups is deprotonated and coordinated to the metal centers, μ–κO1:κO2, while the other remains protonated inside the channels of

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[64] An, J. et al. *J. Am. Chem. Soc.* **2010**, *132*, 38.

[65] Pérez–Yáñez, S. et al. *Inorg. Chem.* **2011**, *50*, 5330.

[66] (a) Pérez–Yáñez, S. et al. *Eur. J. Inorg. Chem.* **2012**, 5921. (b) Li, T. et al. *Chem. Sci.* **2013**, *4*, 1746. (c) Xie, Z. et al. *J. Mat. Chem. A*, **2014**, *2*, 1239.

[67] Li, T. et al. *J. Am. Chem. Soc.* **2013**, *135*, 9984.

[68] Pérez–Yáñez, S. et al *Chem. Commun.* **2012**, *48*, 907.

[69] Pérez–Yáñez, S. et al. *Cryst. Growth Des.* **2012**, *12*, 3324.

the crystal structure in such a way that the dicarboxylic ligands do not join the dimeric fragments as it could in principle be expected. Only when short chain dicarboxylic acids are employed, a different crystal structure is obtained. In this last case, the great tendency of these acids to chelate metal ions hinders the paddle–wheel shaped SBUs providing crystal structures based on discrete complex entities.[70]
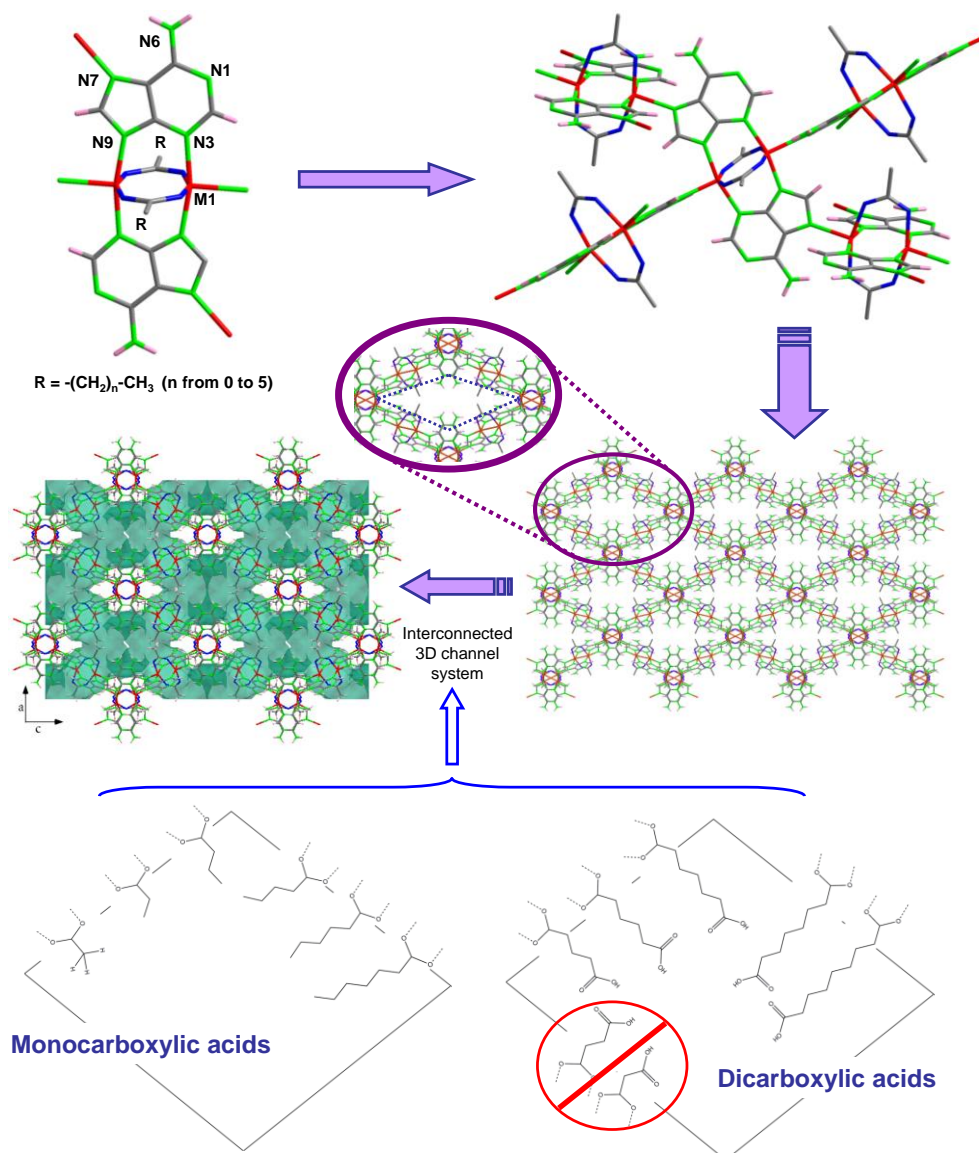
Figure 1.15: Porous crystal structure of $[M_2(\mu_3–adeninato)_2(\mu_2–carboxylato)_2]_n$ compounds (M being Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}).

Other examples of collaborative nucleobase/non–nucleobase bridging ligands sustained MOFs are $[Co_3(\mu–OH)_4(\mu_5–hypoxanthinato–\kappa N3{:}\kappa N7{:}\kappa N9{:}\kappa O6{:}\kappa O6)_2]_n$, with

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[70] Pérez–Yáñez, S. et al. *Eur. J. Inorg. Chem.* **2009**, 3889.

the hypoxanthinato ligand that shows spin canting, metamagnetism, and heterogeneous catalytic ability for the selective oxidation of cis–cyclooctene,[71] and the anionic $[Cd_4(\mu–Cl)(\mu_4–adeninato–\kappa N1:\kappa N3:\kappa N7:\kappa N9)_2Cl_6]_n^{n-}$ network counterbalanced by the presence of H^+/H_3O^+ cations in the channels.[72] All the above examples share in common that the purine nucleobase employs at least N3, N7 and N9 positions to join the metal centers, providing in this way a rigid linker that favors the presence of voids in the resulting structure.

Among nucleobase based MOFs, we can also underline zeolitic type frameworks in which the purine adopts a $\mu–\kappa N7:\kappa N9$ coordination mode (Figure 1.16a). $[M(\mu–purinato–\kappa N7:\kappa N9)_2]_n$ was the first example of a MOF based on this purine nucleobase coordination mode, in which cobalt(II) or zinc(II) tetrahedral nodes are connected through *N7,N9*–purinate bridging ligands.[73] Similarly, a 2–nitroimidazole and purine mixed ligand zinc(II) ZIF, $[Zn(\mu–nitroimidazolato–\kappa N1:\kappa N3)(\mu–purinato–\kappa N7:\kappa N9)]_n$, was later reported.[74] Furthermore, the use of pyridinecarboxylate ligands together with adenine gave rise as well to zeolitic type metal–organic frameworks (Figure 1.16b). In fact, two compounds showing the same network were achieved with isonicotinato, $[Zn(\mu–adeninato–\kappa N7:\kappa N9)(\mu–isonicotinato–\kappa N:\kappa O)]_n,$ [75] and 2–aminoisonicotinato, $[Zn(\mu–adeninato–\kappa N7:\kappa N9)(\mu–2–aminoisonicotinato–\kappa N:\kappa O)]_n.$[76] The functionalization of the isonicotinato ligand with an amino group resulted in a significant enhance of the adsorption selectivity towards CO_2. Finally, $[Zn_{1.33}(O,OH)_{0.33}(\mu–nitroimidazolato–\kappa N1:\kappa N3)_{1.167}(\mu_3–purinato–\kappa N1:\kappa N7:\kappa N9)]_n$ represents another example of this family in which the usual $\mu–\kappa N7:\kappa N9$ coordination mode is reinforced by the coordination through N1 position.[74]

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[71] (a) Zhang, X.–H. et al. *Chem. Eur. J.* **2011**, *17*, 5588. (b) Zhang, G. et al. *Dalton Trans.* **2013**, *42*, 9423.
[72] Song, Y. et al. *CrystEngComm.* **2014**, *16*, 3082.
[73] Hayashi, H. et al. *Nat. Mater.* **2007**, *6*, 501.
[74] Kahr, J. et al. *Chem. Commun.* **2012**, *48*, 6690.
[75] (a) Wang, F. et al. *Chem. Commun.* **2011**, *47*, 5828. (b) Wang, F. et al. *J. Mater. Chem.* **2012**, *22*, 19732.
[76] Yang, E. et al. *CrystEngComm.* **2013**, *15*, 658.

(a)

(b)
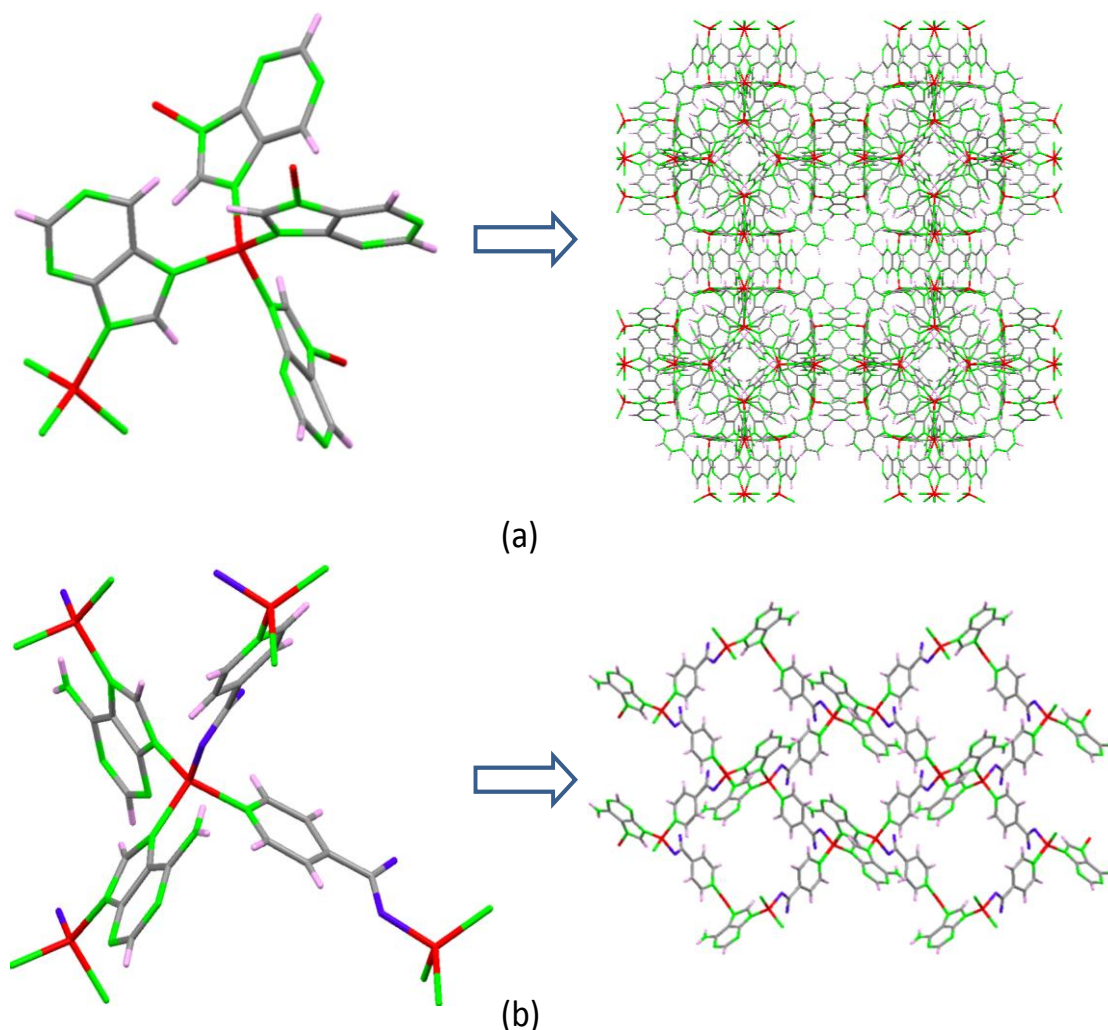
Figure 1.16: Metal coordination environment and final crystal structures of compounds (a) [Zn(μ–purinato–$\kappa N7$:$\kappa N9$)$_2$]$_n$, and (b) [Zn(μ–adeninato–$\kappa N7$:$\kappa N9$)(μ–isonicotinato–κN:κO)]$_n$.

All above mentioned results emphasize the suitability of purine nucleobases as framework components of MOFs due to their multiple available coordination positions and the stiffness of their molecular structure. In fact the lower coordination positions of the pyrimidinic nucleobases did not yet allow the isolation of a MOF based on these ligands as linkers.

1.5   NUCLEOBASES AS HYDROGEN BONDING LINKERS

The formation of duplex DNA from its single stranded constituents is a result of an assemblage of intermolecular forces including aromatic π–stacking, van der Waals forces and hydrophobic effects.[77] However, the high constancy observed in the pairing

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[77] Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991.

of complemetary DNA sequences is greatly due to the unique molecular recognition capability of naturally occurring nucleobases through Watson–Crick pairing hydrogen bonding interactions,[78] while triple helix DNA and G–quartets are formed through Hoogsteen base pairing interactions.

In order to have a better understanding of different synthetic structures that can be constructed through nucleobase interactions, a brief note of the various modes of hydrogen bonding interactions between nucleobases are given in the following part. Till date, various naturally occurring hydrogen bonding motifs and additionally many synthetic hydrogen bonding systems have been reported. However, the nucleobases are considered versatile and known for their capability to sustain hydrogen bond mediated self–assembly or to establish the so called complementary base–pairing interactions.[79] In both DNA and RNA, the purine bases pair with the pyrimidine bases, that is Adenine–Thymine and Cytosine–Guanine in DNA and Adenine–Uracil and Cytosine–Guanine in RNA forming Watson–Crick motifs which are the widely recognised hydrogen bonding interaction in nature. Adenine base has the capacity to form two–point hydrogen bonding either with Thymine or with Uracil, while Guanine forms three–point hydrogen bonding with Cytosine,[80] being therefore a stronger base–pairing motif (Figure 1.17). Hence, in the broader sense, hydrogen–bonding interactions involving base pairs must be considered as playing a salient role in many critical areas such as genetic coding, biological information storage and protein synthesis.[81]

In addition to the conventional G–C and A–T Watson–Crick type base pairing interactions seen in the nucleic acids, the nucleobases are able to establish alternative modes of hydrogen bonding interactions including Hoogsteen and Wobble (mismatched) pairs, two–point homodimers, higher order base–triplets and guanine quartets.[82] Moreover, nucleobases are able to establish hydrogen bonding interactions among the same type of nucleobases. Figure 1.18 shows the hydrogen bonding interactions established along the Watson–Crick and sugar–edges of two adenine

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[78] Watson, J. D.; Crick, F. H. *Nature* **1953**, *171*, 737.
[79] Prins, L. J. et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 2382.
[80] Verma, S. et al. *Acc. Chem. Res*. **2010**, *43*, 79.
[81] (a) Blackburn, G. M. et al. *Nucleic Acids in Chemistry and Biology*; *RSC Publishing*: Cambridge, UK, 2006, p. 470. (b) Bloomfield, V. A. et al. *Nucleic Acids: Structures, Properties and Functions*; *University Science Books*: Sausalito, USA, 2000.
[82] Sessler J. L. et al. *Chem. Soc. Rev*. **2007**, *36*, 314.

moieties. Mimicking the unique ability of DNA to form well–defined assemblies, whose underlying chemistry is governed by the rules of base pairing, is a major area of research in supramolecular chemistry.[83] The high fidelity, directionality, and the effectiveness for establishing multiple pairing interactions have resulted in the concept of base pairing being transported out of the biological realm to the field of supramolecular chemistry.[82]
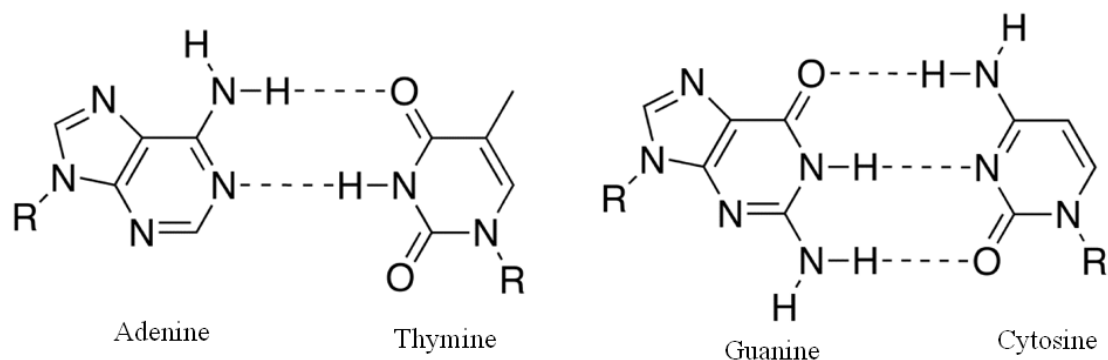
Figure 1.17: Canonical Adenine···Thymine and Guanine···Cytosine complementary base pairing pattern through Watson–Crick faces.
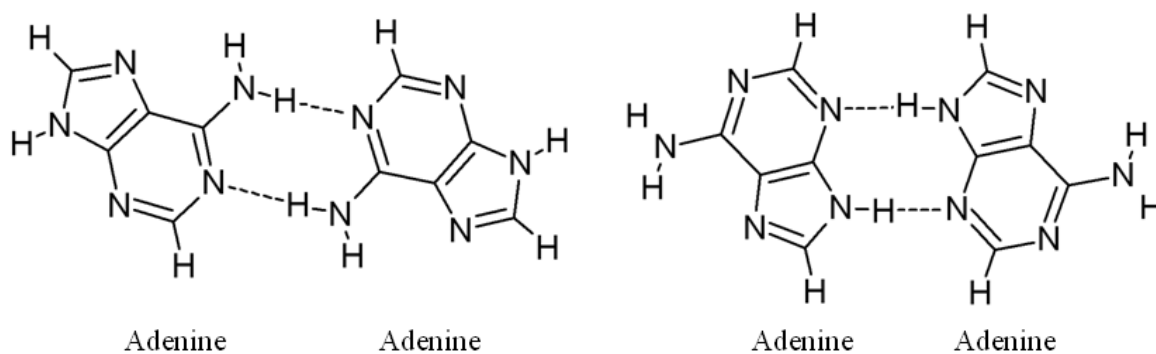
Figure 1.18: The hydrogen bonding interactions established between the same types of nucleobases with adenine as an example.

In addition to these primary nucleobases, there exists other modified nucleobases or nucleobase derivatives. Some examples of them are given in Figure 1.19.

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[83] (a) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9. (b) Sessler, J. L. et al. *J. Chem. Soc. Rev.* **2007**, *36*, 314. (c) Fathalla, M. et al. *J. Chem. Soc. Rev.* **2009**, *38*, 1608.
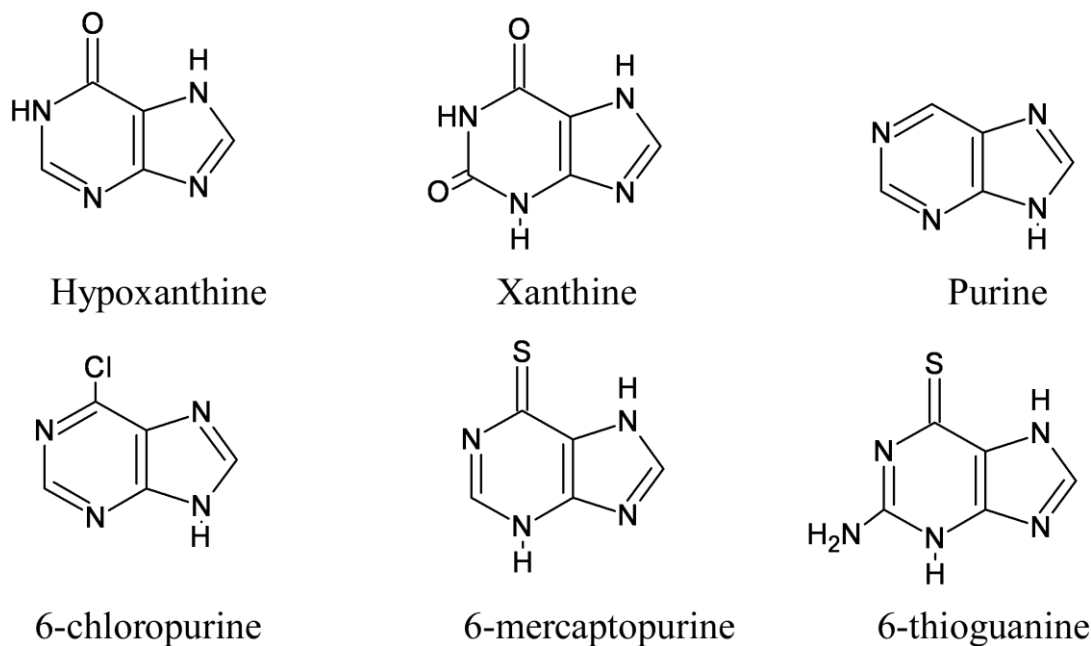
Figure 1.19: Examples of other nucleobases derivatives.

The capacity of the nucleobases to anchor to metal centers through multiple positions at the same time, both acting as bridging or terminal ligand, and their ability to establish complementary interactions makes them suitable for the tailoring of supramolecular arrays based on discrete metal–nucleobase entities. The association patterns between the nucleobases in these discrete entities are directed by a variety of factors like the possible hydrogen bonding scheme, additional stabilization by stacking interactions, the interactions between counterions and also with solvent molecules.[84] On the other hand, the coordination mode versatility of the nucleobases provides a chart of metal–nucleobase discrete entities with different geometries. It also allows them to form complexes of different nuclearity and among which (a) monomers[85] and (b) dimers[86] are very common. However higher nuclearity complexes like (c) trimers,[87] (d) tetramers,[88] (e) hexamers[89] and (f) octamers[90] are also found (Figures 1.20 and 1.21).

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[84] Amo–Ochoa, P. et al. *J. Biol. Inorg. Chem.* **2007**, *12*, 543.

[85] de Meester, P.; Skapski, A. C. *J. Chem. Soc. Dalton Trans.* **1973**, 1596.

[86] Terzis, A. et al. *Inorg. Chem.* **1973**, *12*, 1166.

[87] de Meester, P. et al. *J. Chem. Soc. Dalton Trans.* **1972**, 2400.

[88] Sheldrick, W. S. et al. *Inorg. Chim. Acta* **1993**, *206*, 15.

[89] (a) González–Pérez, J. M. et al. *Inorg. Chem.* **2006**, *45*, 877. (b) An, J. et al. *J. Am. Chem. Soc*. **2009**, *131*, 8401.

[90] Thomas–Gipson, J. et al. *Cryst. Growth Des.* **2015**, *15*, 975.
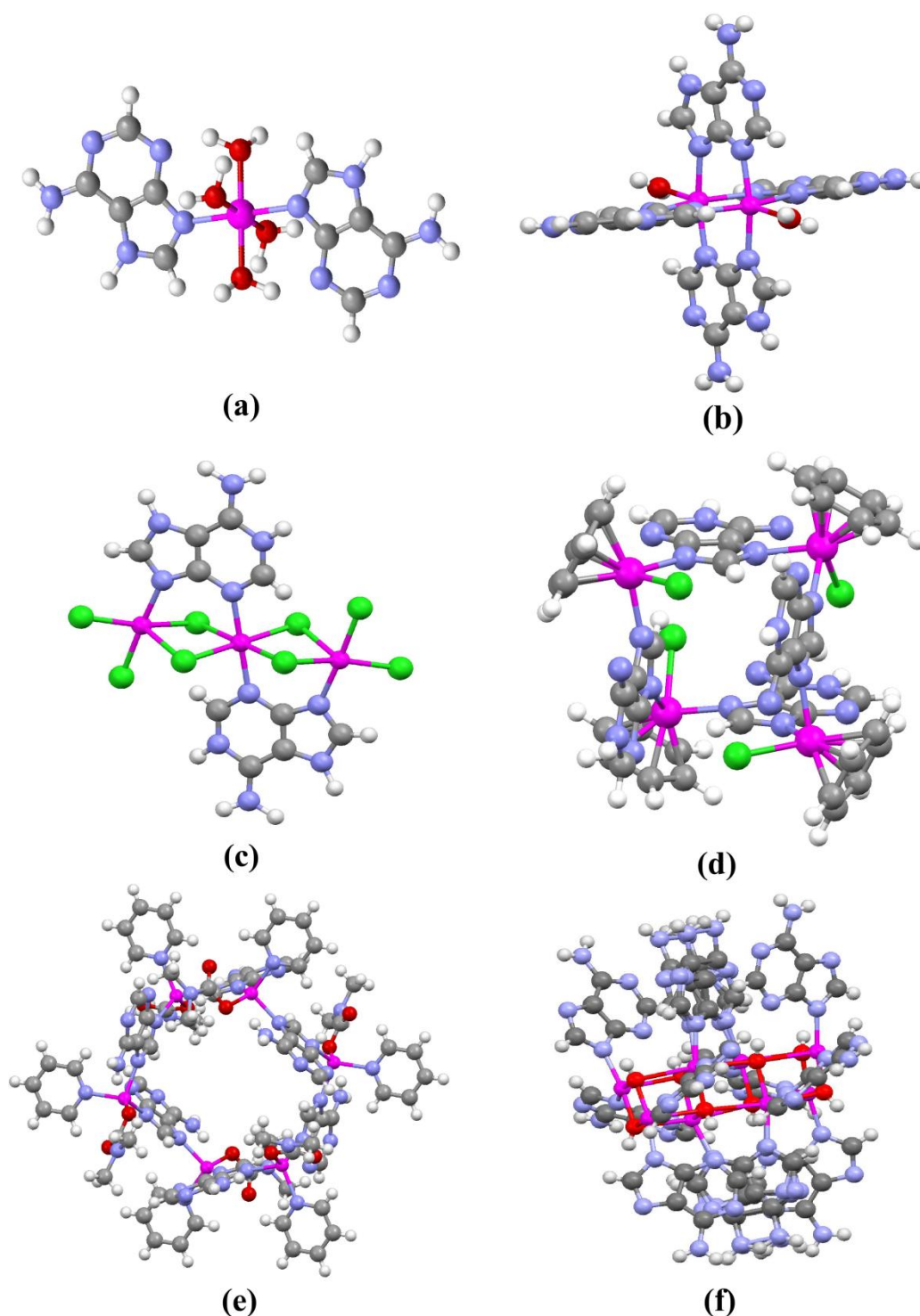
Figure 1.20: Discrete entities of adenine with different nuclearities: (a) monomers,[85] (b) dimers,[86] (c) trimers,[87] (d) tetramers,[88] (e) hexamers[89b] and (f) octamers.[90]

One of the appealing applications of the nucleobase self assembly proccesses involves the generation of supramolecular polymers via hydrogen bonding. Base pairing represents a particularly attractive approach to the construction of supramolecular networks because these hydrogen bonding motifs have the potential to confer both directionality and predictability to the incipient array.
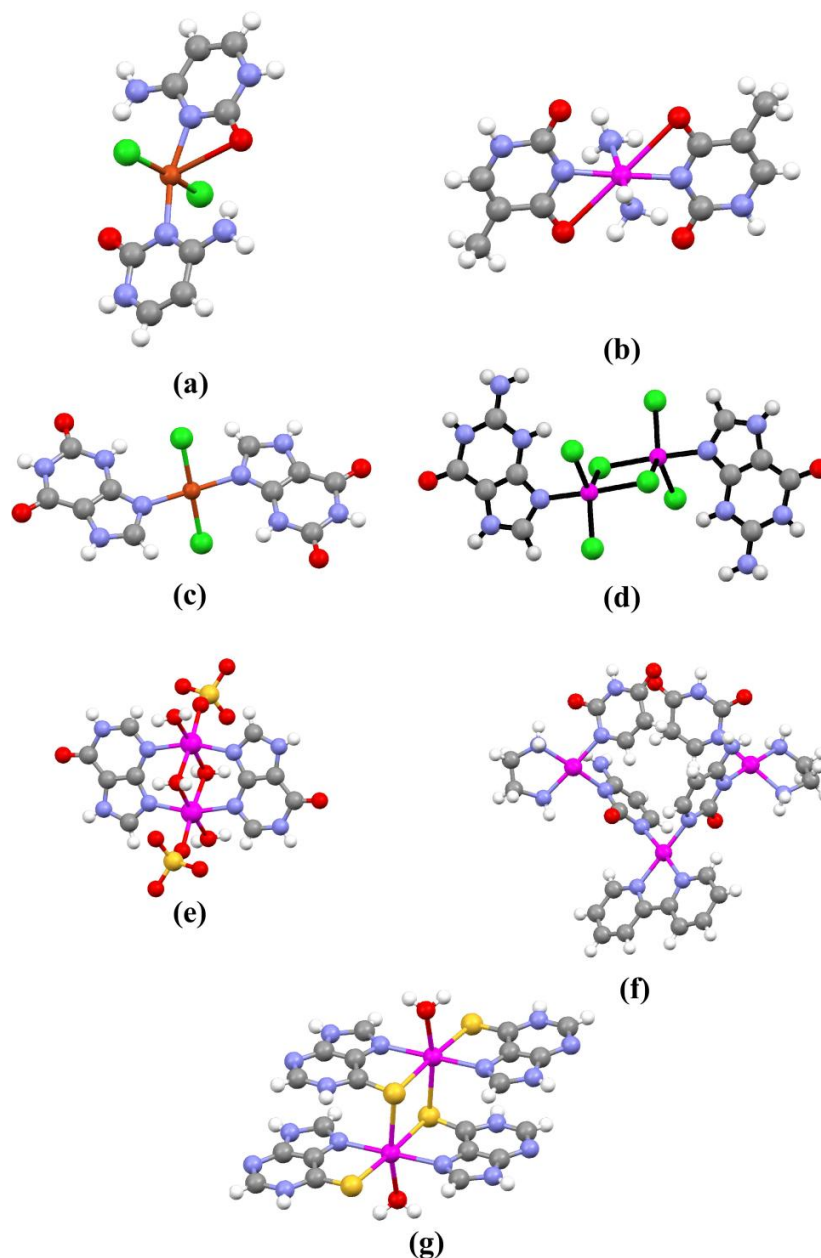
Figure 1.21: Discrete entities of other nucleobases; (a) momomeric compound of cytosine,[91] (b) momomeric compound of thymine,[92] (c) monomeric compound of xanthine,[93] (d) dimeric compound of guanine,[94] (e) dimeric compound of hypoxanthine,[95] and (f) trimeric compound of uracil and cytosine[96] and (g) dimeric compound of 6–mercaptopurine.[97]

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[91] Tran Qui, D.; Palacios, E. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1220.

[92] Parvez, M.; Birdsall, W. J. *Acta Crystallogr. Sect. C, Cryst. Struct. Commun.* **1994**, *50*, 540.

[93] Dubler, E. et al. *Inorg. Chem.* **1992**, *31*, 3728.

[94] Sundaralingam, M.; Carrabine, J. A. *J. Mol. Bio.* **1971**, *61*, 287.

[95] Hänggi, G. et al. *Acta Crystallogr.* **1992**, *C48*, 1008.

[96] Bardají, E. G. et al. *Chem. Eur. J.* **2007**, *13*, 6019.

[97] Amo–Ochoa, P. et al. *Inorg. Chem.* **2006**, *45*, 7642.

There are some examples of non–porous supramolecular polymers based on complementary hydrogen bonded base pairing interactions among transition metal–nucleobase supramolecular building units. Figure 1.22 shows some examples of supramolecular polymers where the complementary base pairing interactions are crucial in forming supramolecular arrays. These examples include, (a) trans–bis(adeninato)–bis(tri–n–butylphosphine)–palladium(II) methanol solvate, [98] (b) (adeninato–N9)–methyl–mercury(II) monohydrate, [99] (c) tetra–aqua–bis(9–methyladenine)–copper(II) dichloride dehydrate, [100] (d) dichloro–bis(cytosine–N3)–copper(II),[91] (e) bis(9–methylguanine)–tetraaqua–cadmium(II) dinitrate, [101] (f) tetrakis(cytosine)–copper(II) diperchlorate dehydrate, [102] and (g) trans–bis(guanine)–aqua–(formato)–copper(II) perchlorate formic acid solvate monohydrate.[103]

Sessler and co–workers[82] pointed out the relevance of the solvent in designing self assembled structures based on hydrogen bonding interactions. It is to be noted that, in polar protic solvents, monomeric nucleobases do not exist as hydrogen bonded pairs. Rather, they tend to form extended columns as a result of π–stacking and hydrophobic interactions. Thus, the solvent competes with the acceptor and donor sites on the nucleobases leading to decreased hydrogen bonding interactions with the complementary base. Therefore aprotic solvents such as CH_2Cl_2 and $CHCl_3$ were preferably used to synthesise synthetic self assembled structures as they do not compete appreciably with the donor/acceptor sites needed to establish the base pairing interactions. However, the solubility of the parent nucleobases in these foresaid solvents is still a challenge to be met. Nonetheless, this solvent dependency is rather attractive as the formation and subsequent break–up of such aggregates can be controlled by changing the reaction medium by switching from non–polar to highly competitive hydrogen bonding solvents.

[98] Beck, W. M. et al. *Inorg.Chem.* **1979**, *18*, 176.
[99] Prizant, L. et al. *Can. J. Chem.* **1981**, *59*, 1311.
[100] Sletten, E.; Ruud, M. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 982.
[101] Amo–Ochoa, P. et al. *J. Inorg. Biochem.* **2005**, *99*, 1540.
[102] Palaniandavar, M. et al. *J. Chem. Soc. Dalton Trans.* **1996**, 1333.
[103] Mastropietro, T. F. et al. *Dalton Trans.* **2008**, 514.
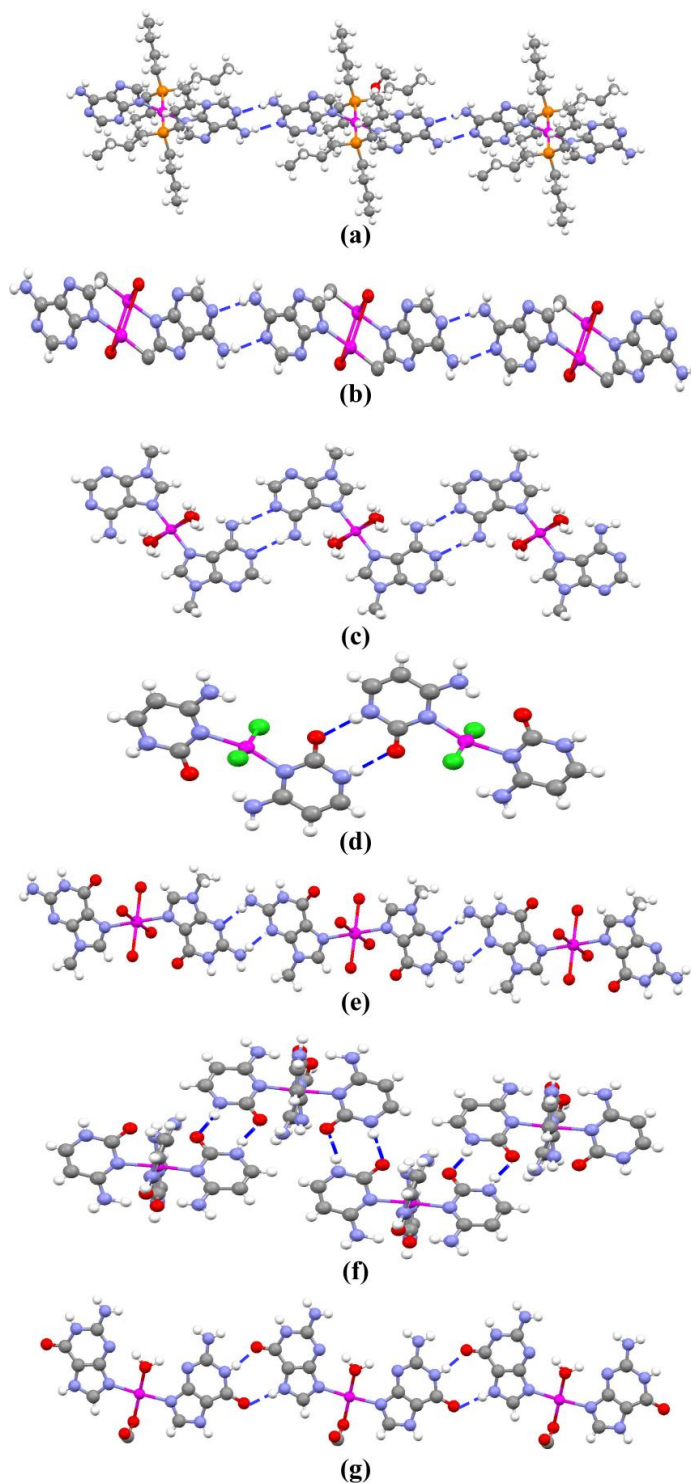
Figure 1.22: Examples of compounds in which base–pairing interactions lead to supramolecular polymerization (a) trans–bis(adeninato)–bis(tri–n–butylphosphine)–palladium(II) methanol solvate,[98] (b) (adeninato–N9)–methyl–mercury(II) monohydrate,[99] (c) tetra–aqua–bis(9–methyladenine)–copper(II) dichloride dehydrate,[100] (d) dichloro–bis(cytosine–N3)–copper(II),[91] (e) bis(9–methylguanine)–tetraaqua–cadmium(II) dinitrate,[101] (f) tetrakis(cytosine)–copper(II) diperchlorate dehydrate,[102] and (g) trans–bis(guanine)–aqua–(formato)–copper(II) perchlorate formic acid solvate monohydrate.[103]

1.6   OBJECTIVE

Taking into account the great potentials of MOFs, herein we decided to explore a novel, but related, type of materials, Supramolecular Metal–Organic Framewroks (***SMOFs***) in which the bridging coordination bonds are replaced with hydrogen bonds, which are also directional and predictable interactions, to sustain the 3D crystal building (Figure 1.23). Although, such kind of alternative materials can arouse an alike fascination to that of MOFs, the crystal engineering principles and the synthetic approach are not yet settled, and examples of this kind of materials have not been yet reported.
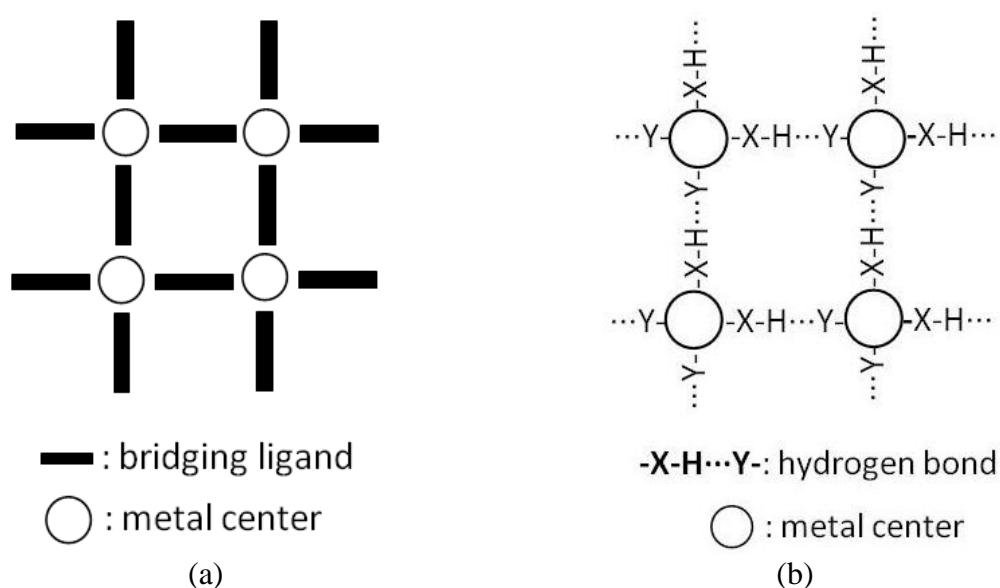
Figure 1.23: Similarity between (a) coordination bonds and (b) hydrogen bonding interactions.

We consider nucleobases as best candidates for this purpose due to their multiple binding positions and capability to establish doubly and triply hydrogen bonded complementary base pairing interactions. Therefore, the original idea is to employ discrete metal–nucleobase complexes in which the nucleobase is tightly anchored to the metal centres but exposing, at the same time, several hydrogen bond donor and acceptor positions to establish base pairing interactions that could sustain a robust supramolecular synthon. It is also expected that the geometrical restrain imposed by the base pairing interactions could led to an inefficient space occupation giving rise to a new family of porous materials.

Chapter 2

Supramolecular architectures based on metal/cytosine systems

2.1 Introduction

2.2 Synthesis and Characterisation

2.3 Results and Discussion

2.4 Conclusions

2.1   INTRODUCTION

The primary objective at the beginning of this work was to develop extended systems of porous supramolecular metal–organic frameworks based on first row transition metal ions and nucleobases. Preference was given to pyrimidine bases due to their high solubility in almost all the solvents and also because there are interesting examples of cytosine derivatives coordinated to transition metal complexes.[104] However, the number of reported examples of such compounds in which unsubstituted neutral cytosine is coordinated to a metal centre is lower.[105]

[104] (a) Pacifico, C. et al. *Bioinorg. Chem. Appl.* **2010**, *2010*, 102863. (b) Britten, J. F. et al. *Inorg. Chem.* **1982**, *21*, 1936. (c) Orbell, J. D. et al. *J. Am. Chem. Soc.* **1981**, *103*, 5126. (d) Houlton, A. et al. *J. Chem. Soc. Dalton Trans.* **1999**, 3229. (e) Sabat, M. et al. *J. Am. Chem. Soc.* **1983**, *105*, 976. (f) Cosar, S. et al. *J. Chem. Soc. Dalton Trans.* **1999**, 2329. (g) Amo–Ochoa, P. et al. *J. Inorg. Biochem.* **2008**, *102*, 203. (h) Vijay–Kumar, S. et al. *Nucleic Acids Res.* **1984**, *12*, 3649. (i) Louie, S. et al. *J. Am. Chem. Soc.* **1977**, *99*, 3874. (j) Lippert, B. et al. *Inorg. Chem.* **1981**, *20*, 335. (k) Aoki, K. *Chem. Commun.* **1979**, 589. (l) Aoki, K. *Biochim. Biophys. Acta.* **1976**, *447*, 379. (m) Holowczak, M. S. et al. *J. Am. Chem. Soc.* **1985**, *107*, 5789. (n) Khutia, A. et al. *Chem. Eur. J.* **2011**, *17*, 4195. (o) Miller, S. K. et al. *Inorg. Chem.* **1986**, *25*, 4272. (p) Schollhorn, H. et al. *J. Am. Chem. Soc.* **1986**, *108*, 3680. (q) Jitsukawa, K. et al. *Chem. Lett.* **2004**, *33*, 1302. (r) Grehl, M; Krebs, B. *Inorg. Chem.* **1994**, *33*, 3877. (s) Djinovic, V. M. et al. *Dalton Trans.* **2010**, *39*, 3633. (t) Miguel, P. J. S. et al. *J. Inorg. Biochem.* **2006**, *100*, 980. (u) Galstyan, A. et al. *Eur. J. Inorg. Chem.* **2011**, 1649. (v) Krumm, M. et al. *Inorg. Chem.* **1991**, *30*, 884. (w) Mastropietro, T. F. et al. *Cryst. Growth Des.* **2007**, *7*, 609. (x) Fusch, E. C.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 7204. (y) Ruiz, J. et al. *Inorg. Chem.* **2005**, *44*, 7365. (z) De Munno, G. et al. *J. Chem. Soc. Dalton Trans.* **2000**, 1625. (aa) Kistenmacher, T. J. et al. *Inorg. Chem.* **1979**, *18*, 240. (ab) Trovo, G. et al. *Dalton Trans.* **1993**, 669. (ac) Longato, B. et al. *Inorg. Chem.* **2006**, *45*, 8179. (ad) Montagner, D. et al. *Inorg. Chem.* **2008**, *47*, 2688. (ae).Wu, S.–M.; Bau, R. *Biochem. Biophys. Res. Comm.* **1979**, *88*, 1435. (af) Fusch, G. et al. *Inorg. Chim. Acta.* **1996**, *252*, 167. (ag) Holthenrich, D. et al. *Inorg. Chim. Acta* **1996**, *248*, 175. (ah) Freisinger, E. et al. *Proc. Nat. Acad. Sci. USA*, **2003**, *100*, 3748. (ai) Anzellotti, A. I. et al. Inorg. *Chem.* **2006**, *45*, 1638. (aj) Schwarz, F. et al. *Chem. Commun.* **1990**, 1282. (ak) Smith, D. P. et al. *Organometallics* **1993**, *12*, 593. (al) Wienken, M. et al, *J. Chem. Soc. Dalton Trans.* **1993**, 3349. (am) Purohit, P. S. et al. *Appl. Catal. A,* **2007**, *316*, 100. (an) Aoki, K. *Chem. Commun.* **1976**, 748.

[105] (a) Garcia, B. et al. *J. Inorg. Biochem.* **2008**, *102*, 1892. (b) Sundaralingam, M.; Carrabine, J. A. *J. Mol. Biol.* **1971**, *61*, 287. (c) Khutia, A. et al. *Chem. Eur. J.* **2011**, *17*, 4195. (d) Garcia–Raso, A. et al. *Polyhedron* **2006**, *25*, 2295. (e) Panfil, A. et al. *Polyhedron* **1994**, *13*, 2513. (f) Klein, A. et al. *Organometallics* **2007**, *26*, 230. (g) Cervantes, G. et al. *Inorg. Chem.* **1990**, *29*, 5168. (h) Hollis, L. S. et al. *J. Med. Chem.* **1989**, *32*, 128. (i) De Munno, G. et al. *J. Chem. Soc. Dalton Trans.* **2000**, 1625. (j) Capllonch, M. C. et al. *J. Inorg. Biochem.* **2001**, *85*, 173. (k) Aoki, K.; Salam, M. A. *Inorg. Chim. Acta* **2001**, *316*, 50. (l) Brüning, W. et al. *Inorg. Chim. Acta* **2002**, *339*, 400. (m) De Munno, G. et al. *J. Chem. Soc. Dalton Trans.* **1993**, 1113. (n) Kickham, J. E. et al. *J. Am. Chem. Soc.* **1993**, *115*, 7031. (o) Szalda, D. J. et al. *Inorg. Chem.* **1975**, *14*, 2076. (p) Tran Qui, D.; Bagieu, M. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 1645. (q) Bardaji, E. G. et al. *Chem. Eur. J.* **2007**, *13*, 6019. (r) Karthikeyan, A. et al. *Acta Crystallogr. Sect. E: Struct. Rep. Online*, **2010**, *66*, m1693. (s) Brüning, W. et al. *Chem. Eur. J.* **2002**, *8*, 4681. (t) Palaniandavar, M. et al. *J. Chem. Soc. Dalton Trans.* **1996**, 1333.

Neutral cytosine, although presenting different donor positions, shows a relatively predictable coordination mode through N3. In fact, in a search at the CSD database (version February 2015) this coordination mode showed 26 hits from a total of 34 registered crystal structures for neutral cytosine coordinated to a transition metal center. Less common coordination modes involve bonding through the exocyclic O2, N1 or even in two cases it links simultaneously through N3 and O2 both as chelates or bridging ligand. The usually accepted numbering scheme of cytosine is shown in Figure 2.1 altogether with its coordination modes.
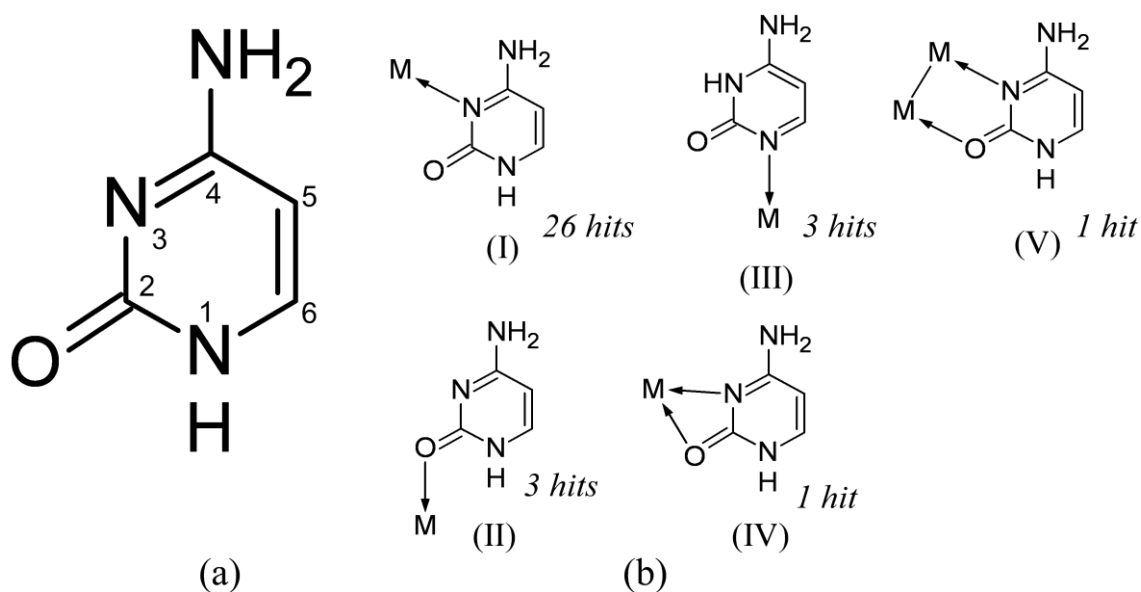
Figure 2.1: (a) The numbering scheme of cytosine and (b) coordination modes of neutral cytosine.

On the other hand, the deprotonation of the cytosine reinforces its coordination capability being relatively common the μ–cytosinato–κ*N1*: κ*N3* (Figure 2.2).
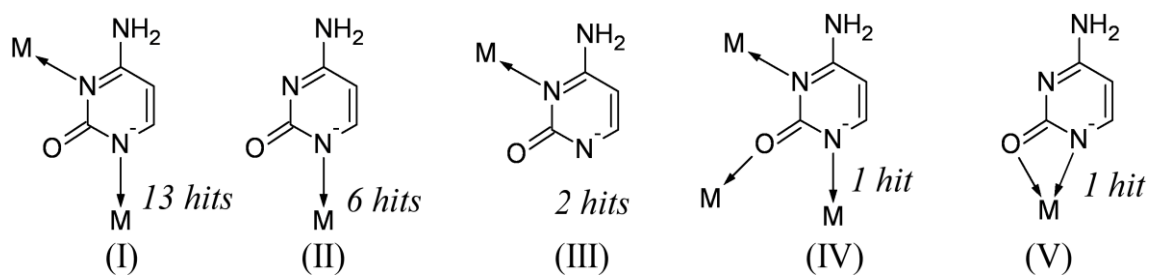
Figure 2.2: Coordination modes of cytosinate anion.

The resulting coordination complexes that emerge from the predominant cytosine–κ*N3* coordination mode, are basically restricted to monomeric entities as those depicted in Figure 2.3, which expose the sugar edge (N1–O2 side) of the nucleobase to

establish complementary hydrogen bonds and therefore they could develop self–assembled *supramolecular MOFs*. Cytosine is able to form three complimentary hydrogen bonds at a time with the guanine molecule, but it is also able to establish cytosine···cytosine self–complementary hydrogen bonding patterns that involves the Watson–Crick and sugar edges (Figure 2.4).[106]

[Pt(cytosine)Cl₃][107]   *[Zn(cytosine)₂Br₂]*[108]

[Cu(cytosine)₂Cl₂][91]

[Cu(cytosine)₄]²⁺[102]
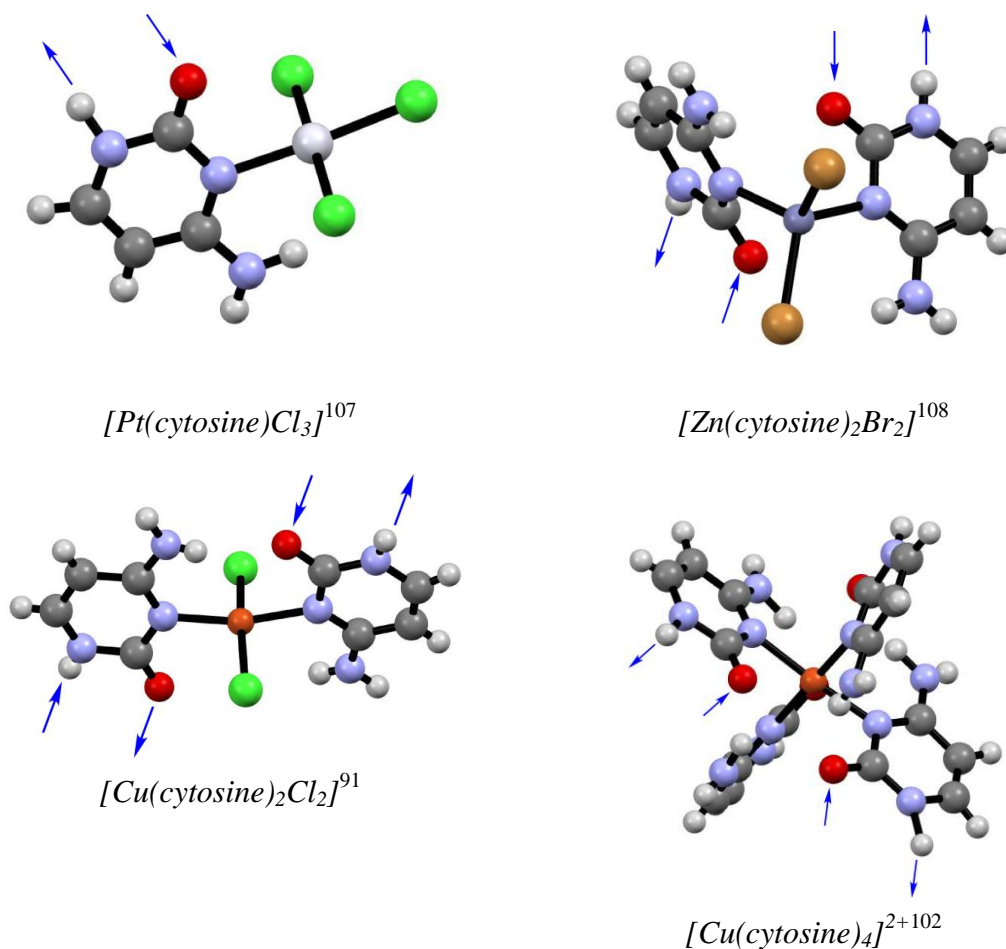
Figure 2.3: Examples of cytosine–κ*N3* coordinated transition metal complexes.

[106] Frey, J. A. et al. *J. Phys. Chem. B*, **2014,** *118*, 682.
[107] Jaworski, S. et al. *Inorg. Chim. Acta* **1988**, *153*, 31.
[108] Karthikeyan, A. et al. *Acta Crystallogr. Sect. E: Struct. Rep. Online*, **2010,** *66,* m1693.
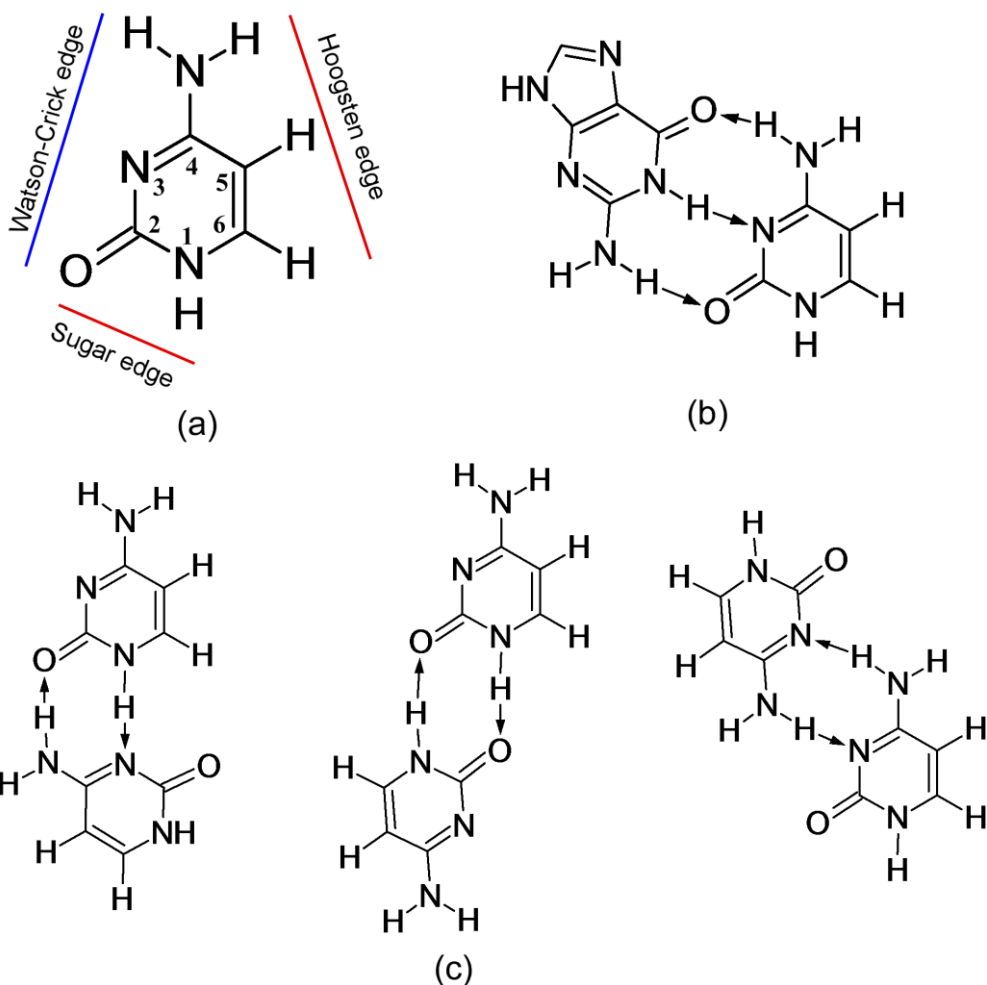
Figure 2.4: (a) Cytosine nucleobase edges, (b) guanine···cytosine triple complementary hydrogen bonds and (c) cytosine···cytosine double complementary hydrogen bonding patterns.

The Figure 2.5 is an example of complementary hydrogen bonding interaction between coordinated cytosine–κ*N3* nucleobases. The objective of this chapter is to explore the use of cytosine as ligand in order to take advantage of its hydrogen bonding capability to form supramolecular networks sustained by noncovalent interactions.
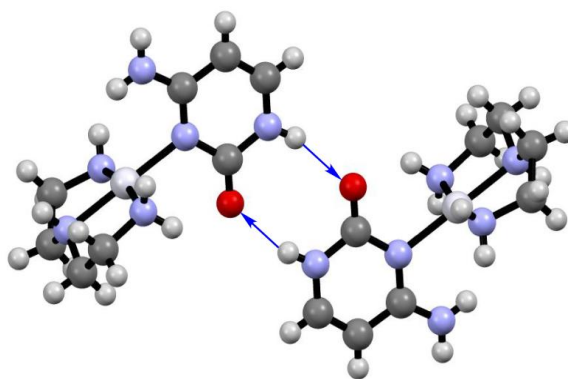
Figure 2.5: Hydrogen bonding interaction between coordinated cytosine–κ*N3* nucleobases.[109]

[109] Brüning, W. et al. *Inorg. Chim. Acta* **2002**, *339*, 400.

2.2   SYNTHESIS AND CHARACTERISATION

2.2.1   Synthesis

The Table 2.1 shows the compounds obtained for the metal/halide/cytosine system. A common feature of syntheses is the use of alcoholic solvents instead of water to promote the direct hydrogen bonding interactions among the cytosines. The purity of all samples has been checked by means of X–ray diffraction techniques, elemental analysis and ICP analysis.

Table 2.1: Synthesised new compounds.[a]

Compound[a]	Code
$(H_2Cyt)_2[CoCl_4]\cdot2(HCyt)$ Cytosinium tetrachloridocobaltate(II)–cytosine (1/2)	*COCYTCL*
$[CoBr_2(HCyt)_2]$ Dibromidobis(cytosine–κ*N3*)cobalt(II)	*COCYTBR*
$[ZnCl_2(HCyt)_2]$ Dichloridobis(cytosine–κ*N3*)zinc(II)	*ZNCYTCL*
$[CuCl_2(HCyt)_2]$ Dichloridobis(cytosine–κ*N3*)copper(II)	*CUCYTCL–B*
$[CuBr_2(HCyt)_2]$ Dibromidobis(cytosine–κ*N3*)copper(II)	*CUCYTBR*
$[Cu(HCyt)_4](SO_4)\cdot2(CH_3OH)$ tetrakis(cytosine–κ*N3*)copper(II) sulphate–methanol (1/2)	*CUCYTSO4*

[a] HCyt = $C_4H_5N_3O$; $H_2Cyt = C_4H_6N_3O$

2.2.1.1 *Synthesis of COCYTCL*

A solution of 0.1 mmol of $CoCl_2\cdot6H_2O$ (0.0239 g) in 5 mL propanol was added dropwise into a solution of 0.2 mmol of cytosine (0.0237 g) in 35 mL propanol containing 0.2 mmol of hydrochloric acid (37%) and stirred for two hours at 80 ºC. A small quantity of a light blue precipitate of *COCYTCL* was obtained and filtered out. The mother liquid was then left evaporating at room temperature and blue good quality single crystals appeared in one week. They were filtered off, washed thoroughly with cold ethanol and left drying under vacuum.

Yield (based on metal): 40%. Anal. Calcd (found) for $C_{16}H_{22}Cl_4CoN_{12}O_4$: C, 29.69 (29.82); H, 3.43 (3.50); N, 25.97 (26.07), Co, 9.11 (9.08). IR selected data (KBr, cm^{-1}): 3430w, 3076w, 1860m, 1826w, 1796w, 1740vs, 1726sh, 1688vs, 1650vs, 1516m, 1488s, 1455s, 1445sh, 1411w, 1386w, 1372sh, 1294w, 1283sh, 1241vs, 1233sh,

1130w, 1113w, 1091w, 1011m, 988m, 947m, 841w, 808m, 781vs, 758sh, 701m, 668m, 596m, 586s, 570s, 553m, 535s, 471w, 425m.

2.2.1.2 *Synthesis of COCYTBR*

Single crystals were grown by the addition of 0.05 mmol solution of $CoBr_2$ (0.0120 g) in 10 mL propanol over a 10 mL propanolic solution of 0.1 mmol of cytosine (0.0116 g). The solution was stirred for 2 hours and left evaporating at room temperature. Blue single crystals of **COCYTBR** were obtained after one week.

Yield: 55%. Anal. Calcd (found) for $C_8H_{10}Br_2CoN_6O_2$: C, 21.79 (21.87); H, 2.29 (2.34); N, 19.06 (19.03), Co, 13.37 (13.31). IR selected data (KBr, cm^{-1}): 3430m, 3386m, 3313m, 3233m, 3213sh*, 3086m, 3016w, 2956w, 2923w, 2883w, 2836w, 1669vs, 1676vs, 1629vs, 1600sh, 1529m, 1500sh*, 1475m, 1437m, 1383w, 1362w, 1275m, 1237s, 1216s, 1116w, 1110w, 1004w, 975w, 958w, 850m, 800s, 779s, 750s, 704m, 666w, 640m, 608m, 600w, 578m, 551s, 541s, 530sh, 443m, 436m.

2.2.1.3 *Synthesis of ZNCYTCL*

A solution of 0.1 mmol of $ZnCl_2$ (0.0140 g) dissolved in 5 mL methanol was added dropwise to a stirring solution of 0.4 mmol of cytosine (0.0450 g) dissolved in 40 mL of methanol. The solution was stirred for one hour and left eveporating at room temperature. Colourless crystals started appearing after one week of evaporation.

Yield: 15%. Anal. Calcd (found) for $C_8H_{10}Cl_2N_6O_2Zn$: C, 26.80 (26.87); H, 2.81 (2.76); N, 23.44 (23.47), Zn, 18.24 (18.21). IR selected data (KBr, cm^{-1}): 3427s, 3367s, 3172s, 3094s, 2922s, 2844s, 2805s, 1672vs, 1633vs, 1505s, 1461s, 1372m, 1288m, 1238m, 1150w, 1105w, 1005w, 977w, 877m, 805s, 788s, 750w, 655m, 600m, 573w, 546m, 433m, 414m.

2.2.1.4 *Synthesis of CUCYTCL–B*

0.1 mmol of $CuCl_2 \cdot 2H_2O$ (0.0170 g) dissolved in 5 mL methanol was added dropwise to a solution of 35 mL methanol containing 0.2 mmol of cytosine (0.0230 g) and 0.2 mmol hydrochloric acid. A blue precipitate appeared on stirring while heating for 10 minutes. The reaction mixture was stirred for one hour at 80 ºC. The precipitate was filtered off. X–ray diffraction data showed that this precipitate corresponds to the previously reported compound $[CuCl_2(C_4H_5N_3O)_2]$.[91,94] The still blue coloured mother

liquid was left evaporating at room conditions and after one week, purple good quality single crystals of **CUCYTCL–B** started appearing.

Yield: 15%, Anal. Calcd (found) for $C_8H_{10}Cl_2CuN_6O_2$: C, 26.94 (26.99); H, 2.83 (2.75); N, 23.56 (23.62), Cu, 17.82(17.87). IR selected data (KBr, cm^{-1}): 3373s, 3340s, 3163s, 2960w, 2880w, 1720w,1680m, 1683s, 1630vs, 1519s, 1497s, 1463w, 1441w, 1419w, 1402w, 1383w, 1363m, 1294m, 1261w, 1230s, 1214s, 1136m, 1100s, 861w, 813w, 795m, 776s, 762m, 667m, 616w, 591w, 576w, 564m, 537m, 447s, 434w.

2.2.1.5 *Synthesis of CUCYTBR*

Single crystals of this compound were grown by the addition of a solution of 0.1 mmol of $CuBr_2$ (0.0248 g) in 5 mL propanol into a 35 mL propanolic solution of 0.2 mmols of cytosine (0.0230 g). Green single crystals were formed on three weeks of slow evaporation.

Yield: 35%, Anal. Calcd (found) for $C_8H_{10}Br_2CuN_6O_2$: C, 21.57 (26.51); H, 2.26(2.34); N, 18.86 (18.97), Cu, 14.26 (14.17). IR selected data (KBr, cm^{-1}): 3448vs, 3377vs, 3177s, 3066w, 2866w, 1627vs, 1515s, 1466w, 1435w, 1380s, 1280w, 1262w, 1217m, 1137w, 1102w, 1022w, 986w, 857w, 791m, 746m, 608w, 560sh, 422m.

2.2.1.6 *Synthesis of CUCYTSO4*

Single crystals were grown by layering a methanolic solution of 0.2 mmol of cytosine (0.0223 g in 20 mL methanol) over 0.1 mmol $CuSO_4·5H_2O$ (0.0270 g) dissolved in 15 mL methanol. Purple single crystals started growing on slow diffusion over one week time. The crystals decomposed upon removal from the mother liquid.

Yield: 20%, Anal. Calcd (found) for $C_{20}H_{36}CuN_{12}O_{12}S$: C, 32.81 (32.76); H, 4.96 (4.91); N, 22.96 (22.99); Cu, 8.68 (8.63). IR selected data (KBr, cm^{-1}): 3372s, 3171s, 1727s, 1651s, 1637s, 1516m, 1496w, 1460w, 1403w, 1383m, 1286w, 1233m, 1196w, 1113s, 1086s, 1013w, 963w, 876w, 780m, 756w, 616m, 601w, 577m, 531m, 484w, 426w.

2.3 RESULTS AND DISCUSSION

2.3.1 Crystallographic analysis

X–ray diffraction data of single crystals were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer (Mo–Kα λ = 0.71073 Å) and an Agilent

Technologies Supernova (Cu–Kα λ = 1.54184 Å). The data reduction was done with CrysAlis RED[110] program. Structures were solved by direct methods using the SIR92 program[111] and refined by full–matrix least–squares on F^2 including all reflections (SHELXL97).[112] All calculations were performed using the WINGX crystallographic software package.[113] Crystal data and details of the refinement procedure are given in Table 2.2.

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[110] *CrysAlis* PRO, version 1.171.33.55; Oxford Diffraction: Wroclaw, Poland, 2010.

[111] Altomare, A. et. al. *J. Appl. Cryst.* **1993**, *26*, 343.

[112] Sheldrick, G. M. SHELXL–97, *Programs for X–ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

[113] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.

Table 2.2: Single crystal data and structural refinement details of metal–cytosine compounds.

Compound	*COCYTCL*	*COCYTBR*	*ZNCYTCL*	*CUCYTCL–B*	*CUCYTBR*	*CUCYTSO4*
Empirical formula	$C_{16}H_{22}Cl_4CoN_{12}O_4$	$C_8H_{10}Br_2CoN_6O_2$	$C_8H_{10}Cl_2N_6O_2Zn$	$C_8H_{10}Cl_2CuN_6O_2$	$C_8H_{10}Br_2CuN_6O_2$	$C_{20}H_{36}CuN_{12}O_{12}S$
Formula weight	647.19	440.97	358.49	356.66	445.58	732.21
λ (Å)	0.71073	0.71073	1.54184	0.71073	0.71073	0.71073
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	tetragonal
Space group	*C 2/c*	*P* $\bar{1}$	*P* $\bar{1}$	*P* $\bar{1}$	*P 2₁/n*	*P 4₃ 2 2*
a (Å)	6.9633(3)	7.1279(7)	7.0087(11)	6.7760(8)	8.4897(2)	10.3967(1)
b (Å)	15.1746(7)	7.7441(8)	7.5786(10)	6.8411(8)	13.8536(4)	10.3967(1)
c (Å)	23.6381(9)	12.3208(12)	12.277(2)	8.0166(9)	10.7710(3)	27.4900(5)
α (°)	90	87.112(8)	85.740(10)	69.905(9)	90.00	90.00
β (°)	93.819(5)	74.907(8)	75.120(10)	87.064(9)	91.842(2)	90.00
γ (°)	90	87.604(8)	87.470(10)	62.633(8)	90.00	90.00
V (Å³)	2492.18(18)	655.51(11)	628.29(16)	307.38(6)	1266.15(6)	2971.43(7)
Z	4	2	2	1	4	4
ρ_{calcd} (g cm⁻³)	1.725	2.234	1.895	1.927	2.337	1.637
μ (mm⁻¹)	1.170	7.411	6.730	2.218	8.044	0.887
Reflections collected	5386	3730	2070	5287	12426	6234
Unique data/parameters	2398/168	2467/172	1460/172	1660/88	3687/172	3145/212
R_{int}	0.0349	0.0745	0.0390	0.0566	0.0379	0.0207
Goodness of fit (S)[a]	0.888	0.768	0.967	1.036	0.904	1.060
R1[b]/wR2[c] [I>2σ(I)]	0.0337/0.0695	0.0397/0.0660	0.0594/0.1457	0.0375/0.870	0.0262/0.0536	0.0330/0.0780
R1[b]/wR2[c] [all data]	0.0545/0.0719	0.0695/0.0690	0.0728/0.1579	0.0494/0.0900	0.0416/0.0547	0.0355/0.0791

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. [c] $wR2 = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (max(F_0^2, 0) + 2Fc^2)/3$ with a = 0.0314 (***COCYTCL***); a = 0.0021 (***COCYTBR***); a = 0.1147 (***ZNCYTCL***); a = 0.0536 (***CUCYTCL***); a = 0.0229 (***CUCYTBR***); a = 0.0352, b = 1.7493 (***CUCYTSO4***).

2.3.2   Structural Description

2.3.2.1 *Structure of COCYTCL*

The crystal structure of this compound consists of $[CoCl_4]^{2-}$ units, cytosinium counterions (H_2Cyt^+) and neutral cytosine molecules (HCyt). Figure 2.6 depicts the ortep drawing of these building units, showing their labelling scheme. The $[CoCl_4]^{2-}$ anion, that lies on a two fold axis, presents the usual tetrahedral geometry with Co–Cl bond distances and Cl–Co–Cl bond angles around 2.25–2.28 Å and 106–120º, respectively (Table 2.3). The continuous shape measurements (CShM) carried out by the program SHAPE [114] show a geometry close to an ideal tetrahedron ($S_{tetrahedron}$: 0.31 and S_{square}: 28.68).
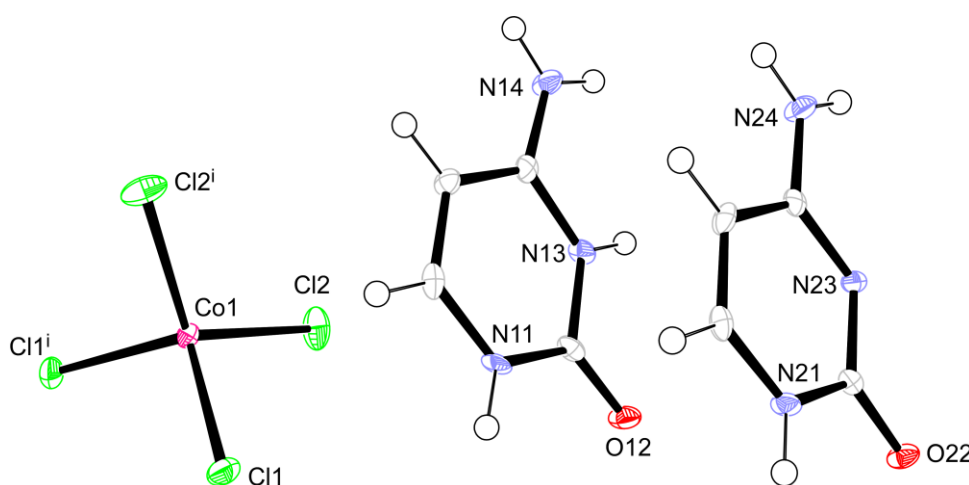
Figure 2.6: Building units of compound *COCYTCL* showing the labelling scheme.

Table 2.3: Selected coordination bond lengths (Å) and angles (º) in compound *COCYTCL*.

Co1–Cl1	2.2813(8)	Cl1–Co1–Cl1^i	110.80(4)	Cl1–Co1–Cl2i^i	106.46(3)
Co1–Cl2	2.2584(7)	Cl1–Co1–Cl2	106.62(3)	Cl2–Co1–Cl2^i	119.82(5)

Symmetry code: (i) –x, y, –z+3/2.

The overall structure is dominated by electrostatic interactions and by supramolecular hydrogen bonding interactions established between the *1H,3H–cytosinium* cation and the neutral *1H–cytosine* molecule through their Watson–Crick and sugar edges (Figure 2.7, Table 2.4). These complementary interactions give rise to zig–zag supramolecular ribbons in which neutral and cationic cytosine molecules alternate. In fact,

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[114] Llunell, M. et al. SHAPE v1.7, **2010**

the protonation of N3 in cytosinium makes its Watson–Crick edge to be fully complementary (three simultaneous hydrogen bonds) with the non protonated Watson–Crick edge of the neutral cytosine. These cationic ribbons establish additional interactions with the $[CoCl_4]^{2-}$ entity through N14–H···Cl1, C25–H···Cl1 and C26–H···Cl2 hydrogen bonds. Additionally, adjacent supramolecular ribbons establish off–set face–to–face π–π stacking interactions (Table 2.4) to reinforce the 3D supramolecular structure.

Table 2.4: Supramolecular interactions (Å, °) of ***COCYTCL***.

Hydrogen bonding interactions.[a]

D–H···A[b]	H···A	D···A	D–H···A
N11–H11···O22[i]	1.97	2.818(3)	169
N13–H13···N23[ii]	2.00	2.857(3)	171
N14–H14A···O22[ii]	1.92	2.783(3)	178
N14–H14B···Cl1[iii]	2.43	3.272(2)	166
N21–H21···O12[i]	1.92	2.781(3)	176
N24–H24A···O12[ii]	2.10	2.944(3)	168

π–π stacking interactions.[c]

Ring···Ring[d]	Angle	DC	α	DZ	DXY
H$_2$Cyt1–HCyt2	2.84(12)	3.745(1)	30.5	3.210(1)	1.923
HCyt2–H$_2$Cyt1	2.84(12)	3.745(1)	31.0	3.226(1)	1.902
HCyt2–HCyt2[iv]	0	3.447(2)	21.3	3.213(1)	1.249

[a] Symmetry: (i) –x+1, –y, –z+1; (ii) –x+1/2, –y+1/2, –z+1; (iii) –x+1/2, y+1/2, –z+3/2; (iv) –x+3/2, –y+1/2,–z+1. [b] **D**: donor, **A**: acceptor. [c] Angle: Dihedral angle between planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] H$_2$Cyt1: N11, C12, N13, C14, C15, C16; HCyt2: N21, C22, N23, C24, C25, C26.

The analysis of the crystal structure shows that employing an acidic media for the synthesis of materials based on the complementary hydrogen interactions between cytosine coordinated discrete comples is not a good option. First of all, it promotes the protonation of the cytosine reducing its capability to coordinate metal centre, and secondly the combination of cytosinium cation and cytosine neutral molecule allows establishing a very stable complementary hydrogen bonding interaction that involves Watson–Crick edge which inhibits or at least makes difficult the coordination of the neutral cytosine to the metal center. In other words, the two easy coordinating positions are protonated (N1) or involved in the above mentioned hydrogen bonding interaction (N3). In fact, other previous studies have shown that the direct binding of a *3d* transition metal to the iminic nitrogen atoms of the nucleobases is rather unusual as a result of the competition between

H bonds to form direct cytosine–cytosine base pairing and the Co–cytosine coordination bond.[91]

(a)

(b)

(c)
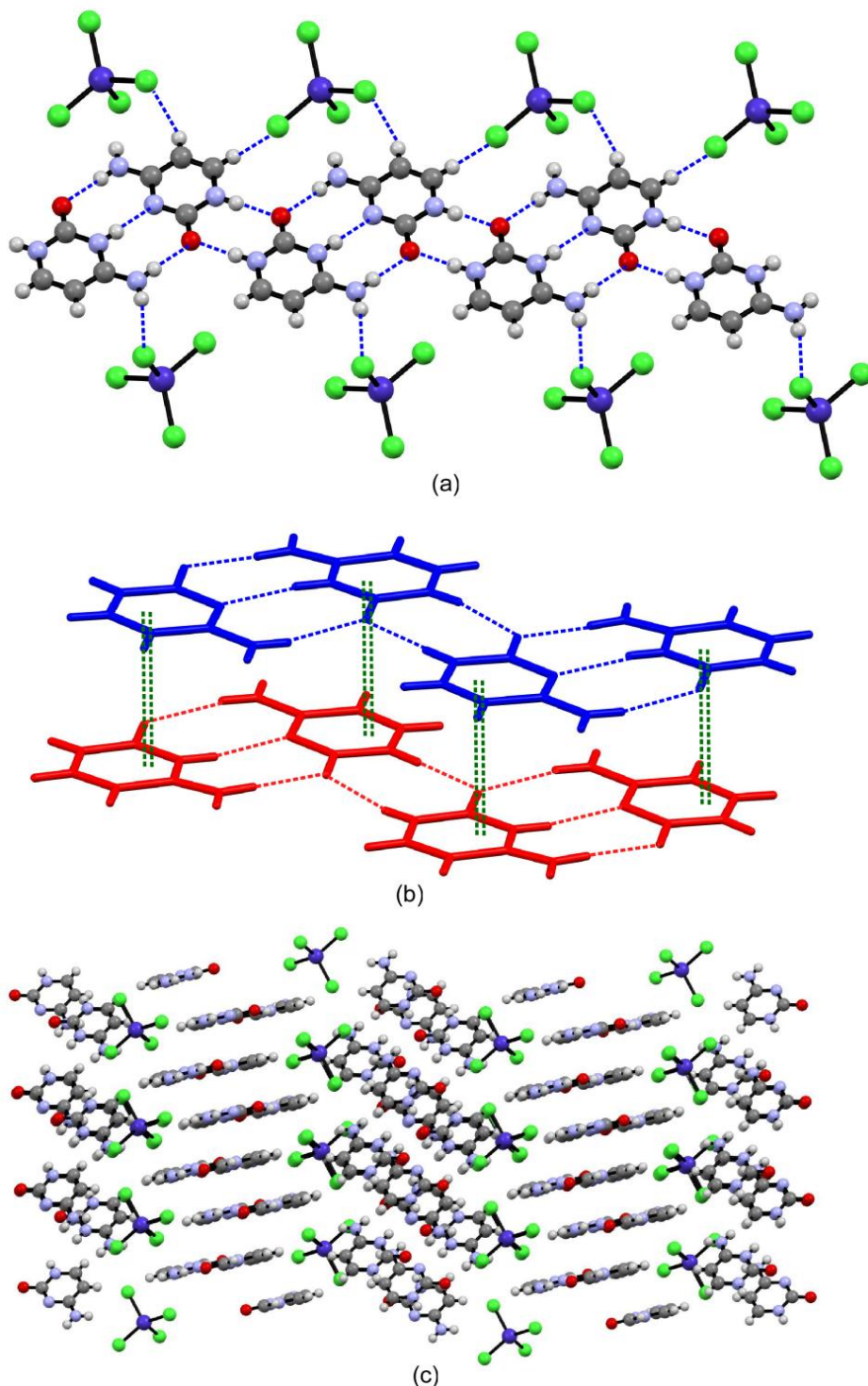
Figure 2.7: (a) Supramolecular ribbons of cytosinium cations and cytosine molecules. (b) π–π stacking interactions among adjacent supramolecular ribbons. (c) Crystal packing of **COCYTCL** viewed along [1 $\bar{1}$ 0] direction. Single dashed lines indicate H–bonds whereas doubles dashed ones correspond to π–π stacking interactions.

2.3.2.2 *Structures of COCYTBR and ZNCYTCL*

The synthesis in non–acidic media permits the coordination of the cytosines through N3 donor positions to give neutral $[CoBr_2(C_4H_5N_3O)_2]$ or $[ZnCl_2(C_4H_5N_3O)_2]$ entities (Figure 2.8). The complex units show a distorted tetrahedral geometry [$S_{tetrahedron}$: 0.67 and S_{square}: 29.09 for *COCYTBR*; $S_{tetrahedron}$: 0.46 and S_{square}: 29.23 for *ZNCYTCL*]. The coordination of the cytosine is reinforced by an intramolecular N–H···X hydrogen bond involving the amine group. These structures are isostructural to those of $[CoCl_2(C_4H_5N_3O)_2]$,[115] $[ZnBr_2(C_4H_5N_3O)_2]$[108] and $[CdBr_2(C_4H_5N_3O)_2]$[116] complexes.

(a) **(b)**
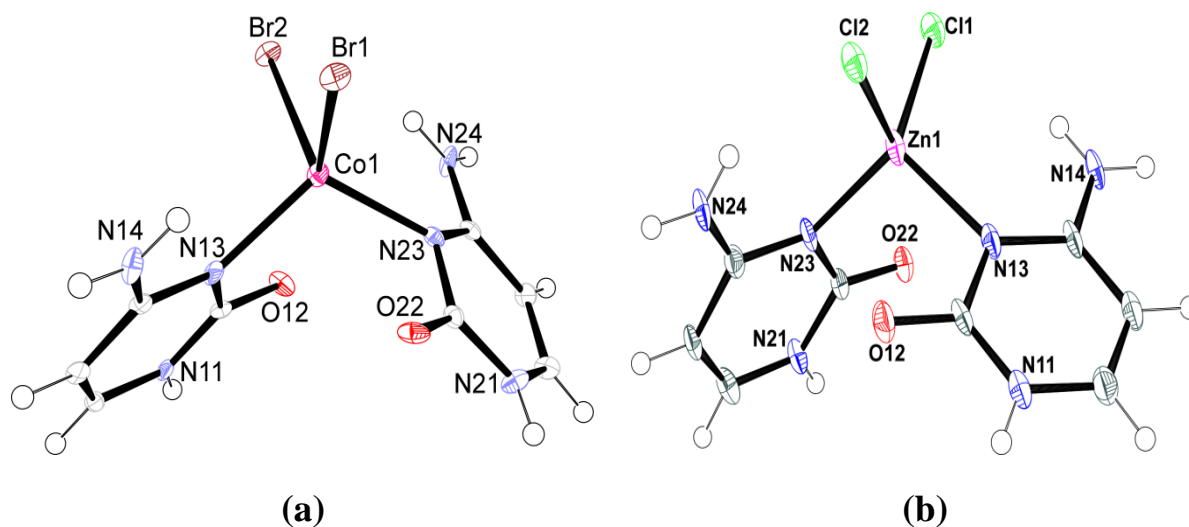
Figure 2.8: Ortep drawing of (**a**) $[CoBr_2(C_4H_5N_3O_2)_2]$ and (**b**) $[ZnCl_2(C_4H_5N_3O_2)_2]$ entities in *COCYTBR* and *ZNCYTCL*, respectively.

The coordination bond distances for Co–N and Zn–N are around 2.037–2.049 Å and 2.045–2.056 Å, respectively, while the Co–Br and Zn–Cl distances are 2.435–2.449 Å and 2.274 and 2.287 Å, respectively. The angles around the metal centre are wider for X–M–X than for N–M–N, which is in agreement with the greater size of halide in comparison with the nitrogen donor atom (Table 2.5).

The cytosine ligands expose the sugar and Hoogsteen edges outwards the monomeric entity, being ready to establish hydrogen bonding interactions. Only one of the coordinated cytosine is able to establish double complementary hydrogen bonds with the sugar edge of an adjacent cytosine. This allows the formation of supramolecular dimers of these discrete

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[115] Tran Qui, D.; Bagieu, M. *Acta Crystallogr. Sect.C:Cryst. Struct. Commun*. **1990**, *46*, 1645.

[116] Muthiah, P. T. et al. *Acta Crystallogr. Sect. E, Struct. Rep. Online*, **2001**, *E57*, m558.

entities (Figure 2.9a), but it is far from the final goal of obtaining a 3D self assembled material through complementary hydrogen bonding interactions. However, taking into account that in compound *COCYTCL*, we could not achieve even a metal–nucleobase discrete entity, compounds *COCYTBR* and *ZNCYTCL* can be considered as a step forward in the intended direction.

Table 2.5: Selected coordination bonds (Å) and angles (º) in compounds *COCYTBR* and *ZNCYTCL*.

COCYTBR					*ZNCYTCL*		
Co1–Br1	2.4487(12)	Br1–Co1–Br2	102.21(4)	Zn1–Cl1	2.287(2)	Cl1–Zn1–Cl2	105.44(7)
Co1–Br2	2.4353(11)	Br1–Co1–N13	114.39(14)	Zn1–Cl2	2.274(2)	Cl1–Zn1–N13	115.04(17)
Co1–N13	2.049(5)	Br1–Co1–N23	111.41(15)	Zn1–N13	2.056(5)	Cl1–Zn1–N23	111.64(19)
Co1–N23	2.037(5)	Br2–Co1–N13	102.84(15)	Zn1–N23	2.045(5)	Cl2–Zn1–N13	104.09(19)
		Br2–Co1–N23	114.77(14)			Cl2–Zn1–N23	114.33(17)
		N13–Co1–N23	110.78(19)			N13–Zn1–N23	106.3(2)

Anyway, on moving forward with the supramolecular crystal structure of this compound, it can be observed that the 3D cohesiveness is ensured by π–π stacking interactions and a exhaustive network of non complementary hydrogen bonding interactions taking place between the sugar edge of the second cytosine, the amine group of the cytosines and the bromide anions of adjacent complex entities (Figure 2.9b–d; Table 2.6).

Table 2.6: Supramolecular interactions (Å, º) of *COCYTBR*/*ZNCYTCL*.

Hydrogen bonding interactions.[a]

D–H···A[b]	*H···A*	*D···A*	*D–H···A*
N11–H11···O12[i]	1.89/1.98	2.740(6)/ 2.784(8)	162/151
N14–H14A···Br1/Cl1	2.73/2.56	3.588(5)/ 3.419(6)	165/165
N14–H14B···Br2[ii]/Cl2 [ii]	3.12/3.32	3.877(5)/ 4.024(6)	146/139
N21–H21···Br1 [iii] /Cl1 [iii]	2.65/2.54	3.434(5)/ 3.326(6)	150/149
N24–H24A···Br2/Cl2	2.62/2.46	3.455(5)/ 3.281(6)	158/155
N24–H24B···O22[iv]	2.16/2.10	2.995(7)/ 2.928(7)	158/156

π–π stacking interactions.[c]

Ring···Ring [d]	Angle	DC	α	DZ	DXY
HCyt1–HCyt1^v (*COCYTBR*)	0	3.557(3)	23.71	3.257(2)	1.430
HCyt1–HCyt1^v (*ZNCYTCL*)	0	3.576(4)	25.56	3.226(3)	1.543

[a] Symmetry: (i) −x+1, −y,−z; (ii) −x, −y+1, −z; (iii) x, y−1, z; (iv) x+1, y, z; (v) −x, −y, −z. [b] **D**: donor, **A**: acceptor. [c] Angle: Dihedral angle between planes I and J (º), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] HCyt1: N11, C12, N13, C14, C15, C16.
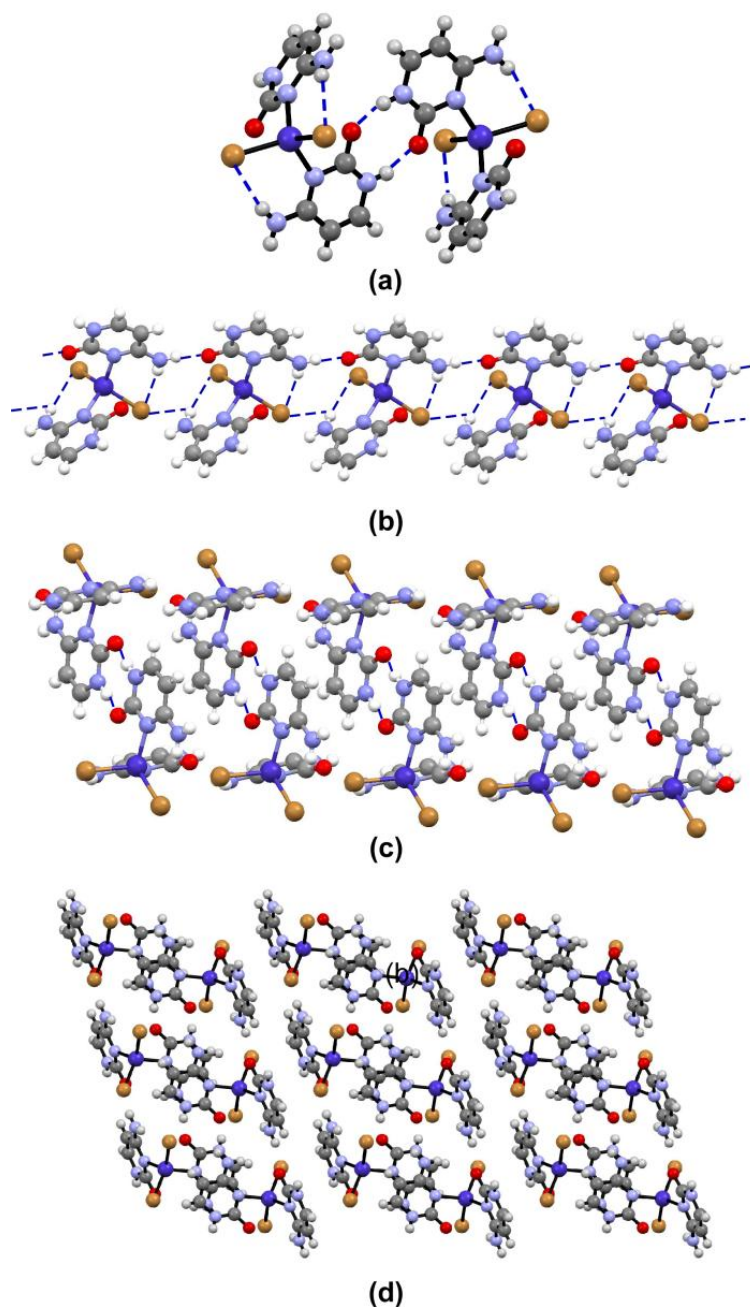
Figure 2.9: (a) Supramolecular dimeric entity. (b) Infinite chains joined by non–complementary supramolecular interactions. (c) Supramolecular ladder like chains as the result of hydrogen bonding interactions. (d) Crystal packing of *COCYTBR* viewed along the crystallographic b axis.

2.3.2.3 *Structure of CUCYTCL–B*

The crystal structure of compound **CUCYTCL–B** contains $[CuCl_2(C_4H_5N_3O)_2]$ neutral units. Previously, Tran Qui and Palacios reported the crystal structure of a different polymorph of the same compound, $[CuCl_2(C_4H_5N_3O)_2]$ (**CUCYTCL–A**).[91] The synthesis procedure seems to indicate that **CUCYTCL–A** corresponds to a kinetically preferred crystal structure, as it is obtained immediately after mixing the reagents. The crystal structure of the novel polymorph that is reported here (**CUCYTCL–B**) seems to correspond to the thermodynamically preferred one as it is obtained upon slow evaporation of the mother liquid after filtering out the blue powder belonging to **CUCYTCL–A**. We have also performed several attempts modifying the synthesis temperature but in all cases the result is the same: first **CUCYTCL–A** precipitates out and crystals belonging to **CUCYTCL–B** appears only after subsequent slow evaporation of the filtrate. Additionally, we have performed thermodiffractometric measurements to identify any possible phase transition between the two polymorphs but both of them remain unaltered upon cooling or moderate heating. The crystal structure of both polymorphs is comprised of $[CuCl_2(C_4H_5N_3O)_2]$ complexes in which the central copper(II) ion is coordinated to two chloride ions and to the endocyclic N3 nitrogen atom of two cytosine molecules. However, the space group changes from $P2_1/n$ to $P\bar{1}$. However, both crystal structures show a nearly planar copper(II) coordination environment, the deviation from the ideal geometry is greater for the first polymorph than for **CUCYTCL–B** [**CUCYTCL–A**: S_{square}: 2.37 and $S_{tetrahedron}$: 27.50; **CUCYTCL–B**: S_{square}: 0.57 and $S_{tetrahedron}$: 33.71]. In both crystal structures, the cytosine mean plane is twisted with respect to the coordination mean plane, with dihedral angles of 88.38/84.56º for **CUCYTCL–A** and 75.96º for **CUCYTCL–B**. The two coordinated cytosines are strictly coplanar for **CUCYTCL–B** and nearly coplanar for **CUCYTCL–A** (dihedral angle of 7.56º). Additionally, **CUCYTCL–A** presents an intramolecular hydrogen bond, which is not present in **CUCYTCL–B**. This could be probably because of the shortening of the coordination bond distances (Table 2.7; Figure 2.10a–b) that generates a greater steric hindrance which hinders the amine and keto groups of the two coordinated cytosines to get closer enough to establish hydrogen bonding interactions. The presence of the intramolecular hydrogen bond in the compound **CUCYTCL–A**, deviates the N–Cu–N angle from 180º and as a consequence significant differences can also be observed at the semi–coordination contacts: two contacts are found for **CUCYTCL–B** but only one, although shorter, is present in **CUCYTCL–A**. Figure 2.10c

shows a superposition of both crystal structures in which these differences are observable. The cytosine molecules of the compound ***CUCYTCL–B*** self assemble through complementary hydrogen bonding interactions along the sugar edges, giving rise to a 1D chain (Table 2.8, Figure 2.11).
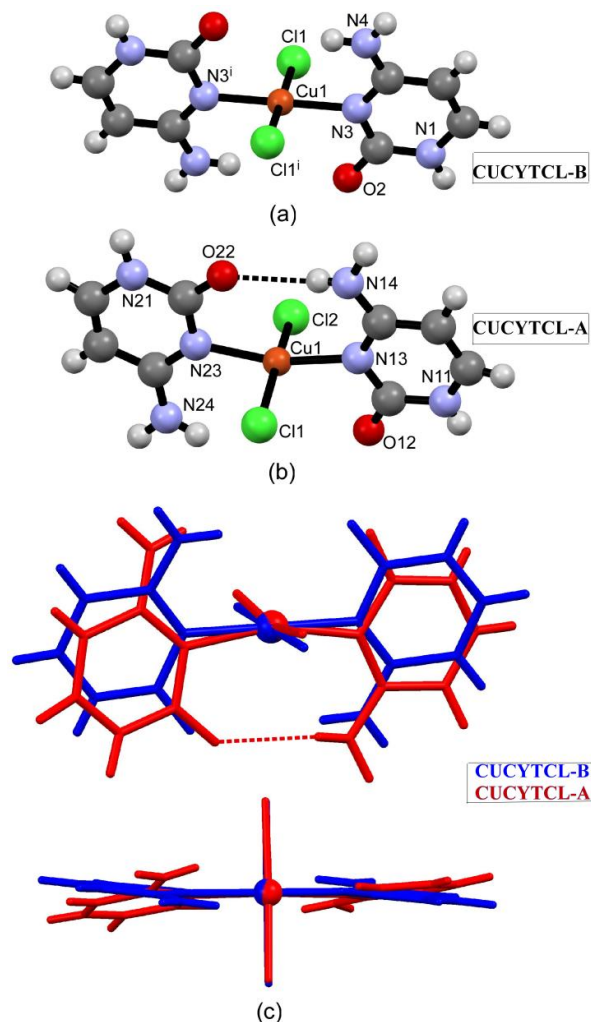
Figure 2.10: Drawing showing the structure of the $[CuCl_2(C_4H_5N_3O)_2]$ discrete entity of (a) ***CUCYTCL–B*** and (b) ***CUCYTCL–A***. (c) Overlay of both structures.

Table 2.7: Selected coordination bond lengths (Å) and angles (º) in compound ***CUCYTCL–A***[a] and ***CUCYTCL–B***.[b]

CUCYTCL–A[a]				*CUCYTCL–B*[b]			
Cu1–Cl1	2.299(1)	Cl1–Cu1–Cl2	165.74(6)	Cu1–Cl1	2.2990(7)	Cl1–Cu1–Cl1^i	180(–)
Cu1–Cl2	2.267(1)	Cl1–Cu1–N13	92.17(12)	Cu1–N3	1.975(2)	Cl1–Cu1–N3^i	90.26(7)
Cu1–N13	1.985(4)	Cl1–Cu1–N23	89.66(12)	Cu1···O2	2.824(2)	Cl1^i–Cu1–N3^i	89.74(7)
Cu1–N23	1.996(3)	Cl2–Cu1–N13	92.40(12)			N3–Cu1–N3^i	180(–)
Cu1···O22	2.779(5)	Cl2–Cu1–N23	90.14(12)				
		N13–Cu1–N23	162.11(16)				

[a] Data taken from reference [91]. [b] Symmetry: (i) –x+2, –y, –z+2.

(a)

(b)
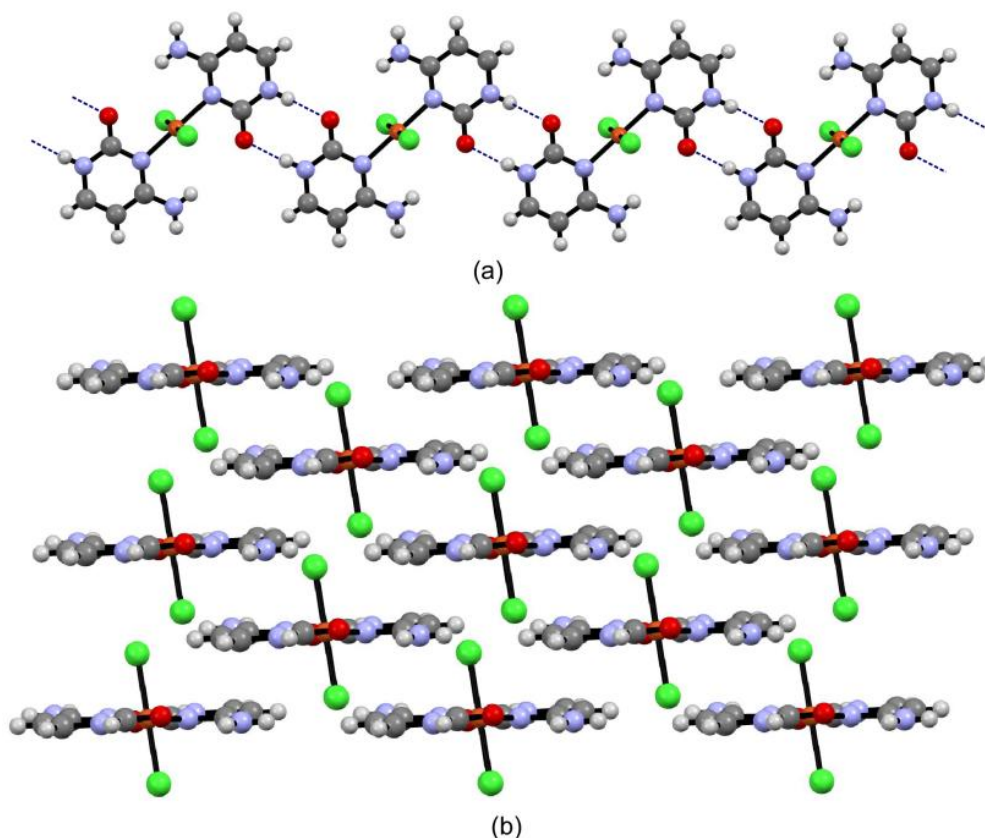
Figure 2.11: (a) Supramolecular chain of cytosine···cytosine complementary hydrogen bonded [CuCl$_2$(C$_4$H$_5$N$_3$O)$_2$] discrete entities and (b) crystal packing in *CUCYTCl–B*.

Table 2.8: Supramolecular interactions (Å, °) of *CUCYTCL*.

Hydrogen bonding interactions.[a]

D–H···A[b]	H···A	D···A	D–H···A
N1–H1···O2^i	1.93	2.784(3)	175
N4–H4B···Cl1^{ii}	2.59	3.391(2)	154

π–π stacking interactions.[c]

Ring···Ring [d]	Angle	DC	α	DZ	DXY
HCyt–HCyt^{iii}	0	3.457(2)	18.22	3.284(1)	1.081

[a] Symmetry: (i) –x+1, –y+1, –z+1; (ii) x, y+1, z;(iii) –x+2, –y+1, –z+1. [b] **D**: donor, **A**: acceptor. [c] Angle: Dihedral angle between planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I–> Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] HCyt: N11, C12, N13, C14, C15, C16.

2.3.2.4 *Structure of CUCYTBR*

The crystal structure of compound *CUCYTBR* is isostructural to the crystal structure of *CUCYTCL–A*. There is no reported case of a second polymorph isostructural to

CUCYTCL–B and the attempts to obtain this polymorph were not successful although many different synthetic conditions were tried. The crystal structure is comprised of $[CuBr_2(C_4H_5N_3O)_2]$ complexes in which the central copper(II) ion is coordinated to two bromide ions and to the endocyclic N3 nitrogen atom of two cytosine molecules (Figure 2.12). Selected bond angles and bond lengths are given in Table 2.9. Due to the greater steric hindrance of the bromide ions in comparison to chloride, the coordination geometry is more distorted but still closer to a square planar one than to a tetrahedron [S_{square}: 2.54 and $S_{tetrahedron}$: 23.14]. The two coordinated cytosines are nearly coplanar (dihedral angle of 7.45°) but almost perpendicular to the coordination mean plane with dihedral angles of 84.13 and 88.72°. An intramolecular hydrogen bond is established between the amino and keto groups of the two coordinated cytosine molecules at one side of the complex but not at the other. The supramolecular crystal structure is like that of the previously described example ***CUCYTCL–A***. The hydrogen bonding parameters are given in Table 2.10.
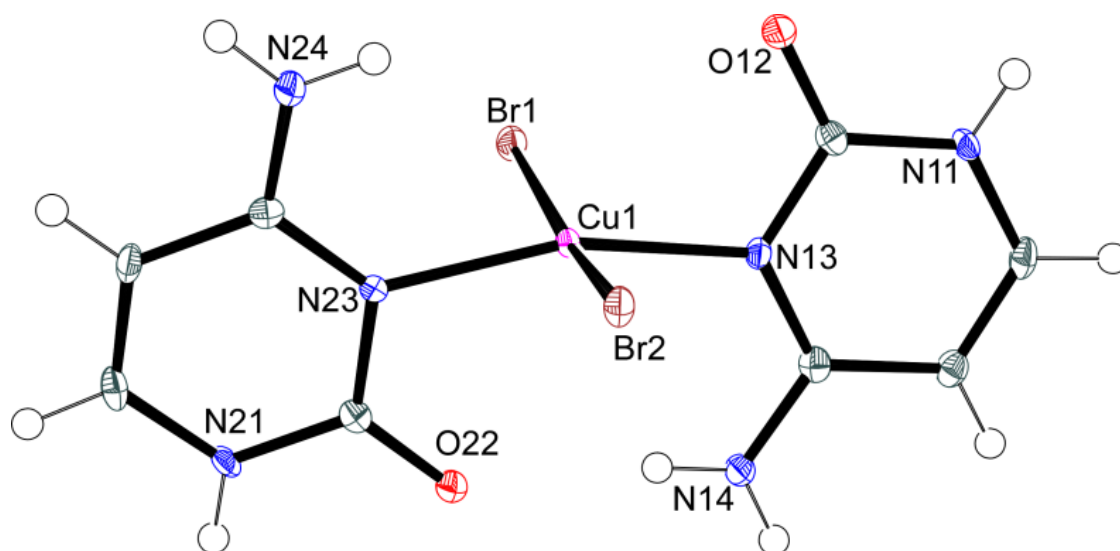
Figure 2.12: Ortep drawing of $[CuBr_2(C_4H_5N_3O)_2]$ complex with labelling scheme.

Table 2.9: Selected coordination bond lengths (Å) and angles (°) in compound ***CUCYTBR***.[a]

Cu1–Br1	2.4024(5)	Br1–Cu1–Br2	168.03(2)
Cu1–Br2	2.4294(5)	Br1–Cu1–N13	92.62(7)
Cu1⋯O22	2.761(2)	Br1–Cu1–N23	89.92(7)
Cu1–N13	1.970(2)	Br2–Cu1–N13	91.80(7)
Cu1–N23	1.985(2)	Br2–Cu1–N23	89.12(7)
		N13–Cu1–N23	162.86(10)

Table 2.10: Supramolecular interactions (Å, °) of *CUCYTBR*.

Hydrogen bonding interactions.[a]

D–H⋯A[b]	H⋯A	D⋯A	D–H⋯A
N11–H⋯O12[i]	2.01	2.843(3)	162
N14–H⋯O22	2.12	2.976(3)	173
N14–H⋯Br1[ii]	2.75	3.520(2)	150
N21–H⋯Br2[iii]	2.47	3.245(2)	150
N24–H⋯Br2[iv]	2.61	3.388(2)	151
N24–H⋯O22	2.12	2.971(3)	170

π–π stacking interactions.[c]

Ring⋯Ring[d]	Angle	DC	α	DZ	DXY
HCyt1–HCyt2[v]	6.66(14)	3.609(2)	22.62	3.439	1.388
HCyt2–HCyt1[vi]	6.66(14)	3.609(2)	17.65	3.311	1.094

[a] Symmetry: (i) –x+2, –y+1, –z; (ii) –x+3/2, y–1/2, –z+1/2; (iii) x–1/2, –y+1/2, z+1/2; (iv) –x+1, –y+1,–z; (v) 1+x, y, z; (vi) 1+x, y, z: [b] **D**: donor, **A**: acceptor. [c] Angle: Dihedral angle between planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] HCyt1: N11, C12, N13, C14, C15, C16; HCyt2: N21, C22, N23, C24, C25, C26.

2.3.2.5 *Structure of CUCYTSO4*

The crystal structure of **CUCYTSO4** $\{[Cu(C_4H_5N_3O)_4](SO_4)\cdot2(MeOH)\}$ consists of $[Cu(HCyt)_4]^{2+}$ cationic units where the N3 nitrogen atoms of the four cytosines are coordinated to the equatorial positions of the central copper atom. These four nitrogen atoms define the equatorial plane with a maximum deviation of 0.014 Å from planarity. The metal atom is placed over a binary rotation axis and show no deviation from the equatorial mean plane. The oxygen atoms of the cytosine keto group establishes four additional short contacts of 2.6037(18) and 2.9543(17) Å to provide a relatively unusual (4 + 2) + 2 coordination surrounding (Figure 2.13; Table 2.11).

The molecular structure of the $[Cu(C_4H_5N_3O)_4]^{2+}$ discrete entity is reinforced by the presence of bifurcated intramolecular hydrogen bonds among the amine and keto groups of the cytosines (Figure 2.14), which increases its rigidity with the presence of four cytosines able to establish complementary hydrogen bonding interactions through their sugar edges in four non–coplanar directions (Figure 2.15). Therefore, if the predicted supramolecular interactions would take place, the resulting material probably would be porous because of

an inefficient occupation of the space due to the rigidity of both the secondary building unit and the synthons.

(a)
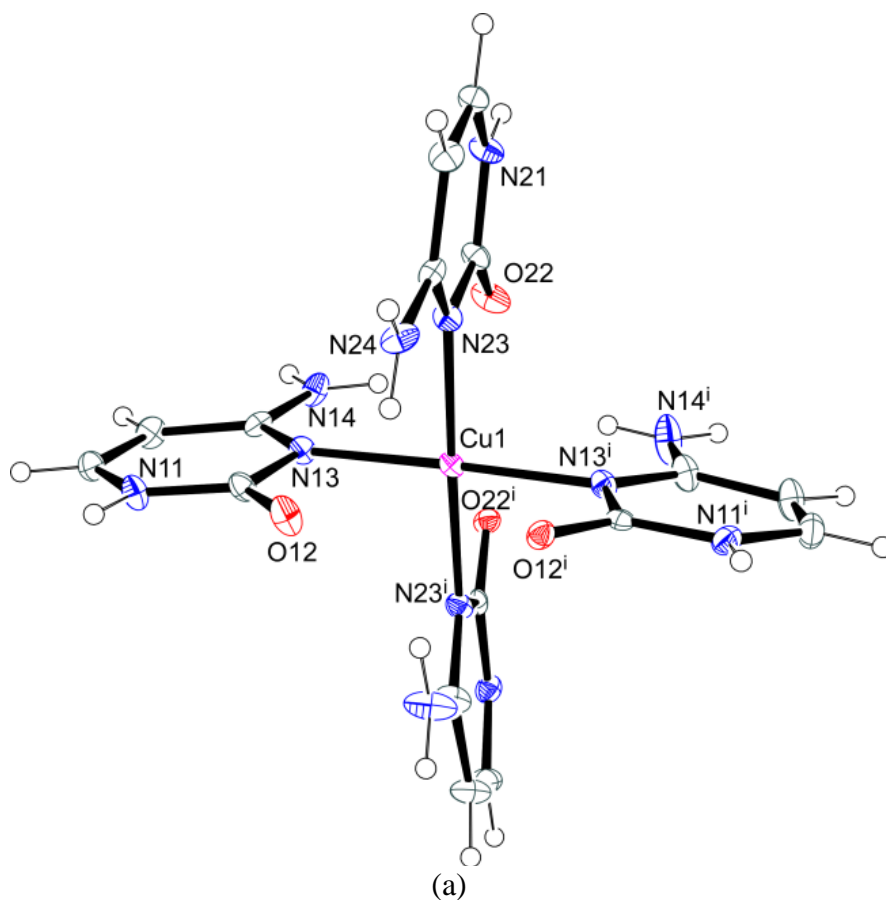
Figure 2.13: Ortep drawing of $[Cu(C_4H_5N_3O)_4]^{2+}$ complex entity in *CUCYTSO4*.
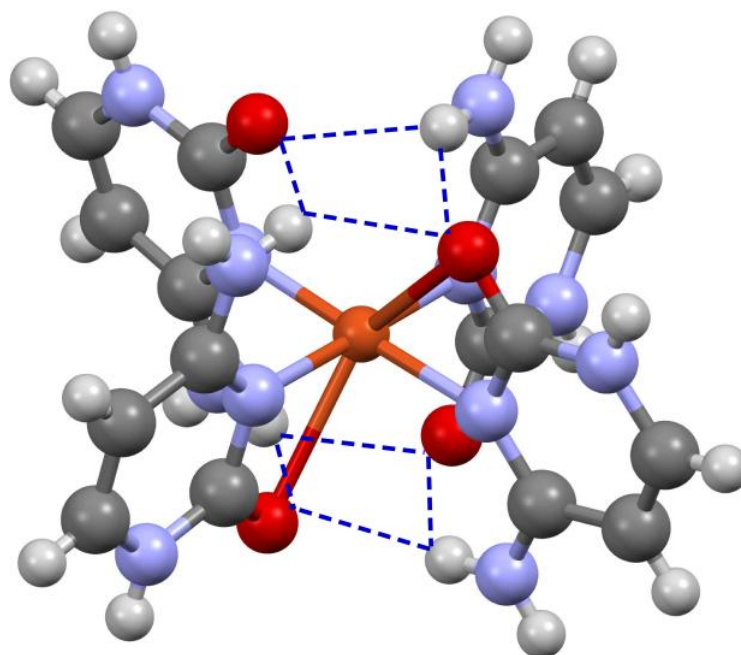
Figure 2.14: Intramolecular bifurcated hydrogen bonding.
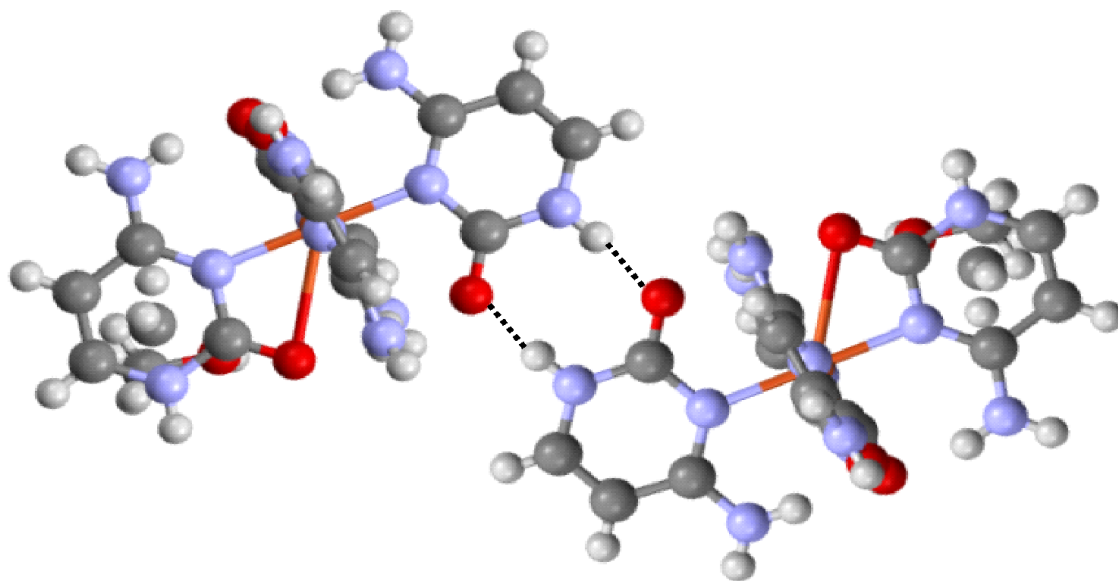
Figure 2.15: Hypothetical complementary base pairing interactions between the sugar edges of cytosine moeties in *CUCYTSO4*.

However, the presence of solvent molecules or counterions can disrupt the complementary base pairing interactions that we are trying to use as the structure directing agents. This could be especially relevant when strong hydrogen bond donor or acceptor molecules/ions are present. This happens in the case of the compound *CUCYTSO4* in which, instead of establishing the predicted cytosine···cytosine interaction, the sulphate counterion interacts with the sugar edge of the nucleobase giving rise to a different crystal structure. As a result, the interactions between adjacent cytosines follow a non conventional hydrogen bonding pattern as shown in Figure 2.16, that involves the presence of an, otherwise repulsive, close contact between keto···keto groups. This interaction gives rises to supramolecular ribbons of $[Cu(C_4H_5N_3O)_4]^{2+}$ discrete entities. Methanol solvent molecules and sulphate counterions occupy the voids within the packing of the supramolecular ribbons, establishing hydrogen bonding interactions by acting as acceptors with the iminium and amine groups of the cytosine.

In addition to this complex network, there exists hydrogen bonding interactions between the oxygen atoms of the sulphate anion and solvated methanol molecule as acceptors and the N4–H and N1–H of cytosines as donors. Further, there are intermolecular interactions occurring between adjacent $[Cu(C_4H_5N_3O)_4]^{2+}$ complexes in a head to tail arrangement. Hydrogen bonding parameters are given in Table 2.12.

(a)   (b)
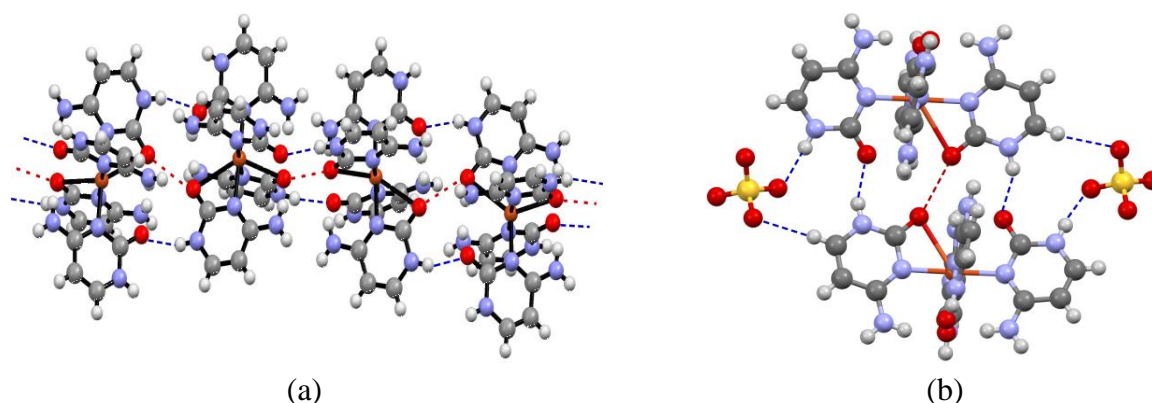
Figure 2.16: (a) Hydrogen bonding interactions between the $[Cu(C_4H_5N_3O)_4]^{2+}$ complex entity in ***CUCYTSO4***. (b) Hydrogen bonding interactions of the $[Cu(C_4H_5N_3O)_4]^{2+}$ units with the sulphate counterions.

Table 2.11: Selected coordination bond lengths (Å) and angles (º) in compound ***CUCYTSO4***.[a]

Cu1–N13	2.029(2)	N13–Cu1–N13[i]	90.89(13)
Cu1–N23	2.021(2)	N13–Cu1–N23	90.59(9)
Cu1···O12	2.604(2)	N13–Cu1–N23[i]	178.32(9)
Cu1···O22	2.954 (2)	N23–Cu1–N23[i]	87.94(13)

[a]Symmetry codes: (i) –x+2, y, –z+2.

Table 2.12: Hydrogen bonding interactions (Å, º) of ***COCYTSO4***.[a]

D–H···A[b]	H···A	D···A	D–H···A
N11–H11···O22[i]	2.03	2.847(3)	159
N14–H14B···O3[ii]	2.03	2.866(3)	164
N14– H14A···O12[iii]	2.30	3.000(3)	138
N14 –H14A···O22	2.38	2.928(3)	122
N21–H21···O2	1.98	2.833(3)	170
N21–H21···S1	2.82	3.593(2)	151
N24–H24A···O22[iii]	2.32	2.956(3)	131
N24–H24A ··O12	2.32	2.991(4)	135
N24–H24B ··O4[iv]	1.99	2.843(3)	172
O3–H3 ··O1	2.00	2.850(3)	162
O3–H3···S1	2.72	3.428(2)	138
O4–H4···O2[v]	1.86	2.788(3)	171

[a]Symmetry codes: (i) y, –x+2, z+1/4; (ii) –y+1, –x+2, –z+7/4; (iii) –x+2, y, –z+2; (iv) y, x, –z+9/4; (v) –x+1, y, –z+2. [b] **D**: donor, **A**: acceptor.

As briefly described in previous paragraph, the hydrogen bonding scheme depicts that, the neighbouring monomeric units are sequentially bound by a double hydrogen bond

among the pyrimidinic proton and the exocyclic oxygen atom (N11–H11···O22). However, these array of monomers present oxygen···oxygen distances of 2.719 Å between neighbouring entities, which is relatively short and accounts for a repulsive interaction that would make the supramolecular strip unstable unless other interactions coming from the array itself or from the crystal packing overcome it. Thus, in order to determine the structural features that make these array stable in the crystal structure, geometry optimization calculations were performed on a finite structural model consisting of two interacting monomers by using dispersion–corrected density–functional theory calculations with the code DMOL3.[117] The PBE exchange–correlation functional was used in the calculations,[118] together with the "D2" flavour of the dispersion correction scheme proposed by Grimme.[119] Figure 2.17 shows the computed structural model together with the numbering scheme and monitored intermolecular interactions.
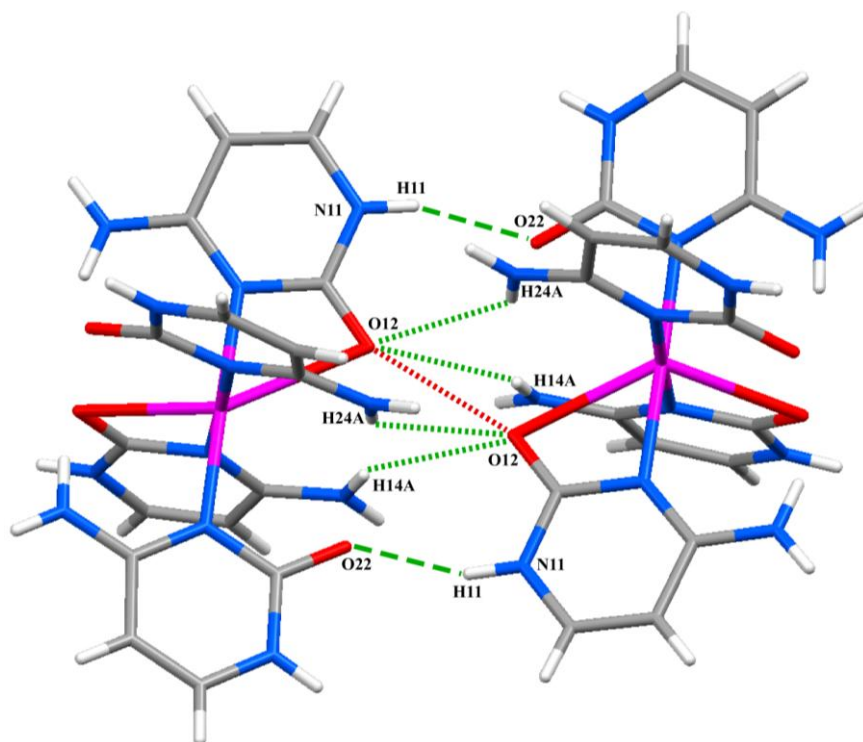
Figure 2.17: Structural model for the DFT–D geometry optimization showing the numbering scheme.

Table 2.13 shows a comparison between relevant distances belonging to the pristine crystal structure and to the computed structure. The similarity among the coordination

[117] (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. (b) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.
[118] Perdew, J. P. et al. *Phys. Rev. Lett.* **1996**, *77*, 3865.
[119] Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

bond distances (along with all the intra–monomer distances) of the optimized model and of the experimental structure supports the suitability of the employed computational method. As depicted in Figure 2.17 and Table 2.13, to assess the stability of the these supramolecular aggregates, a hydrogen bonding interaction (N11–H11···O22), three interactions of electrostatic nature (O12···O12, H14A···O12, H24A···O12) and Cu···Cu distances were considered. Figure 2.18 shows the electrostatic potential (ESP) surface and charges on selected atoms.

Table 2.13: Distances for coordination bonds and intermolecular interaction between two $[Cu(Hcyt)_4]^{2+}$ in the optimized structure and crystal structure.

Coordination bond distances (Å)			Intermolecular interactions (Å)		
	Optimized structure	Crystal structure		Optimized structure	Crystal structure
Cu1–N13	2.132	2.029	O12···O12	2.828	2.719
Cu1–N23	2.134	2.021	N11–H11···O22[i]	1.875	2.029
Cu1–O12	2.650	2.604	N14–H14A···O12	2.859	2.916
Cu1–O22	2.925	2.954	N14–H24A···O12	2.409	2.717
			Cu···Cu	6.851	6.942

Symmetry code: y, –x+2, z+1/4

ESP charges

Cu	+0.920
O12	−0.744
O22	−0.693
H14A	+0.470
H24A	+0.483
H11	+0.379
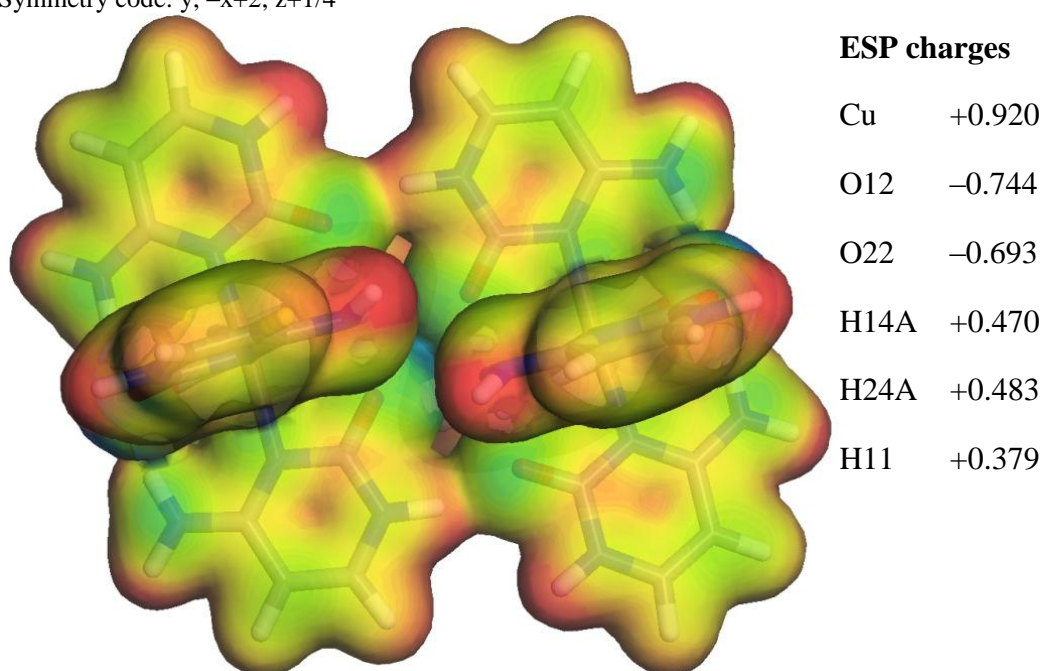
Figure 2.18: (Left) Electrostatic potential upon an electronic isosurface of 0.01 a.u. (Right) Electrostatic potential (ESP) charges for metal center and for atoms implied in the intermolecular interactions.

According to the results, the repulsive 'oxygen···oxygen' interaction leads to a slight increase (*ca*. 0.1 Å) of the O12···O12 distance, while the distances between all the atom pairs involved in attractive interactions are shortened by 0.1–0.3 Å. Moreover, in

agreement with Cu···Cu distance, both the entities get 0.1 Å closer when the supramolecular aggregate is relaxed, which stands for the stability of the 1D array.

2.3.3   Thermal analysis

Figure 2.19 and Table 2.14 show the thermal behaviour (TG/DTA) of the ***COCYTBR***, ***CUCYTCL–B*** and ***CUCYTBR***, performed upon synthetic air atmosphere (79% N_2, 21% O_2).
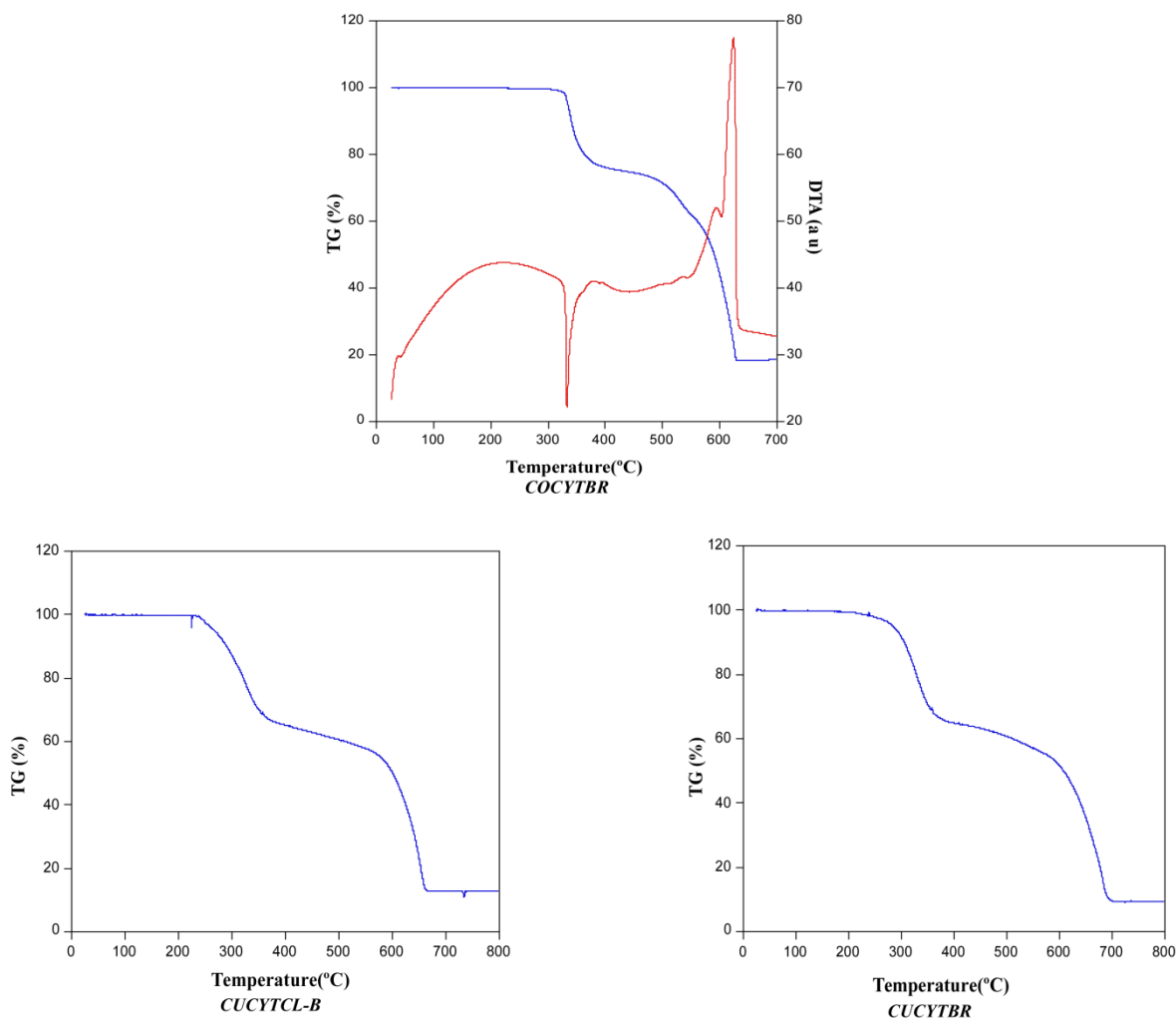
Figure 2.19: Thermogravimetric analysis of ***COCYTBR***, ***CUCYTCL***, ***CUCYTBR***.

All three compounds present a relatively high thermal stability and start decomposing at temperatures above 250–315ºC. This is a relevant aspect because although these crystal structures do not present the desired porous structure, the crystal structures of ***COCYTBR, CUCYTCL–B*** and ***CUCYTBR*** are composed of neutral metal–nucleobase entities that are assembled together by hydrogen bonding interactions. Therefore, these compounds could advance the thermal stability of the supramolecular porous materials that we are pursuing. On the other hand, the first decomposition stage correspond to an

endothermic process for ***COCYTBR***, that may indicate it is not due to a combustion reaction, that are usually exothermic, but to an internal reaction that implies the release of some of the components of the corresponding compound probably as volatile hydrogen halide. For compounds ***CUCYTCL–B*** and ***CUCYTBR***, a similar explanation can be assumed for this first decomposition stage. However the explanation is unsure as this step corresponds to an exothermic process for ***CUCYTCL–B*** and overlapped exo–endothermic processes for ***CUCYTBR***. After this first stage, the thermal decomposition continues further in several, and usually overlapped, processes to provide Co_3O_4 or CuO as final residues.

Table 2.14: Thermoanalytic data for ***COCYTBR***, ***CUCYTCL*** and ***CUCYTBR***.

Step	T_i	T_f	T_{peak}	$\Delta m(\%)$	ΔH	$\Sigma\Delta m(\%)$	$\Sigma\Delta m(\%)_{theor}$
COCYTBR							
1	325	420	331	24.7	Endo	24.7	25.19(–1 $C_4N_3H_5O$)
2	440	660	624	56.97	Exo	81.67	81.79 (1/3 Co_3O_4)
CUCYTCL–B							
1	25	365	–	33	–	33.00	31.15 (–1 $C_4H_5N_3O$)
2	530	665	–	45.98	–	78.98	77.60 (CuO)
CUCYTBR							
1	25	400	–	35.17	–	35.17	36.30 (–2 HBr)
2	540	700	–	48.76	–	83.93	82.15 (CuO)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released fragments and final residue per formula.

2.4 CONCLUSIONS

In order to achieve the first step towards our goal: a porous 3D supramolecular network sustained by complementary hydrogen bonding interactions between discrete metal–nucleobase entities, it is mandatory to use a non–acidic reaction media for cytosine. This is easy understandable as protonation reduces the cytosine coordination capabilities; but even if not all cytosines are protonated, the cytosine···cytosinium complementary hydrogen bonding interactions preclude the coordination of the remaining neutral cytosines to the metal center (***COCYTCL***). On the other hand, when cytosine is coordinated, it uses N3 position to bind metal center and therefore complementary hydrogen bonding

interactions can only take place through the sugar–edge of the cytosine (2 x N1–H and O2).

Under these conditions, if only two cytosines are coordinated, at the most 1D infinite supramolecular chains are obtained through cytosine⋯cytosine complementary hydrogen bonds. Depending on the coordination sphere geometry, these chains would change from zig–zag ones for tetrahedral geometry (Co^{II} metal center) to linear ones for *trans* arranged square planar geometry (Cu^{II}, *CUCYTCL–B*). Apart from that, in many cases other supramolecular interactions such as N–H⋯X (halide) can disrupt these complementary hydrogen bond interactions as seen in compounds *COCYTBR*, *ZNCYTCL*, *CUCYTCL–A* and *CUCYTBR*.

Taking all these previous results into account, it becomes evident that in order to achieve a 3D supramolecular material it would be necessary to increase the number of coordinated cytosines, preferably to four of them in a non–coplanar disposition. This goal was achieved with the synthesis of *CUCYTSO4*, comprised of cationic [Cu(cytosine)$_4$]$^{2+}$ complexes and SO$_4^{2-}$ counterions. However, the crystal structure of this compound did not show the predicted complementary hydrogen bonding interactions between adjacent cytosines because of the presence of the strong hydrogen bond acceptor SO$_4^{2-}$ anions which disrupt these complementary hydrogen bonding interactions. This result shows that not only the design of the supramolecular secondary building units are important but also the presence of other hydrogen bonding competitors in the reaction media, such as counterions or even solvent molecules that could disrupt the direct hydrogen bonding interactions between the nucleobases. Therefore, it becomes clear that in order to achieve the corresponding porous 3D supramolecular network we must design not only the supramolecular building unit but also the synthetic conditions.

Other fact that has become evident is that, each cytosine molecule anchored to the metal centre through N3 (it's preferred coordination position) can only establish complementary hydrogen bonding interactions with just one adjacent cytosine, that limits connectivity and dimensionality of the resulting hydrogen bonding network. This fact makes purine nucleobases specially appealing to meet our objective, because they present more than one edge capable of establishing complementary hydrogen bonding interactions and therefore they can be connected to more than one adjacent nucleobases through hydrogen bonding. It would make easier to achieve the goal of obtaining 3D

supramolecular networks as the number of required coordinated nucleobases per metal centre is reduced.

Chapter 3

Supramolecular metal–organic frameworks based on metal/purine systems

3.1 Introduction

3.2 Synthesis and chemical characterization

3.3 Results and discussion

3.4 Conclusions

3.1 INTRODUCTION

As it was concluded in the previous chapter, using purine nucleobases as ligands take the advantage of their multiple binding and hydrogen bonding positions. It means that the nucleobase can be anchored to the metallic centres through different positions giving rise to extended systems or discrete complex entities. The first case has been previously exploited by our research group to provide MOFs sustained by coordination bonds, usually called as MBioFs.[120] There are many reported examples for discrete complex entities as those depicted in Figure 3.1.[121] Those entities are able to establish complementary hydrogen bonding interactions between adjacent units as it has been seen for the cytosine analogues. However, at one hand they provide the advantage of the increased rigidity of the supramolecular building blocks, because of the coordination through multiple positions, and on the other, they present more edges capable of establishing complementary hydrogen bonding interactions. Therefore, the correct selection of the metal–nucleobase discrete entities in such a way that they provide a non coplanar disposition of the nucleobases could provide the desired supramolecular porous materials that we are looking for.

$[Cu_2(\mu–ade)_4Cl_2]^{2+}$ $[Co(ade)_2Cl_2]$ $[Co(thiogua)_3]$
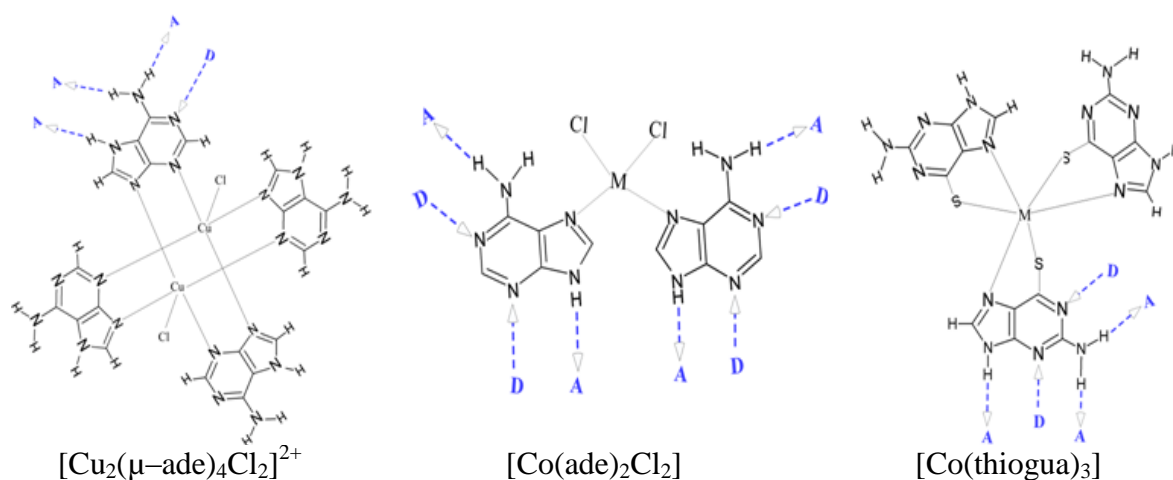
Figure 3.1: Metal–nucleobase discrete entities suitable for the synthesis of *SupraMOFs*.

[120] (a) Pérez–Yáñez, S. et al. *Chem. Commun*. **2012**, *48*, 907. (b) Pérez–Yáñez, S. et al. *Cryst. Growth Des*. **2013**, *13*, 3057.

[121] (a) de Meester, P.; Skapski, A. C. *J. Chem. Soc. A*, **1971**, 2167. (b) Lee, C. F. et al. *J. Chem. Soc. Dalton Trans*. **1993**, *1*, 467. (c) Schmalle, H. W. et al. *Acta Crystallogr. Section C, Cryst. Struct. Commun*. **2000**, *56*, 957.

Adenine (Figure 3.2) is ideal for building up MOFs because it has an imidazolate ring which can imitate the imidazolate derivatives, it is rigid which helps the formation of permanent porous materials, and it has also multiple possible coordination sites allowing the construction of a topologically diverse family of materials.[122,64] As mentioned above, adenine has a wide range of binding possibilities through the endocyclic imino nitrogens, N9, N7, N3, N1 and exocyclic amino nitrogen atom N6, as donor sites.[123] The order of basicity of these five coordinating N atoms are N9 > N1 > N7 > N3 > N6 making adenine a versatile ligand.[124] All the five nitrogen coordination sites are available in a deprotonated adeninate which allows the formation of vast number of coordination polymers. Moreover, adenine can adopt different binding patterns like monodentate N9,[125] N7,[126] and N3,[127] bidentate bridging or chelating through μ–*N7,N9*;[128] μ–*N3,N9*;[129] μ–*N3,N7*;[130] μ–*N1,N9*;[131] and μ–*N6,N7*[132] (with 9–ethyladenine) and also as tridentate μ$_3$–*N3,N7,N9*[133]. There are

[122] Wang, F.; Kang, Y. *Inorg. Chem. Comm.* **2012**, *20*, 266.

[123] (a) Tornita, K. et al. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 96. (b) de Meester, P; Skapski, A. C. *J. Chem. Soc. A*, **1971**, 2167. (c) Terzis, A. et al. *Inorg. Chem.* **1973**, *12*, 1166. (d) Brown, D. B. et al. *Inorg. Chem.* **1977**, *16*, 2675. (e) Sletten, E. *Acta Crystallogr. Sect. B*, **1969**, *25*, 1480. (f) Marzotto, A. et al. *J. Chem. Soc. Dalton Trans.* **1995**, 1461. (g) Prizant, L. et al. *Can. J. Chem.* **1981**, *59*, 1311. (h) Charland, J.–P. et al. *Croat. Chem. Acta* **1984**, *57*, 679. (i) Charland, J.–P.; Beauchamp, A. L. *Inorg. Chem.* **1986**, *25*, 4870. (j) Korn, S.; Scheldrick, W. S. *Inorg. Chim. Acta* **1997**, *254*, 85. (k) Kickham, J. E. et al. *Chem. Eur. J.* **1997**, *3*, 1203. (l) Salam, M. A.; Aoki, K. *Inorg. Chim. Acta* **2000**, *311*, 15.

[124] (a) Lippert, B. *Prog. Inorg. Chem.* **2005**, *54*, 385. (b) de Meester, P.; Skapski, A. C. *J. Chem. Soc. Dalton Trans.* **1973**, 424. (c) Choquesillo–Lazarte, D. et al. *J. Coord. Chem. Rev.* **2008**, *252*, 1241.

[125] (a) Tornita, K. et al. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 96.(b) Brown, D. B. et al. *Inorg. Chem.* **1977**, *16*, 2675.(c) de Meester, P; Skapski, A. C. *J. Chem. Soc. Dalton Trans.* **1973**, 424. (d) Sakaguchi, H. et al. *Chem. Pharm. Bull.* **1978**, *26*, 2465. (e) Marzotto, A. et al. *J. Chem. Soc. Dalton Trans.* **1995**, 1461. (f) de Meester, P; Skapski, A. C. *J. Chem. Soc. Dalton Trans.* **1973**, 1596. (g) Kistenmacher, L. G. et al. *J. Am. Chem. Soc.* **1973**, *95*, 5817. (h) Gagnon, C. et al. *Inorg. Chem.* **1977**, *16*, 2469. (i) Rosopulos, Y. et al. *Chem. Ber.* **1985**, *118*, 931. (i) Prizant, L. et al. *Can. J. Chem.* **1981**, *59*, 1311. (k) Charland, J.–P.; Beauchamp, A. L. *Croat. Chem. Acta* **1984**, *57*, 679.

[126] (a) Taylor, M. R. *Acta Crytstallogr. Sect. B 29*, **1973**, 884. (b) Muthiah, P. T. et al. *J. Inorg. Biochem.* **1983**, *19*, 237. (c) Taylor, M. R.; Westphalen, J. A. *Acta Crystallogr. Sect A 37 (S)*, **1981**, C63.

[127] (a) Marzotto, A. et al. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 119. (b) Kickham, J. E. et al. *Chem. Eur. J.* **1997**, *3*, 1203.

[128] (a) Prizant, L. et al. *Acta Crystallogr. Sect. B 38*, **1982**, 88. (b) Scheldrick, W. S. et al. *Inorg. Chim. Acta* **1993**, *206*, 15.

[129] (a) de Meester, P; Skapski, A. C. *J. Chem. Soc. A*, **1971**, 2167. (b) Terzis, A. et al. *Inorg. Chem.* **1973**, *12*, 1166. (c) de Meester, P; Skapski, A. C. *J. Chem. Soc. Dalton Trans.* **1972**, 2400. (d) Sletten, E. *Acta Crystallogr. Sect. B*, **1969**, *25*, 1480.

[130] (a) Bugella–Altamirano, E. et al. *Inorg. Chim. Acta* **2002**, *339*, 160. (b) Brandi–Blanco, M. P. et al. *J. Inorg. Biochem.* **2013**, *127*, 211.

[131] Das, S. et al. *Inorg. Chim. Acta* **2005**, *358*, 3236.

[132] Day, E. F. et al. *J. Am. Chem. Soc.* **1994**, *116*, 9339.

[133] (a) Wang, F.; Kang, Y.: *Inorg. Chem. Commun.* **2012**, *20*, 266. (b) Song, Y. et al. *CrystEngComm.* **2014**, *16*, 3082. (c) García–Terán, J. P. et al. *Inorg. Chem.* **2004**, *43*, 4549. (d) An, J. et al. *J. Am. Chem. Soc.* **2010**, *132*, 38.

also reported compounds where all the four imino N atoms are coordinated to the metal centre at the same time.[134]

A large number of metal organic complexes of adenine in which adenine is coordinated to one or more metal centres have been reported. Due to the highly versatile nature of adenine, it can adopt different coordination modes and thirteen such coordination modes are represented in Figure 3.3.
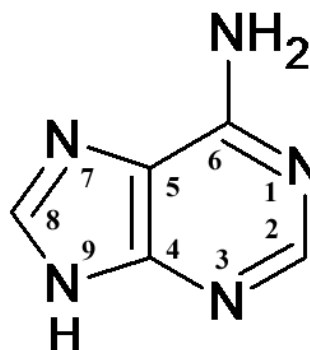
Figure 3.2: Numbering pattern of the atoms in adenine molecule.

Another benefit of using adenine as ligand in the supramolecular synthesis is the presence of the exocyclic primary 6–amino group which enables adenine as a potential connector in the network formation, since the 6–amino group acts as a hydrogen donor in intermolecular hydrogen–bonding interactions and thus spreading the resulting complex into more extended architectures.[135]

Adenine can be found in neutral or ionic forms according to the pH of the medium and thereby modifying its coordinative properties. The pKa values of adenine are 4.2 and 9.8,[136] respectively (Figure 3.4). Adenine in neutral form is capable of forming different types of compounds like, monomers,[85] discrete polynuclear species[86] or one dimensional (1D) polymeric chains.[137] Being a strong base, the adeninate anion has the capacity to form compounds varying form monomeric,[98] polynuclear [138–139] to three dimensional (3D) networks.[86]

[134] (a) Yang, E.–C. et al. *Inorg. Chem.* **2009**, *48*, 3511. (b) Song, Y. et al. *CrystEngComm.* **2014**, *16*, 3082 (c) Li, T. et al. *J. Am. Chem. Soc.* **2013**, *135*, 11688.

[135] Choquesillo–Lazarte, D. et al. *J. Coord. Chem. Rev.* **2008**, *252*, 1241.

[136] Taqui–Khan, M. M.; Krishnamoorthy, C. R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1417.

[137] García–Terán J. P. et al. *Inorg Chem.* **2004** ,*43*, 5761.

[138] Hubert, J.; Beauchamp, A. L. *Acta Crystallogr.* **1980**, *B36*, 2613.

[139] (a) Prizant, L. et al. *Acta Crystallogr.* **1982**, *B38*, 88. (b) Beauchamp, A. L. *J. Cryst. Mol. Struct.* **1980**, *10*, 149.
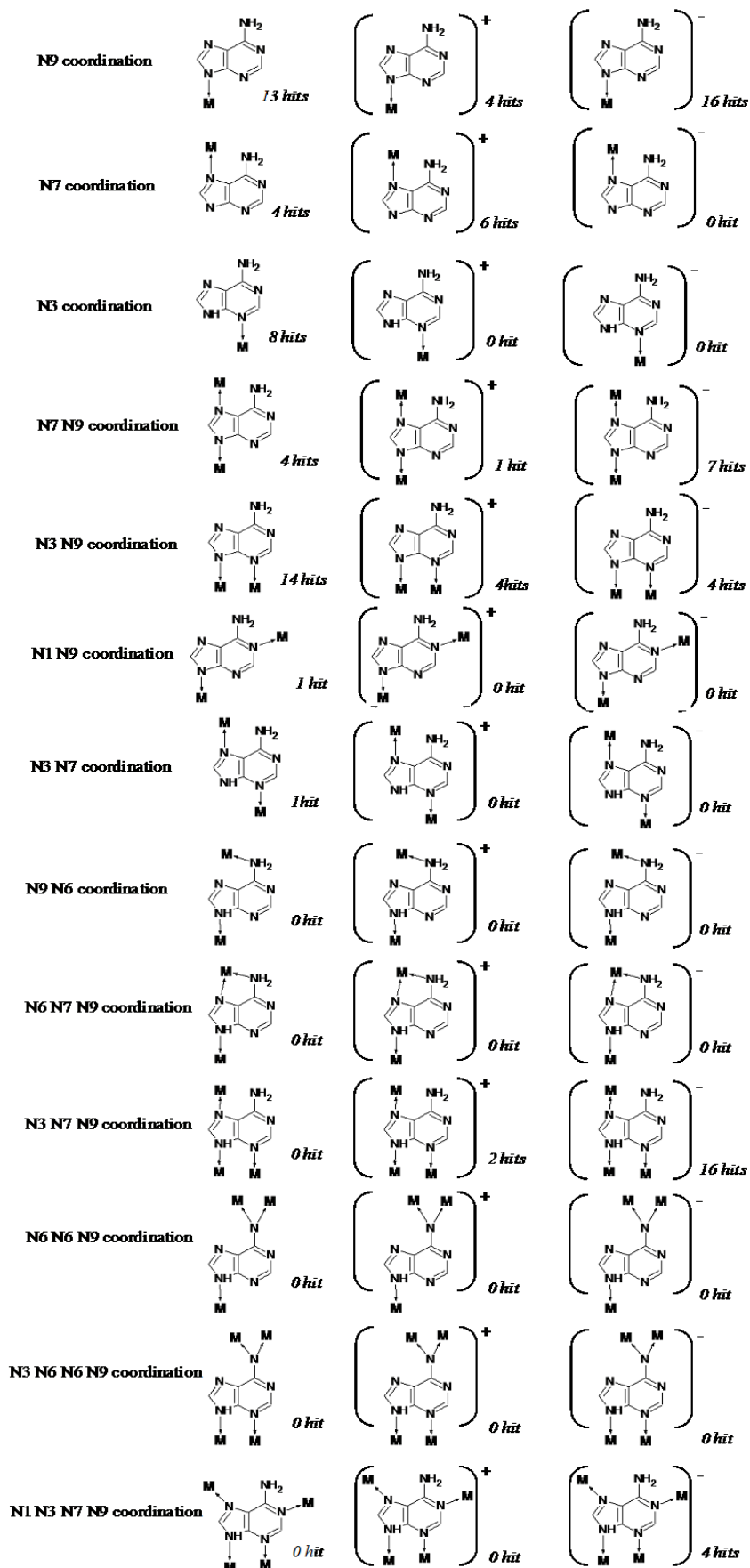
Figure 3.3: Coordination modes of the adenine ligand with the number of examples for each mode found in the CSD.

1H,9H–adeninium   *9H*–adenine   adeninate
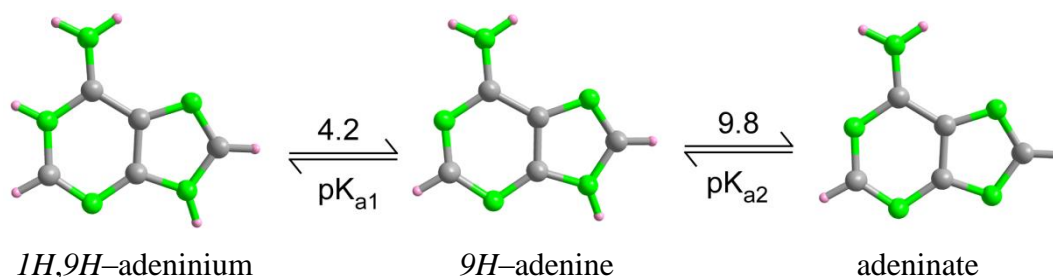
Figure 3.4: The pKa values of adenine.

Guanine nucleobase has the highest number of tautomers among the purine nucleobases.[140] Among which 1H,9H–keto form is the most abundant in the solid state[141] while 1H,7H–keto form is most abundant in the gas phase.[142] In the literature there exist a very large number of structural reports of substituted guanine nucleobase coordinated to a transition metal. However, because of the insoluble nature of guanine in most solvents, only few structures are reported in which guanine itself acts as a ligand.[143] Figure 3.5, shows the usually accepted numbering scheme and the coordination modes found for the guanine nucleobase (as found in the CSD data base version February 2015). In the case of unsubstituted guanine the most preferred binding position is N9 with 6 examples found.[144] The other possible binding modes are through μ–*N7*:*N9* (2 examples),[145] μ–*N3*:*N7* (2 examples)[103] and μ–*N3*:*N9* (1 example).[146]

Crystal engineering through the design of supramolecular network structures is a well known practice in the solid–state supramolecular chemistry.[147] The key to success in such supramolecular network designing is to choose tectons with proper geometry and robust synthons.[148] Adenine fulfils the above requeriments as can be observed in Figure 3.6. Similarly, guanine is also able to establish complementary hydrogen bonds with a second

[140] Gupta, D. et. al. *Dalton Trans*. **2010**, *39*, 73.

[141] Thewalt, U. et. al. *Acta Crystallogra. Sect. B: Struct. Crystallogr. Cryst. Chem*. **1971**, *27*, 2358.

[142] Lippert, B.; Gupta, D. *Dalton Trans*. **2009**, 4619.

[143] (a) Mastropietro, T. F. et. al. *Dalton Trans*. **2008**, 514. (b) Gupta, D. et al. *Dalton Trans*. **2010**, *39*, 73. (c) Turel, I. et. al. *J. Inorg. Biochem*. **2004**, *98*, 393. (d) Gaballa, A. S. et al. *Inorg. Chim. Acta* **2008**, *361*, 2070. (e) Sundaralingam, M.; Carrabine J. A. *J. Mol. Biol*. **1971**, *61*, 287. (f) Colacio, E. et al. *J. Inorg. Biochem*. **2004**, *98*, 595.(f) Declercq, J. P. et. al. *Bull. Soc. Chim. Belg*. **1971**, *80*, 527.

[144] (a) Gupta, D. et al. *Dalton Trans*. **2010**, *39*, 73. (b) Mastropietro, T. F. et al. *Dalton Trans*. **2008**, 514. (c) Turel, I. et al *J. Inorg. Biochem*. **2004**, *98*, 393. (d) Declercq, J. P. et al. *Bull. Soc. Chim. Belg*. **1971**, *80*, 527. (e) Sundaralingam, M.; Carrabine, J. A. *J. Mol. Biol*. **1971**, *61*, 287. (f) Gaballa, A. S. et al. *Inorg. Chim. Acta* **2008**, *361*, 2070.

[145] (a) Gupta, D. et al. *Dalton Trans*. **2010**, *39*, 73. (b) Annen, P. et al. *Inorg. Chim. Acta* **2000**, *307*, 115.

[146] Colacio, E. et al. *J. Inorg. Biochem*. **2004**, *98*, 595.

[147] Han, L. et al. *Cryst. Growth Des*. **2009**, *9*, 660.

[148] Saha, B. K.; Bhattacharya, S. *CrystEngComm.* **2010**, *12*, 2369.

guanine (Figure 3.7). However, some recognition patterns requires the simultaneous presence of neutral and protonated guanines. Additionally, there is a relatively common interaction between the guanines that involves keto group as acceptor and N2–H + N3–H or N1–H + N2–H as donor to form a $R_2^1(6)$. These last interactions does not provide a rigid synthon as the second guanine can rotate retaining this interaction. There are many other purine derivatives not involved in the DNA structure but still retaining most of the hydrogen bonding self–recognition capacities. A brief selection of these purine based molecules has been depicted in Figure 1.19.

GUANINE

N9 Coordination

3 hits

4 hits

N7-N9 Coordination

1 hit

1 hit

N3-N9 Coordination

1 hit

N3-N7 Coordination

2 hits
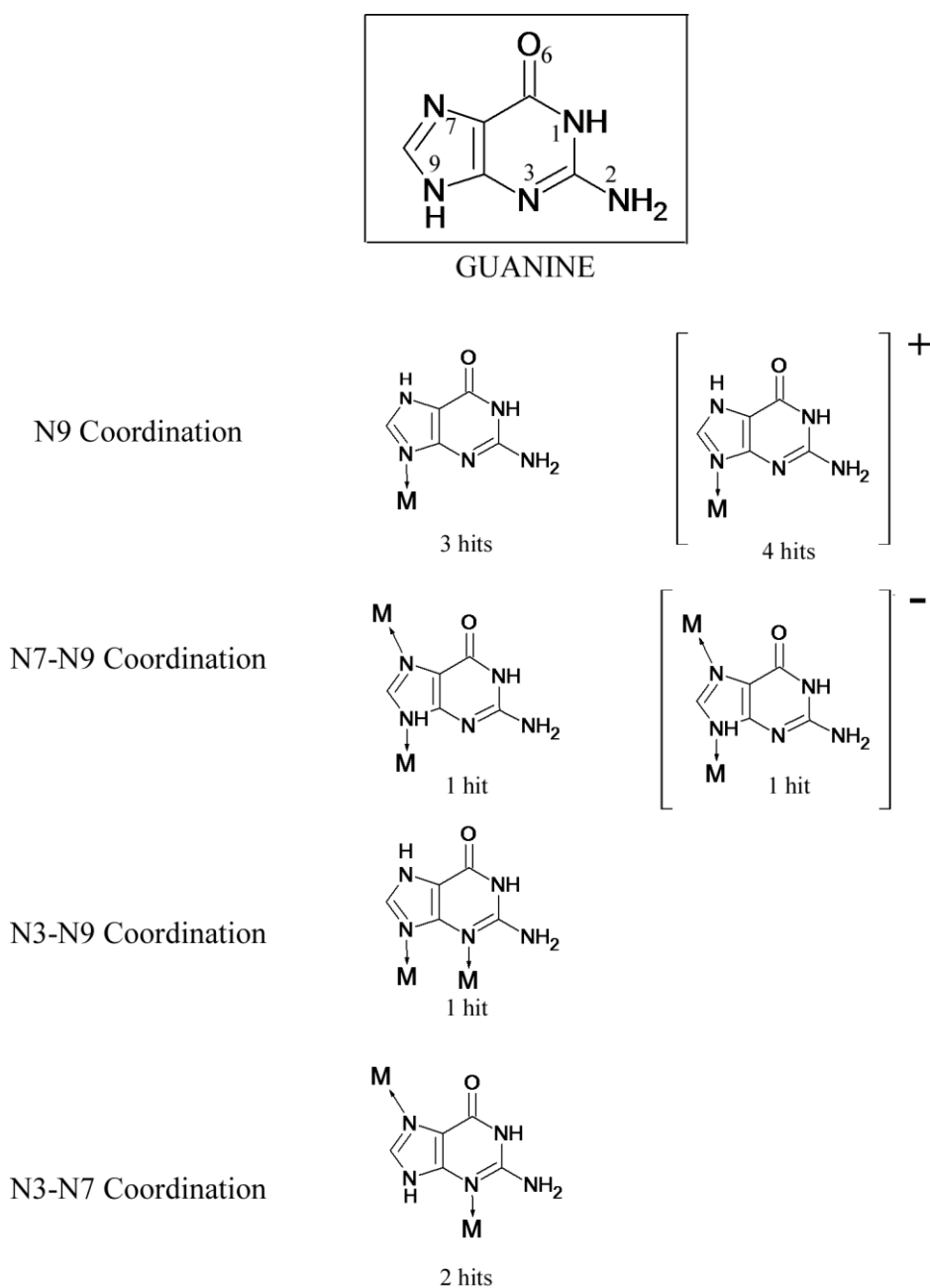
Figure 3.5: (a) Structure and numbering pattern of guanine. (b) Different coordination modes as found in the CSD database.
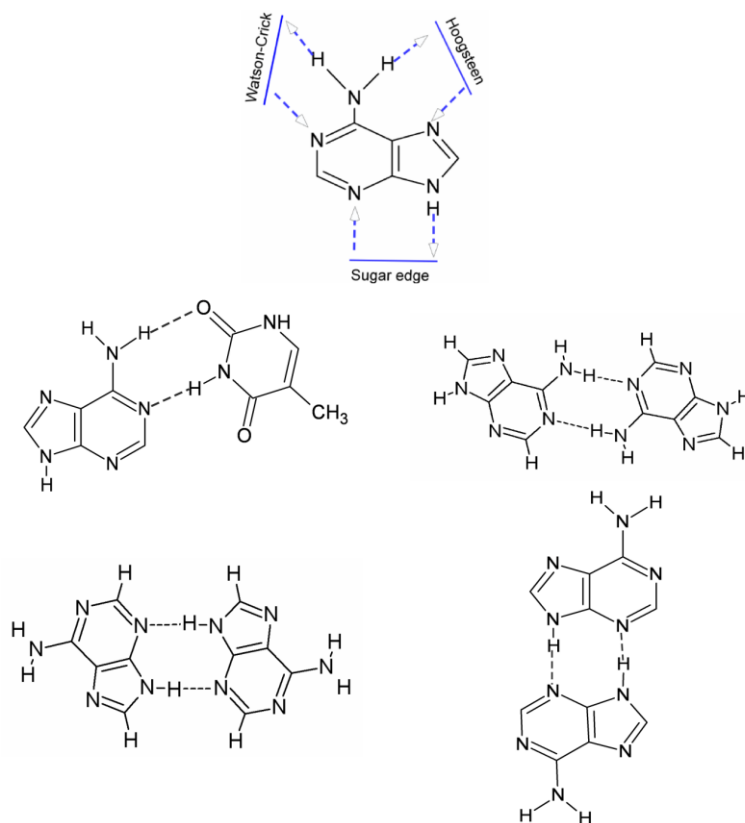
Figure 3.6: Complementary hydrogen bonds between adenines.
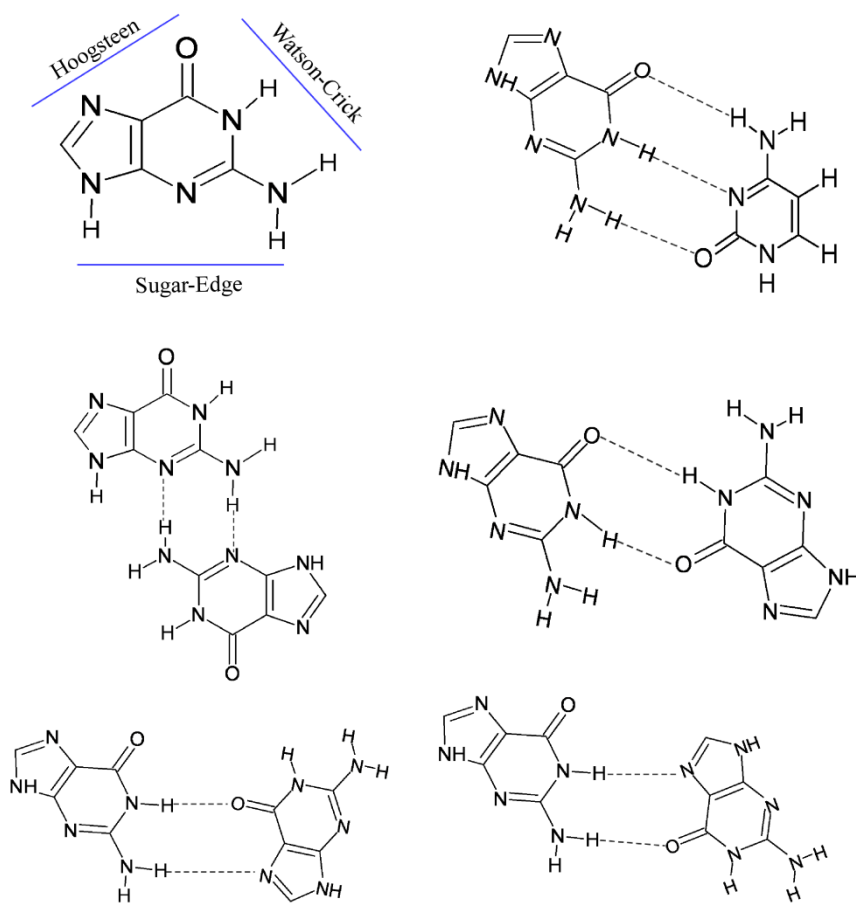
Figure 3.7: Complementary hydrogen bonds between guanines.

3.2 SYNTHESIS AND CHEMICAL CHARACTERISATION

3.2.1 Synthesis

Taking into account the above mentioned ideas, we report herein the synthesis and crystal structures of fifteen compounds with purine derivatives (Table 3.1). Apart from compounds *CUADECL–A*, *CO–6–CLPUR* and *CO–6–THIOG*, all other compounds were obtained using alcohols as solvent to avoid the instability of the 3D supramolecular architectures due to the presence of water mediated hydrogen bonds between the nucleobases.

Table 3.1: Compounds synthesised[a]

Compound[a]	*Code*
[Cu$_2$(μ–Hade)$_4$Cl$_2$]Cl$_2$·8H$_2$O Tetrakis(μ–adenine–$\kappa N3$:$\kappa N9$)bis(chlorido)dicopper(II) chloride–water (1/8)	*CUADECL–A*
[Cu$_2$(μ–Hade)$_4$(Cl)$_2$]Cl$_2$·2MeOH Dichloridotetrakis(μ–adenine–$\kappa N3$:$\kappa N9$)dicopper(II) chloride–methanol (1/2)	*CUADECL–B (SMOF–1)*
[Cu$_2$(μ–Hade)$_4$(Br)$_2$]Br$_2$·~2MeOH Dibromidotetrakis(μ–adenine–$\kappa N3$:$\kappa N9$)dicopper(II) bromide–methanol (1/2)	*CUADEBR–A (SMOF–2)*
[Cu$_2$(μ–Hade)$_2$(Cl)$_4$]·2MeOH Dichloridobis(μ–chlorido)bis(μ–adenine–$\kappa N3$:$\kappa N9$)dicopper(II)–methanol(1/2)	*CUADECL–C (SMOF–3)*
[Cu$_2$(μ–Hade)$_2$(Br)$_4$]·2PrOH Dibromidobis(μ–bromido)bis(μ–adenine–$\kappa N3$:$\kappa N9$)dicopper(II)–propanol (1/2)	*CUADEBR–B*
[Cu$_4$(μ$_3$–ade)$_2$(μ$_2$–ade)$_2$(pentylNH$_2$)$_2$(CH$_3$OH)$_2$(CO$_3$)$_2$(H$_2$O)$_2$]·n(solvent) Tetrakis(μ$_3$–adeninato–$\kappa N3$:$\kappa N7$:$\kappa N9$)(μ$_2$–adeninato–$\kappa N3$:$\kappa N9$)diaquabis(carbonato–κO: $\kappa O\acute{}$)dimethanolbis(pentylamine)tetracopper(II)]–n(solvent)	*CUADECO3 (SMOF–8)*
[Cu$_2$(μ–ade)$_3$(μ–OH)(H$_2$O)(CH$_3$OH)]$_n$·n(solvent) *catena*–poly[Bis(μ–adeninato–$\kappa N3$:$\kappa N9$)(μ–adeninato–$\kappa N7$:$\kappa N9$)aqua(μ–hydroxido)methanoldicopper(II)]–solvent(1/n)	*CUADEOH (SMOF–9)*
[Co$_3$(μ–Hade)$_2$(μ–Cl)$_4$Cl$_2$(H$_2$O)$_4$]·2H$_2$O (μ–adenine–1κN3:3κN9)(μ–adenine–2κN3:3κN9)bis(μ–chlorido–1κCl:3κCl)bis(μ–chlorido–2κCl:3κCl)di(chlorido–1κCl,2κCl)tetra(aqua–1κ2O,2κ2O)tricobalt(II)–water (1/2)	*CO3ADECL*
[Co(Hade)$_2$Cl$_2$] Dichloridobis(adenine–$\kappa N7$)cobalt(II)	*COADECL (SMOF–5)*
[Co(Hade)$_2$Br$_2$] Dibromidobis(adenine–$\kappa N7$)cobalt(II)	*COADEBR (SMOF–6)*
[Co(9–MeAde)$_2$(H$_2$O)$_4$]Cl$_2$·2(H$_2$O). Tetraaquabis(9–methyladenine–$\kappa N7$)cobalt(II) chloride–water (1/2)	*CO–9–MEADECL*
[Cu$_2$(μ–CH$_3$COO)$_4$(μ–9–MeAde)]$_n$·nCH$_3$OH catena–poly[tetrakis(μ–acetato–κO:$\kappa O\acute{}$)(μ–9–methyladenine–$\kappa N1$:$\kappa N7$)dicopper(II)]–methanol (1/1)	*CU–9–MEADEACE*
[Co(6–ClPur)$_2$(H$_2$O)$_4$]·4H$_2$O Tetraaquabis(6–chloropurinato–$\kappa N9$)cobalt(II)–water (1/4)	*CO–6–CLPUR*
[Cu$_2$(Hgua)$_2$(H$_2$gua)$_2$(μ–Cl)$_2$Cl$_2$][CuCl$_4$] Bis(guanine–$\kappa N9$)bis(guaninium–$\kappa N9$)bis(μ–chlorido)bis(chlorido)dicopper(II) tetrachloridocuprate(II)	*CUGUACL*
[Co(Thiogua)$_3$]·nH$_2$O Tris(6–thioguaninato–$\kappa N7$, $\kappa S6$)cobalt(III)–water (1/n)	*CO–6–THIOG (SMOF–4)*

[a] Hade = adenine (C$_5$H$_5$N$_5$); ade = adeninate (C$_5$H$_4$N$_5$); Hgua = guanine (C$_5$H$_5$N$_5$O); H$_2$gua = guaninium (C$_5$H$_6$N$_5$O); 9–MeAde = 9–methyladenine (C$_6$H$_7$N$_5$); 6–ClPur = 6–chloropurinato (C$_5$H$_2$ClN$_4$); Thiogua = 6–thioguaninato (C$_5$H$_4$N$_5$S); MeOH = CH$_3$OH; PrOH = 1–propanol; pentylNH$_2$ = pent–1–amine.

3.2.1.1 *Synthesis of compound CUADECL–A*

0.0852 g of $CuCl_2 \cdot 2H_2O$ (0.5 mmol) dissolved in 5 mL water was added dropwise to the stirring solution of 0.0682 g of adenine (0.5 mmol) dissolved in 30 mL water. After stirring for 30 minutes, a dark blue precipitate corresponding to **CUADECL–A** appeared. It was filtered off and washed thoroughly with water. The filtrate was left evaporating at room temperature for two weeks and good quality blue single crystals were formed.

Yield: 80%. Anal. Calcd (Found) for $C_{20}H_{36}Cl_4Cu_2N_{20}O_8$: C, 25.19 (25.13); H, 3.81 (3.75); N, 29.38 (29.42); Cu, 13.33 (13.27) %. Main IR features (cm^{-1}; KBr pellets): 3440s, 3191s, 2362w, 2338w, 1646vs, 1463m, 1400m, 1343w, 1310w, 1280w, 1203m, 1143m, 1110m, 993w, 906, 791m, 738m, 655m, 619m, 569m, 461m.

3.2.1.2 *Synthesis of compound CUADECL–B (SMOF–1)*

0.0171 g of $CuCl_2 \cdot 2H_2O$ (0.1 mmol) dissolved in 5 mL of methanol was added dropwise to a warm stirring solution (50 ºC) of 0.0277 g of adenine (0.2 mmol) dissolved in 30 mL methanol. The blue precipitate was formed immediately on the addition of the $CuCl_2$ solution. It was filtered, washed with methanol and dried. Single crystals of **CUADECL–B** were obtained by the following diffusion technique. A methanolic solution of 0.0138 g of adenine (0.1 mmol) in 10 mL was layered slowly over a propanolic solution of 0.0086 g of $CuCl_2 \cdot 2H_2O$ (0.05 mmol) in 10 mL in a test tube. Blue crystals suitable for the single crystal X–ray analysis were formed in one week.

Yield: 80%. Anal. Calcd (found) for $C_{22}H_{28}Cl_4Cu_2N_{20}O_2$: C, 30.25 (30.35); H, 3.23 (3.14); N, 32.07 (32.09), Cu, 14.55 (14.62) %. Main IR features (cm^{-1}; KBr pellets): 3360s, 3170s, 1650vs, 1515w, 1460m, 1400m, 1350w, 1210m, 1320m, 1110w, 785w, 740w, 550m.

3.2.1.3 *Synthesis of compound CUADECL–C (SMOF–3)*

0.0702 g of $CuCl_2 \cdot 2H_2O$ (0.4 mmol) dissolved in 10 mL of methanol was added dropwise to the hot stirring solution (50 ºC) of 0.0128 g of adenine (0.1 mmol) dissolved in 20 mL methanol. The light green precipitate formed was filtered, washed with methanol and dried. Diffusion technique was used again to obtain crystals but using a methanolic solution of 0.0136 g of adenine (0.1 mmol in 10 mL) slowly layered over a propanolic solution of 0.0086 g of $CuCl_2 \cdot 2H_2O$ (0.05 mmol in 10 mL) in a diffusion tube. Good

quality green crystals were formed along with blue crystals of the compound **CUADECL–B**, in one week.

Yield: 70%. Anal. Calcd (found) for $C_{12}H_{18}Cl_4Cu_2N_{10}O_2$: C, 23.89 (23.92); H, 3.01 (3.14); N, 23.22 (23.18), Cu, 21.07 (21.03) %. Main IR features (cm^{-1}; KBr pellets): 3387s, 3142sh, 3103sh, 1666vs, 1611m, 1580m, 1520m, 1478m, 1450s, 1404vs, 1383w, 1356sh, 1347sh, 1318vs, 1262w, 1244w, 1215m, 1291w, 1170m, 1111vs, 1016w, 976sh, 970sh, 931m, 788m, 737sh, 722sh, 680m, 633w, 597m, 573w, 548s.

3.2.1.4 *Synthesis of compound CUADEBR–A (SMOF–2)*

0.0112 g of CuBr$_2$ (0.05 mmol) dissolved in 5 mL methanol was added dropwise to the hot stirring solution of 0.0270 g adenine (0.2 mmol) dissolved in 30 mL of methanol at 50 ºC. Precipitation started immediately and the solution was kept stirring for 20 minutes. The blue precipitate corresponds to **CUADEBR–A**. Crystals suitable for single–crystal X–ray diffraction studies were obtained by diffusion of a methanolic solution of adenine (0.0136 g, 0.1 mmol in 10 mL) slowly layered over a propanolic solution of CuBr$_2$ (0.0116 g, 0.05 mmol in 10 mL). With in one week, **CUADEBR–A** crystallized as deep blue colored crystals along with some red crystals corresponding to **CUADEBR–B**.

Yield: 80%. Anal. Calcd (found) for $C_{23}H_{32}Br_4Cu_2N_{20}O_3$: C, 25.13 (25.24); H, 2.68 (2.81); N, 26.65 (26.53), Cu, 12.09 (11.97) %. Main IR features (cm^{-1}; KBr pellets): 3330s, 3170s, 1650vs, 1515w, 1460m, 1348w, 1320m, 1260w, 1215m, 1182w, 1148w, 1117m, 1022w, 970w, 934sh, 922sh, 790m, 738m, 683w, 610w, 563w, 545m.

3.2.1.5 *Synthesis of compound CUADEBR–B*

As mentioned above, single crystals of **CUADEBR–B** were obtained in the diffusion tube along with the crystals of **CUADEBR–B (SMOF–2).** The compound **CUADEBR–B** was obtained in pure form by adding 0.0273 g of adenine (0.2 mmol) dissolved in 40 mL methanol over the solution of 0.0226 g of CuBr$_2$ (0.1 mmol) dissolved in 15 mL of propanol. Red coloured crystals started appearing on evaporating the brown coloured mother liquid for one week.

Yield: 60%. Anal. Calcd (found) for $C_{16}H_{26}Br_4Cu_2N_{10}O_2$: C, 22.96 (22.91); H, 3.13 (3.09); N, 16.73 (16.78); Cu, 15.18 (15.15) %. Main IR features (cm^{-1}; KBr pellets): 3380s, 3226s, 3293s, 3240s, 3193s, 3130s, 2953s, 1666vs, 1612m, 1476w, 1460w, 1405m, 1384w, 1357w, 1344w, 1320s, 1262w, 1220m, 1175w, 1112m, 1050w, 1002s, 972w, 930w, 875m, 802w, 876m, 736m, 711w, 677w, 663w, 613m, 569m, 538w, 472w, 463w.

3.2.1.6 *Synthesis of compound CUADEOH (SMOF–9)*

Single crystals of this compound were obtained by the slow addition of a 10 mL methanolic solution of 0.0199 g of $Cu(OOCCH_3)_2 \cdot H_2O$ (0.1 mmol) into a cold methanolic solution (50 mL) of 0.0546 g of adenine (0.4 mmol) mixed with 0.59 mL of pentylamine stirring in an ice–bath. The green solution was stirred in the ice–bath for 1 hour and left evaporating at room temperature. Blue needle like crystals appeared in one week.

Yield: 5%. Anal. Calcd (found) for $C_{16}H_{19}Cu_2N_{15}O_3$: C, 33.87 (33.77); H, 6.15 (6.08); N, 24.18 (24.09); Cu, 14.63 (14.74) %. Main IR features $(cm^{-1}$; KBr pellets): 3446s, 3356vs, 3123s, 1671s, 1418m, 1398m, 1385m, 1333m, 1308s, 1268m, 1251w, 1191m, 1149m, 1123w, 1022w, 979w, 939m, 910w, 875w, 845w, 797m, 738w, 723s, 641m, 620w, 570w, 541m.

3.2.1.7 *Synthesis of compound CUADECO3 (SMOF–8).*

The synthesis was performed similarly as that of compound **CUADEOH**, but using 0.0206 g of adenine (0.15 mmol) dissolved in 20 mL of cold methanol. On evaporating, the colour of the solution changed to blue–violet and violet prismatic shaped crystals appeared after one week. The crystals were unstable outside the mother liquid. Main IR features $(cm^{-1}$; KBr pellets): 3444s, 2961m, 2930m, 2872w, 1644s, 1506w, 1489w, 1465m, 1397w, 1382m, 1343w, 1308w, 1265w, 1238w, 1191m, 1113m, 991w, 941w, 731w, 657w, 618m, 575w, 556w.

3.2.1.8 *Synthesis of compound CO3ADECL*

Pink coloured single crystals of compound **CO3ADECL** were obtained using diffusion techniques by layering a methanolic solution of 0.0135 g of adenine (0.1 mmol in 10 mL) over an aqueous solution of 0.0119 g of $CoCl_2 \cdot 6H_2O$ (0.05 mmol in 10 mL). Pink crystals were formed with in one week.

Yield: 10%. Anal. Calcd (found) for $C_{10}H_{22}Cl_6Co_3N_{10}O_6$: C, 15.64 (15.67); H, 2.89 (2.83); N, 18.24 (18.27); Co, 23.02 (22.98) %. Main IR features $(cm^{-1}$; KBr pellets): 3444s, 2360vs, 2340s, 2266w, 1650m, 1633m, 1311w, 1244m, 1186w, 1147w, 983w, 719w, 680w, 668m, 649m, 614w, 536w.

3.2.1.9 *Synthesis of compound COADECL* (*SMOF–5*)

This compound was obtained as deep blue polycrystalline sample by the dropwise addition of a propanolic solution 0.0270 g of adenine (0.2 mmol 40 mL) into a stirring

solution of 0.0238 g of $CoCl_2·6H_2O$ (0.1 mmol) dissolved in 5 mL propanol. When the synthesis was performed in methanol low quality crystals were obtained. Then single crystals of good quality were obtained by layering a methanolic solution of 0.0135 g of adenine (0.1 mmol, 10 mL) over a solution of 0.0119 g of $CoCl_2·6H_2O$ (0.05 mmol, 10 mL) in propanol. Blue crystals appeared after two weeks. Polycrystalline sample of this compound was obtained through solvent–free synthesis by heating a 1:2 mixture of $CoCl_2·6H_2O$ and adenine in a closed container up to 130 ºC.

Yield: 70%. Anal. Calcd (found) for $C_{10}H_{10}Cl_2CoN_{10}$: C, 30.02 (30.09); H, 2.52 (2.47); N, 35.01 (34.93); Cu, 14.73 (14.82) %. Main IR features (cm^{-1}; KBr pellets): 3391vs, 3258vs, 3133vs, 3058vs, 2346w, 2280w, 2186w, 2016w, 1943w, 1790w, 1696vs, 1611s, 1498m, 1459w, 1397s, 1327m, 1237m, 1171m, 1105w, 1066w, 1016w, 942m, 895m, 856w, 778m, 712m, 631w, 610m, 530m.

3.2.1.10 *Synthesis of compound COADEBR* (*SMOF–6*)

This compound was obtained as deep blue polycrystalline sample by the dropwise addition of a propanolic solution 0.0270 g of adenine (0.2 mmol) dissolved in 40 mL into a stirring solution of 0.0240 g of $CoBr_2$ (0.1 mmol) in 5 mL propanol. All the attempts to grow single–crystals were unsuccessful.

Yield: 60%. Anal. Calcd (found) for $C_{10}H_{10}Br_2CoN_{10}$: C, 24.56 (24.49); H, 2.06 (2.09); N, 28.68 (28.57); Cu, 12.05 (12.01) %. Main IR features (cm^{-1}; KBr pellets): 3450s, 3341vs, 3066s, 2817w, 2671w, 2284w, 1951w, 1663vs, 1596vs, 1513w, 1480s, 1416s, 1360w, 1343s, 1306s, 1246s, 1170w, 1120w, 1020w, 1063w, 1030w, 973m, 910m, 870w, 791m, 763m, 722s, 680w, 638m, 627m, 557s, 545m, 532s.

3.2.1.11 *Synthesis of compound CO–9–MEADECL*

0.0298 g (0.2 mmol) of 9–methyladenine dissolved in 20 mL of methanol was added dropwise to the stirring solution of 0.0237 g (0.1 mmol) of $CoCl_2·6H_2O$ dissolved in 5 mL of methanol at room temperature. The pink coloured clear solution formed was stirred at room temperature for 2 hours and left for evaporation. Orange–yellow good quality single crystals were formed within one week.

Yield: 40%. Anal. Calcd (found) for $C_{12}H_{26}Cl_2CoN_{10}O_6$: C, 26.88 (26.81); H, 4.88 (4.79); N, 26.12 (26.17); Co, 10.99 (11.03) %. Main IR features (cm^{-1}; KBr pellets): 3417s, 2740w, 2760w, 2275w, 1947m, 1886w, 1793m, 1663vs, 1600vs, 1576vs, 1500s, 1467s, 1426s, 1416s, 1390w, 1373w, 1346s, 1326m, 1300s, 1266m, 1256s, 1230m,

1196m, 1086w, 1063m, 1047m, 1019m, 978w, 945m, 921m, 898s, 843m, 795m, 760w, 742w, 717m, 684w, 641w, 602w, 585w, 542m.

3.2.1.12 *Synthesis of compound CU–9–MEADEACE*

0.0298 g (0.2 mmol) of 9–methyladenine dissolved in 20 mL of methanol was added dropwise to the stirring solution of 0.0199 g (0.1 mmol) of $Cu(OOCCH_3)_2 \cdot H_2O$ dissolved in 5 mL of methanol at room temperature. A green coloured precipitate was obtained immediately. Single crystals were obtained using diffusion techniques. A methanolic solution of 9–methyladenine (0.1 mmol, 0.1490 g in 10 mL) was layered over a methanolic solution of copper(II) acetate monohydrate (0.05 mmol, 0.0099 g in 10 mL). Good quality green crystals were obtained within one week.

Yield: 50%. Anal. Calcd (found) for $C_{15}H_{23}Cu_2N_5O_9$: C, 33.09 (33.01); H, 4.26 (4.39); N, 12.86 (12.77); Cu, 23.34 (23.51) %. Main IR features (cm^{-1}; KBr pellets): 3395s, 3288m, 3195s, 1666s, 1626s, 1603vs, 1530w, 1508w, 1475w, 1433s, 1421s, 1385m, 1336m, 1310m, 1258w, 1230s, 1197m, 1083w, 1067w, 1050m, 1020m, 945w, 902w, 880w, 841w, 795m, 760w, 742w, 720m, 685m, 642w, 626w, 603w, 561w, 540w, 530w.

3.2.1.13 *Synthesis of compound CO–6–CLPUR*

0.0464 g (0.3 mmol) of 6–chloropurine dissolved in 30 mL of water was mixed with 0.59 mL (0.4 mmol) of pentylamine and the mixture was stirred in an ice bath for 1 hour. 0.0291 g (0.1 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 5 mL of water was added dropwise to the cold stirring solution of 6–chloropurine. The orange coloured solution formed was stirred in ice bath for 2 hours more and kept for evaporating. Orange coloured single crystals were formed in three days.

Yield: 60%. Anal. Calcd (found) for $C_{10}H_{20}Cl_2CoN_8O_8$: C, 23.54 (23.63); H, 3.95 (3.87); N, 21.96 (21.99); Co, 11.55 (11.51) %. Main IR features (cm^{-1}; KBr pellets): 3442s, 1717w, 1624s, 1593w, 1511w, 1482w, 1451w, 1384vs, 1330w, 1286w, 1250w, 1230w, 1144m, 1100m, 1064w, 990w, 933w, 920w, 855m, 939m, 785w, 750w, 630w, 606w, 595w, 537w, 500w.

3.2.1.14 *Synthesis of compound CUGUACL*

Good quality green crystals of compound ***CUGUACL*** were obtained by mixing methanolic solutions of 0.0173 g of $CuCl_2 \cdot 2H_2O$ (0.1 mmol in 5 mL) and an acidified

methanolic solution of 0.0337 g of guanine, dissolved in 40 mL methanol, with 34 μl (0.4 mmol) of concentrated HCl (purity: 37%).

Yield: 30%. Anal. Calcd (found) for $C_{20}H_{24}Cl_8Cu_3N_{20}O_5$: C, 21.96 (21.84); H, 2.21 (2.28); N, 25.63 (25.54); Cu, 17.27 (17.36) %. Main IR features (cm^{-1}; KBr pellets): 3450s, 1750vs, 1666vs, 1400m, 1383s, 1361m, 1316w, 1196w, 1160w, 1116w, 1073w, 1046w, 993m, 820w, 800w, 763w, 660w, 593w, 543w, 506m, 426w.

3.2.1.15 *Synthesis of compound CO–6–THIOG* (*SMOF–4*)

0.59 mL (0.4 mmol) of pentylamine was added dropwise to a 0.0685 g (0.4 mmol) of 6–thioguanine dissolved in 20 mL of water and the mixture was stirred in an ice bath for 1 hour. To this mixture a 10 mL aqeuous solution of 0.0291 g (0.1 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ was added. The brown coloured solution was then stirred for 2 hours in ice bath and then left for evaporation. Brown coloured single crystals were obtained after two weeks. The same compound was obtained on replacing $Co(NO_3)_2 \cdot 6H_2O$ with $CoSO_4 \cdot 7H_2O$.

Yield: 60%. Anal. Calcd (found) for $C_{15}H_{12}CoN_{15}S_3$: C, 26.56 (26.68); H, 3.78 (3.70); N, 30.98 (31.29), Co, 14.18 (14.21). IR selected data (KBr, cm^{-1}): 3422s, 1611m, 1498w, 1459w, 1385m, 1306w, 1243vs, 1190m, 1146s, 983s, 933w, 893w, 836w, 803w, 743w, 716w, 680w, 630w, 523w.

3.3   RESULTS AND DISCUSSION

3.3.1   *Crystallographic analysis*

The crystallographic data and the refinement conditions are given in Table 3.2–4. Diffraction data of single crystals were collected on Oxford Diffraction Xcalibur and STOE IPDS II diffractometers. The data reduction was done with CrysAlis RED[110] and X–Area[149] programs, respectively. Structures were solved by direct methods using the SIR92 program[111] and refined by full–matrix least–squares on F^2 including all reflections (SHELXL97).[112] All calculations were performed using the WINGX crystallographic software package.[113]

During the data acquisition of some of these compounds, it become evident that some of them were non–merohedrically twinned: **CO3ADECL**, **CUADECL–C** and

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[149] Stoe & Cie. *X–AREA , Main Menu Version 1.15*, **2001,** Stoe & Cie GmbH, Darmstadt, Germany.

CUADECO3. The corresponding twin laws and percentage of the minor domain are listed below:

CO3ADECL: (0.997 0.007 0.002 0.579 –0.998 0.001 0.942 0.003 –0.999)   47.43%

CUADECL–C: (1.000 0.000 1.986 0.000 –1.000 0.000 0.000 0.000 –1.000) 14.37%

CUADECO3: (1.026 –0.077 0.038 0.070 0.963 0.012 –0.023 –0.000 1.003) 24.32%

Additionally, some other ones presented great voids within the crystal structure that were occupied by solvent molecules in a very disordered manner. Their contribution to the diffraction pattern has been removed using the SQUEEZE subroutine as implemented in PLATON: ***CUADEBR–A***, ***CUADECL–B***, ***CUADECO3*** and ***CUADEOH***.[150]

CUGUACL compound shows a disorder related to the orientation of the Jahn–Teller effect on the dimeric unit. It implies the terminal and bridging chlorido ligands that are disordered over two positions with short and significantly longer Cu–Cl distances. This disorder also implies the presence of a coordination water molecule with an occupation factor of 0.50.

The hydrogen atoms were geometrically positioned or fixed at the position of a maximum of the Fourier difference map. However, for compounds ***CUADECL–C*** and ***CUADEOH*** it was impossible to locate the hydrogen atoms attached to the H_2O, OH^- and MeOH molecules.

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[150] Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

Table 3.2: Single crystal data and structural refinement details of compounds ***CUADECL–A***, ***CUADECL–B (SMOF–1)***, ***CUADEBR–A (SMOF–2)***, ***CUADECL–C (SMOF–3)*** and ***CUADEBR–B***.

Compound	*CUADECL–A*	*CUADECL–B_100K*	*CUADECL–B_293K*	*CUADEBR–A*	*CUADECL–C*	*CUADEBR–B*
Empirical formula	$C_{20}H_{36}Cl_4Cu_2N_{20}O_8$	$C_{22}H_{28}Cl_4Cu_2N_{20}O_2$	$C_{22}H_{28}Cl_4Cu_2N_{20}O_2$	$C_{22}H_{28}Br_4Cu_2N_{20}O_2$	$C_{12}H_{18}Cl_4Cu_2N_{10}O_2$	$C_{16}H_{26}Br_4Cu_2N_{10}O_2$
Formula weight	953.553	873.49	873.49	1051.229	603.24	837.19
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	293(2)	100(2)	293(2)	100(2)	100(2)	100(2)
Diffractometer	IPDS II	IPDS II	IPDS II	Xcalibur	Xcalibur	IPDS II
Crystal system	orthorhombic	trigonal	trigonal	trigonal	monoclinic	monoclinic
Space group	*Pbam*	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	C2/c	P21/c
a (Å)	13.7405(7)	26.9032(17)	26.820(1)	27.1979(9)	22.2245(18)	9.1344(7)
b (Å)	10.3343(6)	26.9032(17)	26.820(1)	27.1979(9)	13.8069(10)	11.0778(10)
c (Å)	12.1024(7)	15.4298(10)	15.528(1)	15.4999(4)	7.0204(6)	13.0778(11)
α (º)	90	90	90	90	90	90
β (°)	90	90	90	90	108.280(6)	103.873(7)
γ (º)	90	120	120	120	90	90
V (Å^3)	1718.52(17)	9671.6(11)	9673(1)	9929.6(5)	2045.5(3)	1284.7(2)
Z	2	9	9	9	4	2
ρ_{calcd} (g cm^{-3})	1.843	1.350	1.349	1.582	1.959	2.164
μ (mm^{-1})	1.627	1.284	1.284	4.630	2.636	7.912
Reflections collected	7022	11165	20165	31767	9439	18741
Unique data/parameters	2073/132	2035/109	2029/109	2837/109	9439/127	3059/161
R_{int}	0.0721	0.0536	0.0598	0.0465	0.0695	0.0942
Goodness of fit (S)[a]	0.918	0.960	1.050	1.234	1.089	1.119
R1[b]/wR2[c] [I>2σ(I)]	0.0519/0.1040	0.0337/0.0822	0.0798/0.2501	0.0927/0.2997	0.0778/0.2048	0.0504/0.0927
R1[b]/wR2[c] [all data]	0.1113/0.1115	0.0500/0.0872	0.1002/0.2601	0.1112/0.3107	0.1119/0.2342	0.0688/0.1005

[a] $S = [\sum w(F_0{}^2 - F_c{}^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R1 = \sum \|F_0| - |F_c\| / \sum|F_0|$. [c] $wR2 = [\sum w(F_0{}^2 - F_c{}^2)^2 / \sum wF_0{}^2]^{1/2}$; $w = 1/[\sigma^2(F_0{}^2) + (aP)^2 + bP]$ where $P = (\max(F_0{}^2,0) + 2Fc^2)/3$ with a = 0.0447 (**CUADECL–A**); a = 0.0548(***CUADECL–B_100K***); a = 0.1794 (***CUADECL–B_293K***); a = 0.2000 (***CUADEBR–A***); a = 0.1437 (***CUADECL–C***); a = 0.0235, b = 9.0683 (***CUADEBR–B***).

Table 3.3: Single crystal data and structural refinement details of compounds *CUADEOH (SMOF–9)*, *CUADECO3 (SMOF–8)*, *CO3ADECL*, *COADECL (SMOF–5)* and *CUGUACL*.

Compound	*CUADEOH*	*CUADECO3*	*CO3ADECL*	*COADECL*	*CUGUACL*
Empirical formula	$C_{16}H_{19}Cu_2N_{15}O_3$	$C_{30.85}H_{46.80}Cu_{3.55}N_{21.55}O_{8.20}$	$C_{10}H_{22}Cl_6Co_3N_{10}O_6$	$C_{10}H_{10}Cl_2CoN_{10}$	$C_{20}H_{24}Cl_8Cu_3N_{20}O_5$
Formula weight	596.54	1076.37	767.87	400.11	1098.81
λ (Å)	1.54184	0.71073	0.71073	1.54184	1.54184
T (K)	100(2)	293(2)	100(2)	100(2)	100(2)
Diffractometer	Xcalibur	Xcalibur	Xcalibur	IPDS II	Xcalibur
Crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
Space group	C2/c	P$\bar{1}$	P$\bar{1}$	C2/c	P$\bar{1}$
a (Å)	23.472(7)	12.646(5)	7.203(2)	11.2442(18)	7.8461(5)
b (Å)	16.398(3)	13.136(5)	9.520(3)	6.9401(7)	8.7590(5)
c (Å)	18.803(5)	13.158(5)	9.659(4)	18.760(2)	13.1716(8)
α (°)	90.00	73.784(5)	82.49(2)	90.00	79.157(5)
β (°)	112.30(3)	81.840(5)	69.47(2)	95.000(13)	77.230(5)
γ (°)	90.00	62.368(5)	77.59(4)	90.00	78.526(5)
V (Å^3)	6696(3)	1859.2(12)	604.7(3)	1458.4(3)	855.28(9)
Z	8	1	1	4	1
ρ_{calcd} (g cm^{-3})	1.184	0.961	2.109	1.822	2.133
μ (mm^{-1})	1.899	1.047	2.748	12.758	8.550
Reflections collected	5529	6909	4885	5201	5856
Unique data/parameters	5529/325	6909/269	4885/161	1462/109	3346/264
R_{int}	0.0972	0.1840	0.0602	0.0656	0.0391
Goodness of fit (S)[a]	0.741	0.773	0.959	1.045	1.048
R1[b]/wR2[c] [I>2σ(I)]	0.0800/0.1840	0.1044/0.2691	0.0288/0.0666	0.0606/0.1560	0.0638/0.1704
R1[b]/wR2[c] [all data]	0.1519/0.2091	0.2330/0.2882	0.0388/0.0681	0.0664/0.1606	0.0820/0.1886

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R1 = \sum \|F_0\|-\|F_c\| / \sum |F_0|$. [c] $wR2 = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (max(F_0^2,0) + 2Fc^2)/3$ with a = 0.0584 (*CUADEOH*); a = 0.1283 (*CUADECO3*); a = 0.0897, b = 4.8645 (*CO3ADECL*); a = 0.1437 (*COADECL–A*); a = 0.1110, b = 2.2530 (*CUGUACL*).

Table 3.4: Single crystal data and structural refinement details of compounds *CO–9–MEADECL*, *CU–9–MEADEACE*, *CO–6–CLPUR*, *CO–6–THIOG (SMOF–4)*.

Compound	*CO–9–MEADECL*	*CU–9–MEADEACE*	*CO–6–CLPUR*	*CO–6–THIOG*
Empirical formula	$C_{12}H_{26}Cl_2CoN_{10}O_6$	$C_{15}H_{23}Cu_2N_5O_9$	$C_{10}H_{20}Cl_2CoN_8O_8$	$C_{15}H_{12}CoN_{15}S_3$
Formula weight	536.26	544.46	510.17	557.51
λ (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	monoclinic	trigonal
Space group	*I2/m*	P$\bar{1}$	*P2₁/c*	P$\bar{3}$
a (Å)	11.3880(14)	7.3349(8)	10.6365(2)	16.7297(14)
b (Å)	6.7307(7)	8.5513(8)	13.20990(10)	16.7297(14)
c (Å)	14.9009(19)	16.8119(12)	7.33780(10)	6.5245(4)
α (°)	90	94.649(7)	90.00	90.00
β (°)	109.960(14)	93.046(7)	110.057(2)	90.00
γ (°)	90	99.041(8)	90.00	120.00
V (Å³)	1073.5(2)	1035.64(17)	968.48(2)	1581.4(2)
Z	2	2	2	2
ρ_{calcd} (g cm⁻³)	1.659	1.746	1.749	1.171
μ (mm⁻¹)	1.101	2.112	1.221	0.769
Reflections collected	3999	6694	6770	4690
Unique data/parameters	1263/93	3849/287	2104/135	2300/103
R_{int}	0.0216	0.0522	0.0210	0.1278
Goodness of fit (S)[a]	1.084	1.083	1.064	1.033
R1[b]/wR2[c] [I>2σ(I)]	0.0254/0.0600	0.0635/0.1085	0.0244/0.0592	0.0646/0.1585
R1[b]/wR2[c] [all data]	0.0278/0.0618	0.1018/0.1237	0.0268/0.0607	0.0924/0.1673

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. [c] $wR2 = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (max(F_0^2, 0) + 2Fc^2)/3$ with a = 0.0244, b = 1.3486 (*CO–9–MEADECL*); a = 0.0341 (*CU–9–MEADEACE*); a = 0.0246, b = 0.6946.; (*CO–6–CLPUR*); a = 0.0691, b = 1.2150 (*CO–6–THIOG).*

3.3.2 Stuctural Description

3.3.2.1 Structural Description of [Cu$_2$(μ–Hade)$_4$Cl$_2$]Cl$_2$·8H$_2$O; (*CUADECL–A*)

The crystal structure of **CUADECL–A**, consists of paddle–wheel shaped [Cu$_2$(μ–adenine)$_4$Cl$_2$]$^{2+}$ complex cations, chloride counterions and disordered water molecules. The structure of the dimeric complex cation is shown in Figure 3.8. The two copper(II) centers are bridged by four adenine moieties through their N3 and N9 nitrogen atoms resulting in a paddle–wheel like structure. The copper(II) centers exhibit a distorted square pyramidal geometry with the N3,N9 atoms of the adenine placed in the basal plane and the chloride ligands in the apical position. The dimeric complex is seated on a 2/m crystallographic position and shows a UUDD conformation, referring the terms U(up) or D(down) to the coordination of each pyrimidinic N3 atoms to the upper or lower metal centre. The dimeric entity resembles the structure of the previously published complex [Cu$_2$(μ–ade)$_4$Cl$_2$]Cl$_2$·6H$_2$O, [151] but its crystal structure differs by the number of entrapped water molecules ([Cu$_2$(μ–ade)$_4$(Cl)$_2$]Cl$_2$·8H$_2$O for **CUADECL–A**). These subtle changes on the number of crystallization water molecules have been also described for other systems and they have been attributed to a difference on the crystallization temperature: lowering the temperature helps increasing the amount of entrapped water molecules. [152] The selected coordination bond lengths and angles are given in Table 3.5.

In this attempt, though we had been successful in obtaining paddle–wheel shaped discrete entity, we had still been away from the final goal of obtaining rigid synthons that could lead to robust supramolecular arrays as water molecules disrupt the desired direct hydrogen bonding interactions between the nucleobases. The [Cu$_2$(μ–adenine)$_4$Cl$_2$]$^{2+}$ units are held together by hydrogen bonding interactions mediated through the crystallization water molecules, that are in fact disordered altogether with the chloride counterions, giving rise to a complex network of hydrogen bonds. The crystal structure can also be described as layers of dimeric entities held together by means of water mediated Cl1···O$_w$···O$_w$···Cl1 and weaker C8–H···N1 hydrogen bonds. Among these complex sheets, disordered chloride and crystallization water molecules are placed. Figure 3.9 provides a better insight into the crystal structure of compound **CUADECL–A.**

[151] de Meester, P.; Skapski, A. C. *J. Chem. Soc. (A)*, **1971**, 2167.
[152] García–Couceiro, U. et al. *Inorg. Chim. Acta* **2004**, *357*, 339.
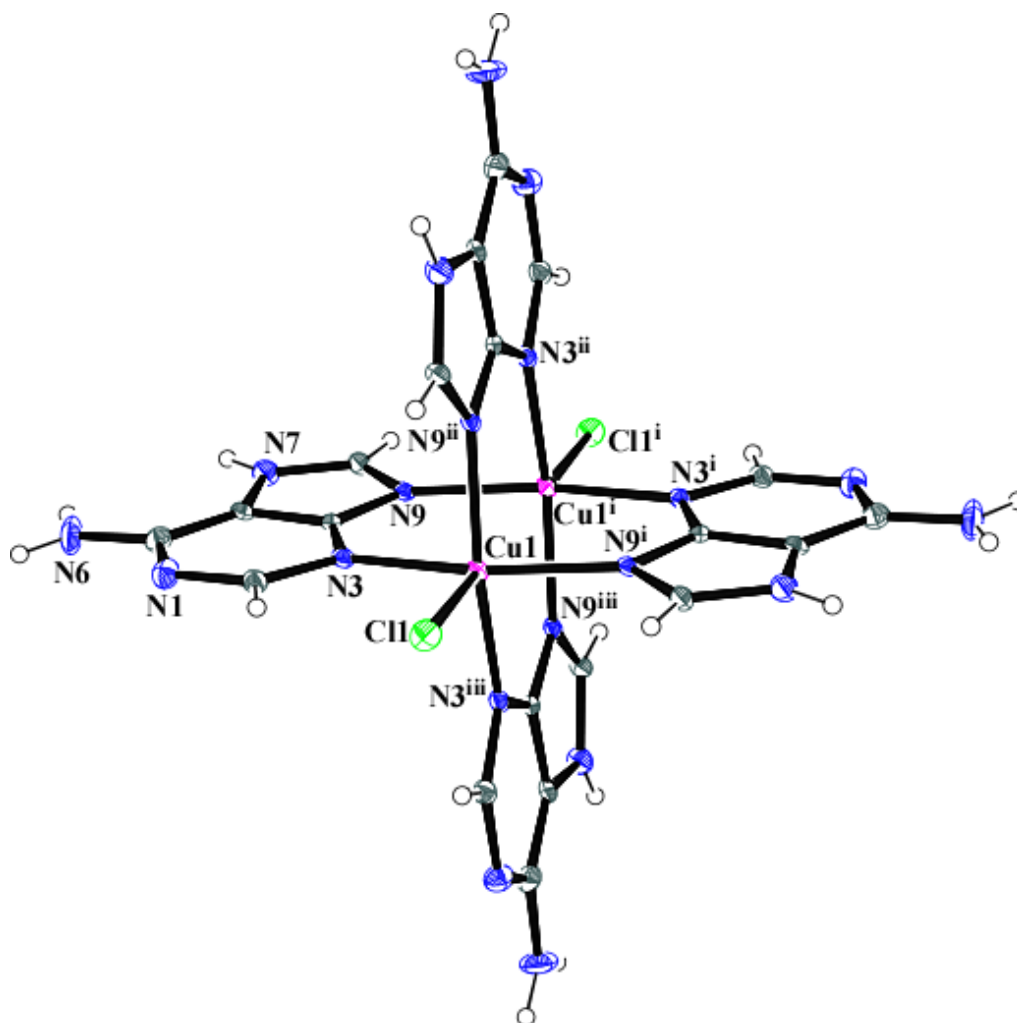
Figure 3.8: Structure of the dimeric complex cation $[Cu_2(\mu–adenine)_4Cl_2]^{2+}$ present in *CUADECL–A* together with labeling scheme.

Table 3.5: Selected bond lengths (Å) and angles (º) of the compound *CUADECL–A*.[a]

Cu1–N3	2.025(4)	N3–Cu1–N3^{iii}	90.2(2)	N3^{iii}–Cu1–Cu1^i	79.99(10)
Cu1–N9^i	2.020(4)	N3–Cu1–N9^i	87.90(13)	N9^i–Cu1–N9^{ii}	89.90(13)
Cu1–Cl1	2.4017(17)	N3–Cu1–N9^{ii}	163.14(15)	N9^i–Cu1–Cl1	97.52(11)
Cu1···Cu1^i	3.0346(15)	N3–Cu1–Cl1	99.32(11)	N9^i–Cu1–Cu1^i	79.99(10)
		N3–Cu1–Cu1^i	79.99(10)	N9^{ii}–Cu1–Cl1	97.52(11)
		N3^{iii}–Cu1–N9^i	163.14(15)	N9^{ii}–Cu1–Cu1^i	79.99(10)
		N3^{iii}–Cu1–N9^{ii}	87.90(13)	Cl1–Cu1–Cu1^i	176.47(6)
		N3^{iii}–Cu1–Cl1	99.32(11)		

[a]Symmetry codes: (i) –x, –y, z; (ii) –x, –y, –z+1; (iii) x, y, –z+1.

(a)

(b)
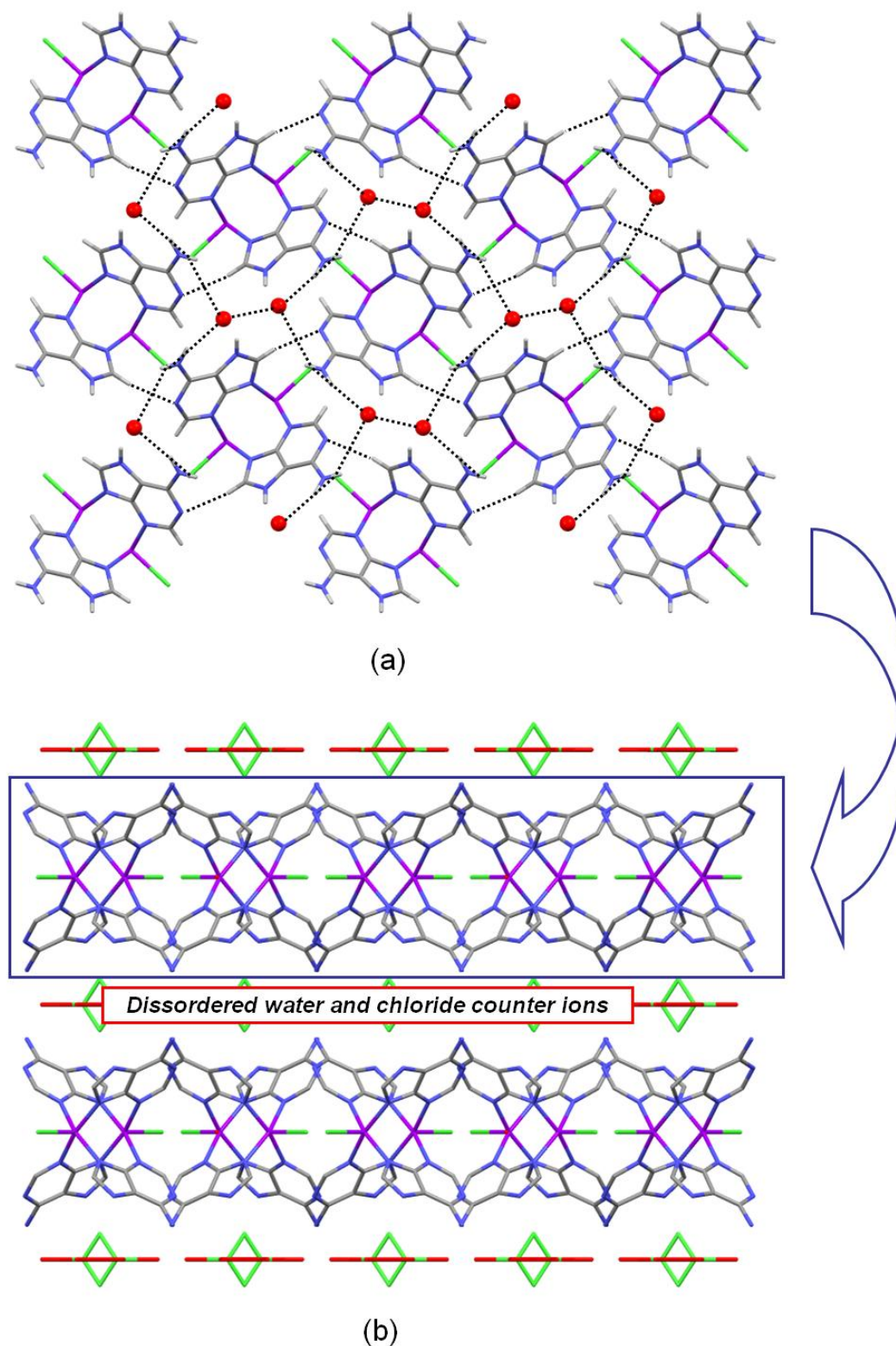
Figure 3.9: Graphical insight into the crystal structure of ***CUADECL–A***. (a) Complex layer of $[Cu_2(\mu{-}adenine)_4Cl_2]^{2+}$ units and water molecules. (b) Projection along the crystallographic *a* axis. Notice that the chloride counterions and interlayer water molecules are disordered.

Not only considering this specific example but also other reported examples[153] with solvated water or any other strong hydrogen bond acceptors shows a general trend of reduced rigidity of the overall network due to solvent mediated flexible hydrogen bonds. From these observations we assume that the presence of strong hydrogen bonding solvents in the reaction media can disrupt the desired direct complementary base pairing interactions between the adenine moieties. Therefore, we focused to avoid the presence of water molecules during the following syntheses and, instead of water, alcohols were employed as solvent.

3.3.2.2 Structural description of [Cu$_2$(μ–Hade)$_4$(Cl)$_2$]Cl$_2$·2MeOH; (CUADECL–B/ SMOF–1) and [Cu$_2$(μ–Hade)$_4$(Br)$_2$]Br$_2$·~2MeOH; (CUADEBR–A/SMOF–2)

The compounds ***CUADECL–B*** (***SMOF–1***) and ***CUADEBR–A*** (***SMOF–2***) are isostructural and their crystal structure consists of windmill–like [Cu$_2$(μ–adenine)$_4$X$_2$]$^{2+}$ complex cations, along with chloride or bromide counterions respectively, and disordered methanol molecules. Figure 3.10 shows a perspective view of the dimeric entity together with the labelling scheme which is conventionally accepted for the adenine nucleobase for chemical and biological purposes (where, X = chlorido or bromido), while coordination bond lengths and angles are gathered in Table 3.6. Four bridging adenine molecules are linked to the copper(II) centers through their N3 and N9 nitrogen atoms to provide the core of the windmill shaped dinuclear entity.[154] Two halide anions occupy the apical positions resulting in an elongated square pyramidal coordination environment of the metal centers. As discussed for ***CUADECL–A***, the dimeric complex is seated on a *2/m* crystallographic position and shows a UUDD conformation. The structural parameters listed in Table 3.6 are similar to those reported for dimeric compounds containing μ–κ*N3*:κ*N9* bridging purine ligands.[155] The shape and structural features of the dimeric cation resembles those reported for the analogous compounds [Cu$_2$(μ–adenine)$_4$Cl$_2$]Cl$_2$·6H$_2$O[151] and the previously mentioned ***CUADECL–A*** which were obtained using a similar synthesis method but employing water as solvent.

[153] (a) de Meester, P.; Skapski, A. C. *J. Chem. Soc(A)*, **1971**, 2167. (b) de Meester, P.; Skapski, A. C. *J. Chem. Soc. Dalton Trans*. **1972**, 2400. (c) González–Pérez, J. M. et al. *Inorg. Chem*. **2006**, *45*, 877. (d) Bugella–Altamirano, E. et al. *Inorg. Chim. Acta* **2002**, *339*, 160.

[154] (a) Cepeda, J. et al. *Eur. J. Inorg. Chem*. **2009**, 2344. (b) González–Pérez, J. M. et al. *Inorg. Chem*. **2006**, *45*, 877.

[155] (a) Suggs, J. W. et al. *J. Chem. Soc. Chem. Commun*. **1993**, 307. (b) Sonnenfroh, D.; Kreilick, R. W. *Inorg. Chem*. **1980**, *19*, 1259. (c) Sletten, E. *Acta Crystallogr*. **1969**, *B25*, 1480.

However, the dissimilar features of the solvation molecules afford dramatic changes in the resulting crystal buildings. In the hydrated compounds the interactions between the complex entities are mediated by water molecules to give a non–porous crystal structure maintained by an intricated network of adenine····water and chloride····water/bromide····water interactions. On the contrary, the weaker ability of methanol to establish hydrogen bonds implies that the crystal packing of *CUADECL–B* and *CUADEBR–A* are essentially sustained by the assembling of the windmill dimeric $[Cu_2(\mu-adenine)_4X_2]^{2+}$ entities through rigid direct intermolecular hydrogen bonds between the adenine molecules, without involving the solvent methanol molecules, together with interactions taking place between the halide anions and the adenine moieties of the cationic complexes. These direct hydrogen bonding interactions provides extra stability and rigidity to the 3D porous supramolecular network and, as a consequence, increasing the robustness of the crystal building.
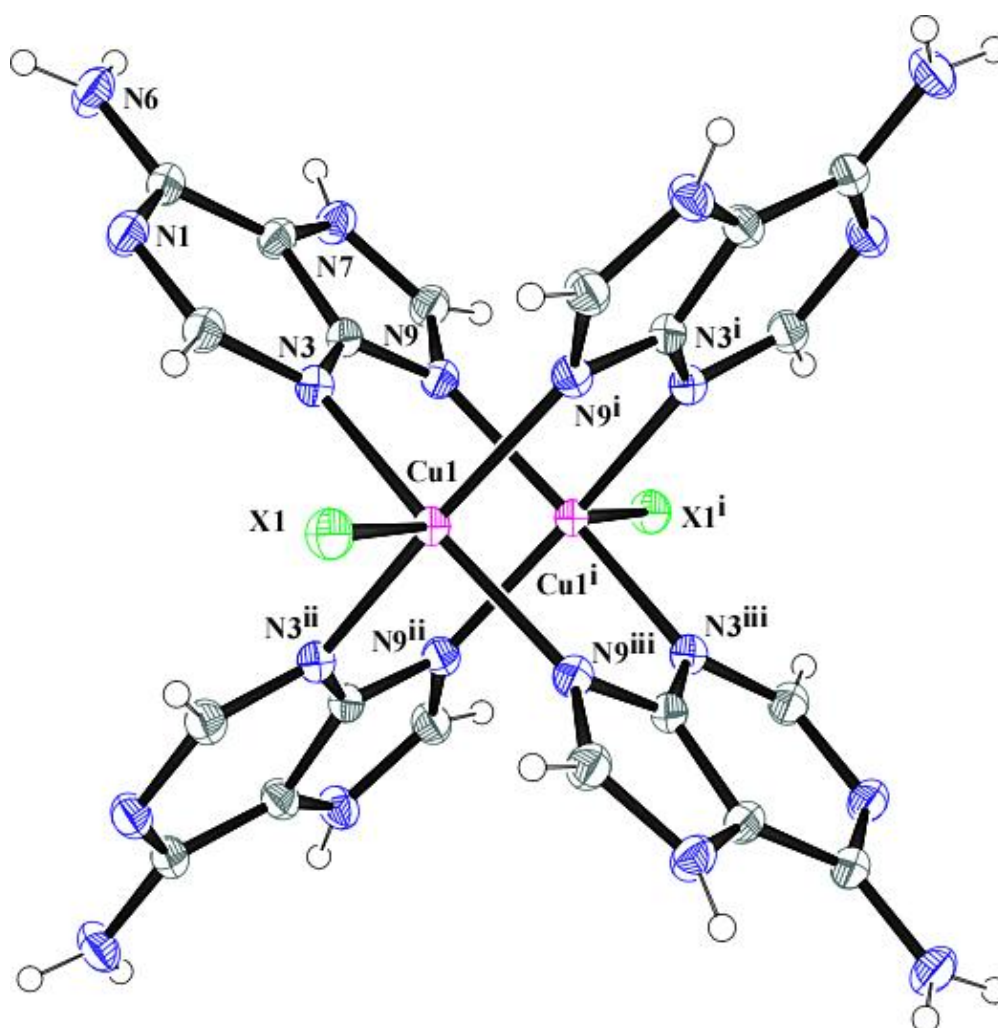
Figure 3.10: Structural unit of *CUADECL–B* and *CUADEBR–A* with the atomic numbering scheme (where $X = Cl^-$ or Br^-).

Table 3.6: Selected bond lengths (Å) and angles (º) for **CUADECL–B** and **CUADEBR–A**.[a]

CUADECL–B (SMOF–1)			CUADEBR–A (SMOF–2)	
	100K	293K		100K
Cu–N3	2.009(2)	2.002(6)	Cu–N3	1.994(5)
Cu–N9^i	2.027(2)	2.031(5)	Cu–N9^i	2.016(6)
Cu–Cl1	2.445(1)	2.466(3)	Cu–Br1	3.080(2)
Cu···Cu^i	3.0761(9)	3.064(2)	Cu···Cu^i	3.082(1)
N3–Cu–N3^{ii}	87.01(13)	86.9(3)	N3–Cu–N3^{ii}	88.1(3)
N3–Cu–N9^i	87.45(9)	87.7(2)	N3–Cu–N9^i	86.5(2)
N3–Cu–N9^{iii}	161.49(9)	162.5(3)	N3–Cu–N9^{iii}	161.6(3)
N3–Cu–Cl1	100.57(7)	99.8(2)	N3–Cu–Br1	100.2(2)
N9^i–Cu–N9^{iii}	92.27(12)	92.5(3)	N9^i–Cu–N9^{iii}	93.1(3)
N9^i–Cu–Cl1	97.80(7)	97.5(2)	N9^i–Cu–Br1	98.0(2)

[a] Symmetry codes: (i) x–y, –y, –z+2; (ii) –x+y+1, y, z; (iii) –x+1, –y, –z+2.

This synthon involving the Watson–Crick faces yields by itself a four–connected uninodal 3 dimensional net with **nbo** topology and $(6^4.8^2)$ point symbol.[156] However, the cohesion of the structure is further strengthened by $R_2^1(7)$ type hydrogen bonding interaction established among the free halide counterions and the Hoogsteen faces of two adenines of neighboring complexes. Considering both types of interactions (Watson–Crick base pairing and Hoogsteen···halide) the supramolecular network can be alternatively described as an eight–connected uninodal with **reo** topology and $(3^8.4^8.5^8.6^4)$ point symbol.

On analysing the supramolecular hydrogen bonding interactions of **CUADECL–B (SMOF–1)** (as can be seen in Figure 3.11), the dinuclear entities of **CUADECL–B (SMOF–1)** are cross–linked together by pairs of symmetry–related N6–H···N1 hydrogen bonding interactions between the Watson–Crick faces of two adjacent nucleobases to give a $R_2^2(8)$ ring, a well–known structural synthon involved in the supramolecular recognition processes which determines the self–assembling pattern of the adenine moieties to form supramolecular aggregates in a great diversity of metal–nucleobase systems.[80,157] Furthermore, coordination

[156] Blatov, V. A. *IUCR CompComm. Newletter* **2006,** 7, 4, (accessed jan. 2012), TOPOS Main Page. http://www.topos.ssu.samara.ru.
[157] See for example: (a) Byres, M. et al. *CrystEngComm*. **2009**, *11*, 135. (b) Galindo, M. A. et al. *Chem. Commun.* **2009**, 2833. (c) Peacock, A. F. A. et al. *J. Am. Chem. Soc*. **2007**, *129*, 3348 (d) Morel, A. C. et al. *Inorg. Chem. Commun.* **2003**, *6*, 1354.

of the adenine through the N9 atom of the pyridine ring produce the proton transfer to the imidazole N7 site to give the non–canonical 7H–adenine tautomer[158] which favours the formation of a hydrogen–bonded $R_2^1(7)$ ring between the Hoogsteen face [N6H, N7H] of the nucleobase as donor and the chloride anion as acceptor.[159] Structural parameters for the supramolecular interactions are listed in Table 3.7. Each chloride counterion is joined to two adenine ligands from adjacent dimeric complexes forming a distorted tetrahedral hydrogen bonding environment.
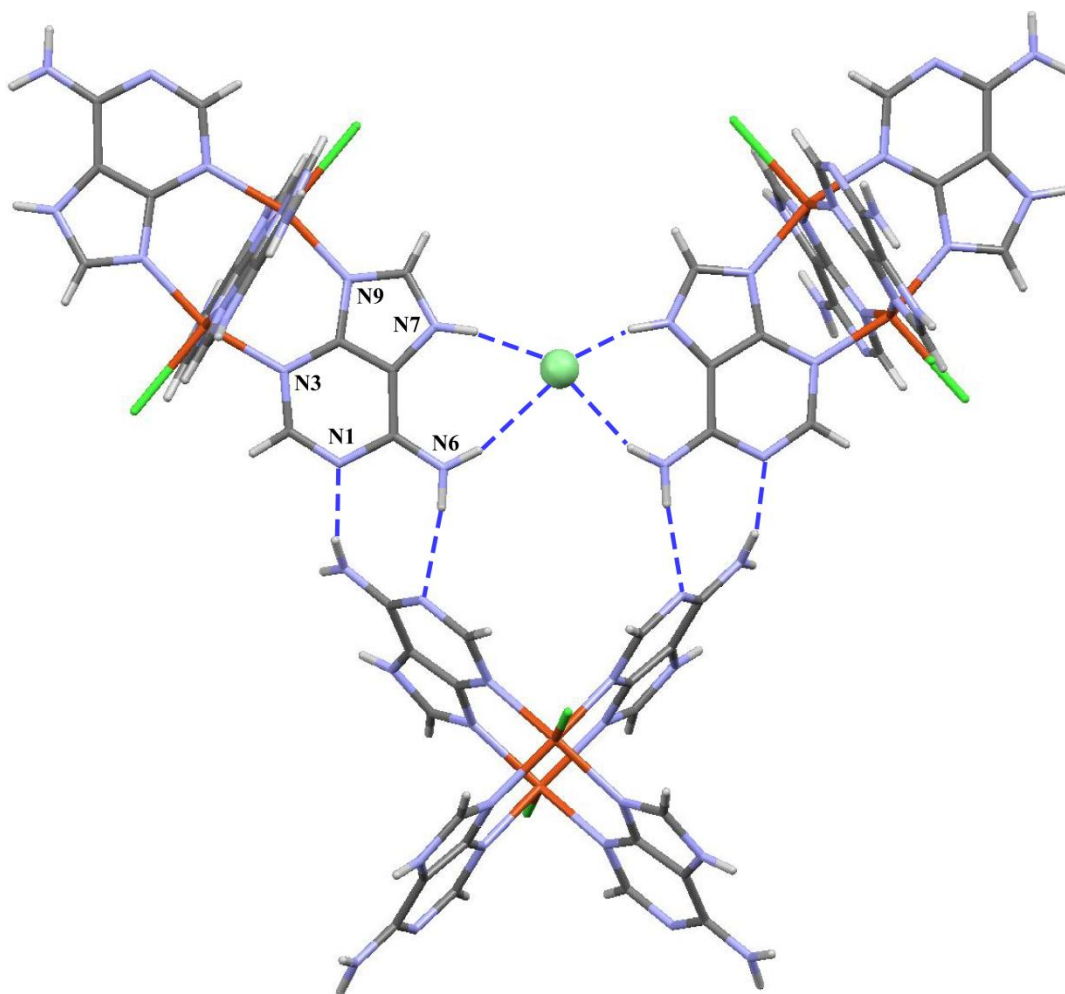
Figure 3.11: Details of the adenine···adenine and adenine···chloride interactions in the crystal packing of ***CUADECL–B (SMOF–1).***

[158] García–Terán, J. P. et al. *Dalton Trans*. **2006**, 902.
[159] See for example: (a) Garcia–Raso, A. et al. *Polyhedron* **2007**, *26*, 949. (b) Mastropietro, T. F. et al. *Polyhedron* **2007**, *26*, 4945. (c) Suzuki, T. et al. *Inorg. Chem*. **2004**, *43*, 6435. (d) de Meester, P.; Skapski, A. C. *J. Chem. Soc. Dalton Trans*. **1973**, 424.

Table 3.7: Hydrogen bonding interactions (Å, º) in ***CUADECL–B*** (***SMOF–1***).[a]

D–H···A[b]	D–H	H···A	D–H···A
100K			
N6–H6A···N1[i]	2.19	3.015(3)	161.1
N6–H6A···Cl2[ii]	2.66	3.466(3)	156.4
N7–H7···Cl2[ii]	2.24	3.034(2)	154.2
293K			
N6–H6A···N1[i]	2.20	3.032(8)	163.3
N6–H6A···Cl2[ii]	2.69	3.505(8)	157.5
N7–H7···Cl2[ii]	2.23	3.032(7)	156.3

[a] Symmetry codes: (i) x–y, –y, –z+1; (ii) y, –x+y, –z; [b] **D**: donor; **A**: acceptor.

The self–assembling process driven by the above–described rigid interactions results in a supramolecular 3D structure containing very large channels along the crystallographic *c* axis with a diameter of ~6.3 Å (Figure 3.12). These channels represent a 36% of the total volume of the unit cell and they are occupied by solvent methanol molecules in a highly disordered manner.

The hydrogen bonding parameters of ***CUADEBR–A (SMOF–2)*** shown in Table 3.8 and Figure 3.13, depict the hydrogen bonding interactions involving the nucleobases and the bromide anions and the resulting porous supramolecular network.

Table 3.8: Hydrogen bonding interactions (Å, º) in ***CUADEBR–A*** (***SMOF–2***).[a]

D–H···A[b]	D–H	H···A	D···A	D–H···A
N6–H6A···N1[i]	0.86	2.23	3.060(9)	162.4
N6–H6B···Br2[i]	0.86	2.76	3.572(8)	158.7
N7–H7···Br2	0.86	2.35	3.140(6)	152.3

[a] Symmetry codes: (i) –x+2/3, –x+y+1/3, –z+4/3. [b] **D**: donor; **A**: acceptor.

As it is depicted in Figure 3.13, the synthon involving the Watson–Crick faces of the adenine nucleobases yields by itself a four–connected uninodal 3 dimensional net with ***nbo*** topology and $(6^4.8^2)$ point symbol[156] same as in the case of the previously mentioned chloride analogue ***CUADECL–B (SMOF–1).*** Similarly, the cohesion of the structure is further

strengthened by the hydrogen bonding interaction established among the free bromide counterions and the Hoogsteen faces of two adenines of neighbouring complexes. A $R_2^1(7)$ hydrogen bonded ring is established for each bromide···Hoogsteen face interaction. Considering both types of interactions (Watson–Crick base pairing and Hoogsteen···bromide) the supramolecular network can be alternatively described as an eight–connected uninodal with *reo* topology and $(3^8.4^8.5^8.6^4)$ point symbol. Representations of the hydrogen bonding nets are shown in Figure 3.14.
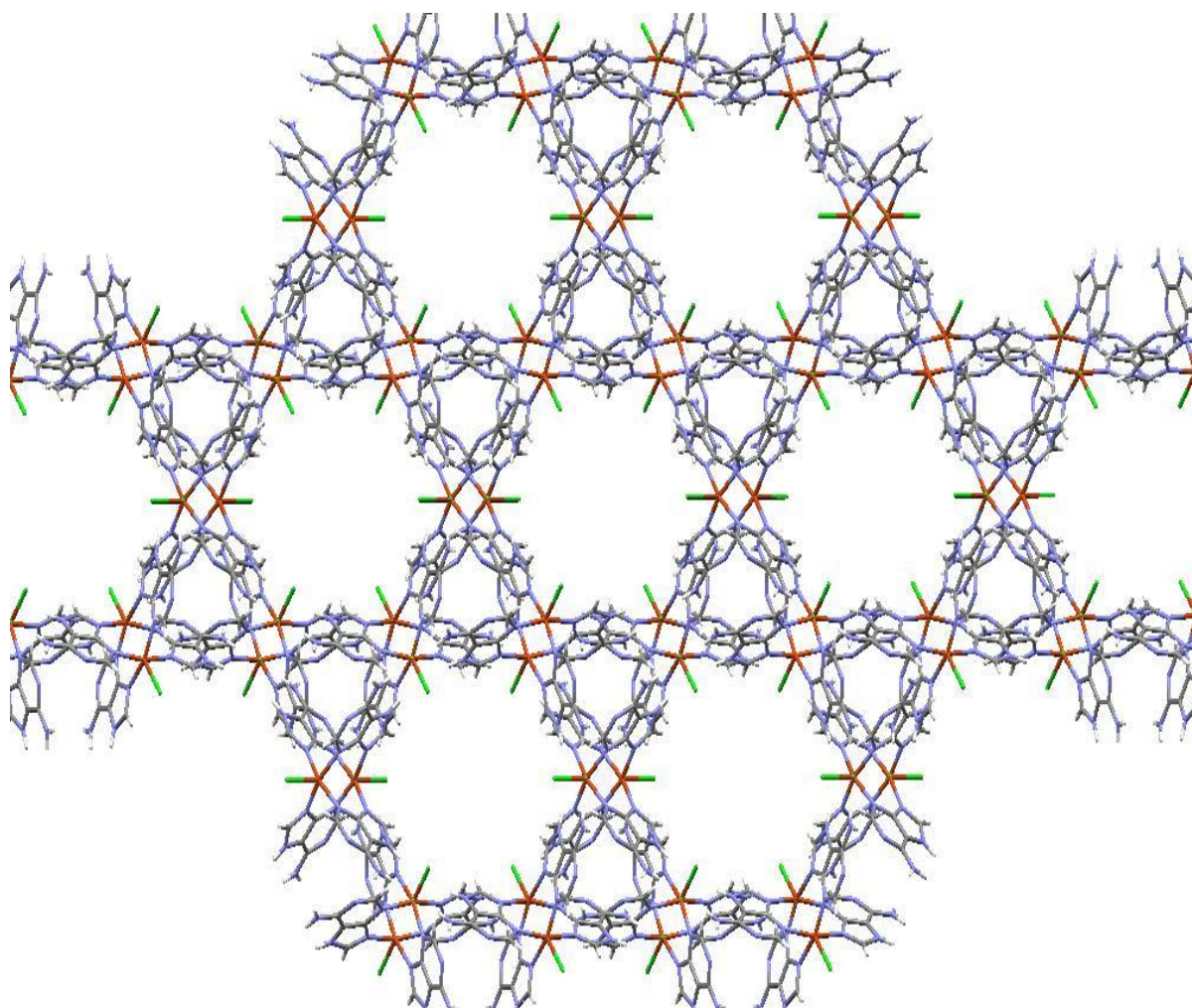
Figure 3.12: Perspective view of the 3D framework along the *c*–axis showing the pores in compound ***CUADECL–B (SMOF–1)***. Solvated methanol molecules are omitted for clarity.

(a)   (b)

(c)
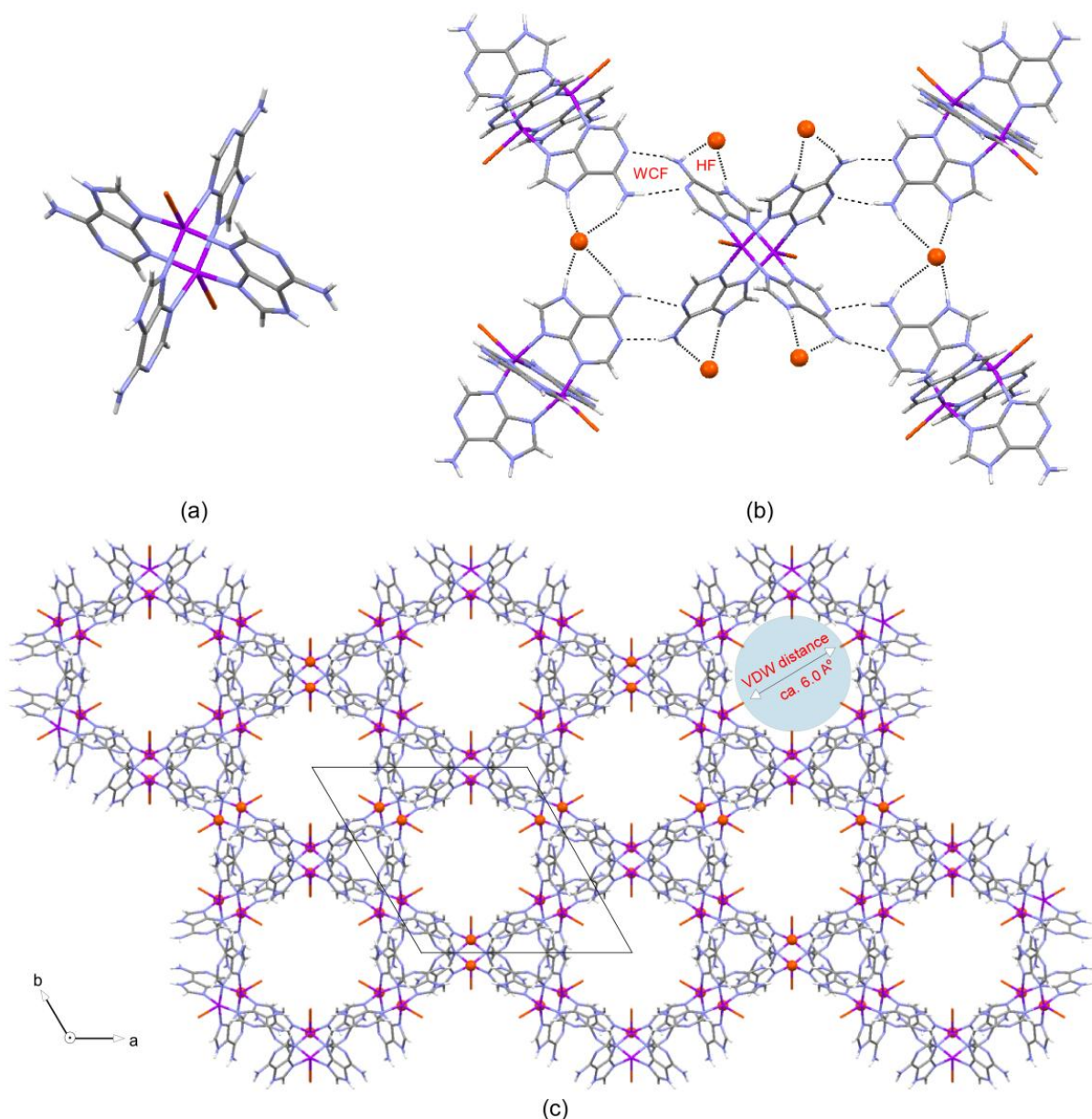
Figure 3.13: Crystal structure features of ***CUADEBR–A (SMOF–2)***: (a) Structural unit. (b)
Details of the adenine base pairing interaction through the Watson–Crick face
(WCF) and of the Hoogsteen Face (HF) mediated adenine⋯bromide
interaction (free bromide anions are represented as orange spheres). (c)
Perspective view of the 3D framework along the *c*–axis showing the pores.

The resulting porous structure consists of 1D tubular channels that run along the
crystallographic *c* axis with a diameter of ~6.0 Å (distance between van der Waals surfaces of
opposite bromide anions). These channels represent 30% of the total crystal volume[150] and
they are occupied by solvent methanol molecules in a highly disordered manner. Due to the
greater size of bromide anion these values are somewhat lower than those found in the case of
CUADECL–B (***SMOF–1***) where the pore diameter is 6.3 Å and the accessible volume is
36%.

(a)

(b)

(c)
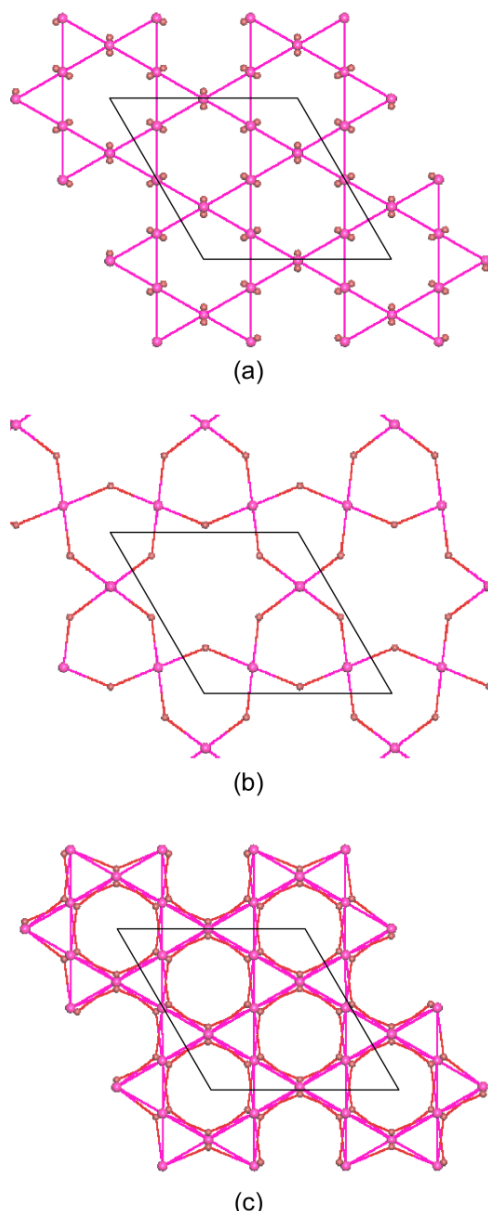
Figure 3.14: (a) Watson-Crick base pairing generated four-connected uninodal 3D net, (b) Hoogsteen edge···bromide hydrogen bond generated net and (c) supramolecular network considering both interactions in ***CUADEBR–A (SMOF–2)***.

3.3.2.2.1   *Thermogravimetric analysis of CUADECL–B (SMOF–1) and CUADEBR–A (SMOF–2)*

The thermal stability of the two compounds was assessed by means of thermogravimetric analysis. Figures 3.15–16 and Table 3.9 show the thermogravimetric and thermodifractometric data of ***CUADECL–B (SMOF–1)*** and ***CUADEBR–A (SMOF–2).*** According to the thermogravimetric data of both compounds, the release of the solvent molecules hosted in the channels takes place between room temperature and 100 ℃, and it involves a weight loss of *ca*. 7.0% (calcd.: 7.32% for two methanol molecules per formula

unit). In both cases the resulting compound remains stable up to 240 ºC and the XRPD patterns at different temperatures (Figure 3.16) do not differ substantially from that corresponding to the starting material, suggesting that the 3D open framework is retained after the removal of the methanol molecules. Above this temperature it undergoes successive exothermic processes leading to CuO as final residue above 500ºC.

CUADECL-B (SMOF-1)   *CUADEBR-A (SMOF-2)*
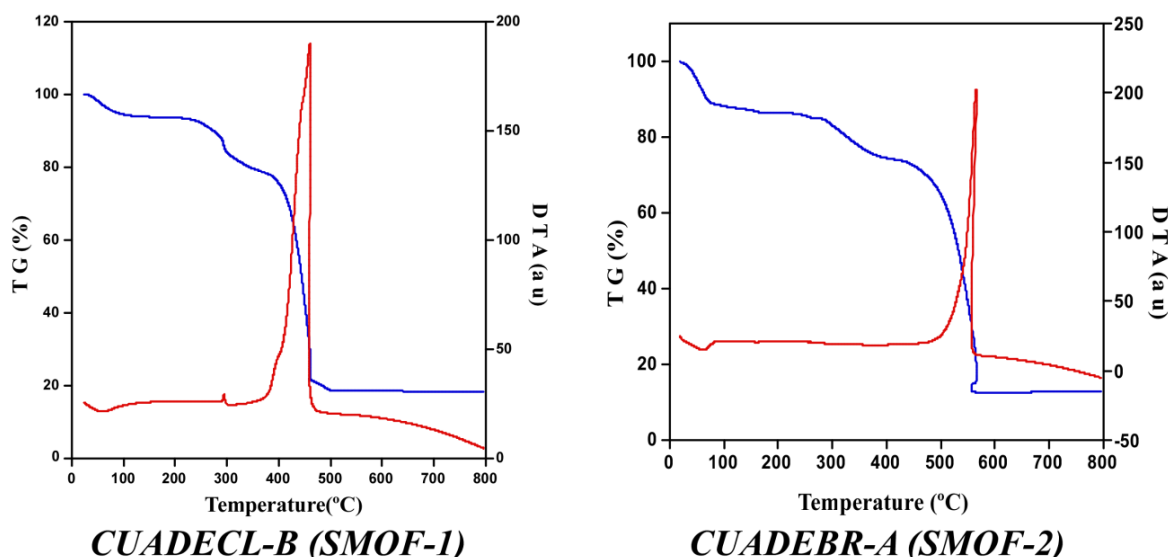
Figure 3.15: Thermoanalytic data for compounds ***CUADECL–B*** (***SMOF–1***) and ***CUADEBR–A*** (***SMOF–2***) performed upon synthetic air atmosphere (79% N_2, 21% O_2).

Table 3.9: Thermogravimetric data of ***CUADECL–B*** (***SMOF–1***) and ***CUADEBR–A*** (***SMOF–2***).[a, b]

Step	T_i	T_f	T_{peak}	$\Delta m(\%)$	ΔH	$\Sigma\Delta m(\%)$	$\Sigma\Delta m(\%)_{theor}$
CUADECL–B							
1	25	155	58	7	Endo	7	7.32 (–2 CH_3OH)
2	205	375	294	15.2	Exo	22.2	12.77 (–1 $C_5H_5N_5$)
3	375	500	460	60	Exo	82.2	81.8 (2 CuO)
CUADEBR–A							
1	25	100	63	11.67	Endo	11.67	12.12 (–4 CH_3OH)
2	100	215	–	2.33	–	14	15.26 (–1 CH_3OH)
3	215	415	–	12.27	–	26.27	28.24 (–1 $C_5H_5N_5$)
4	415	555	566	60.50	Exo	86.77	84.88 (2 CuO)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released molecules/fragments and final residue by formula.
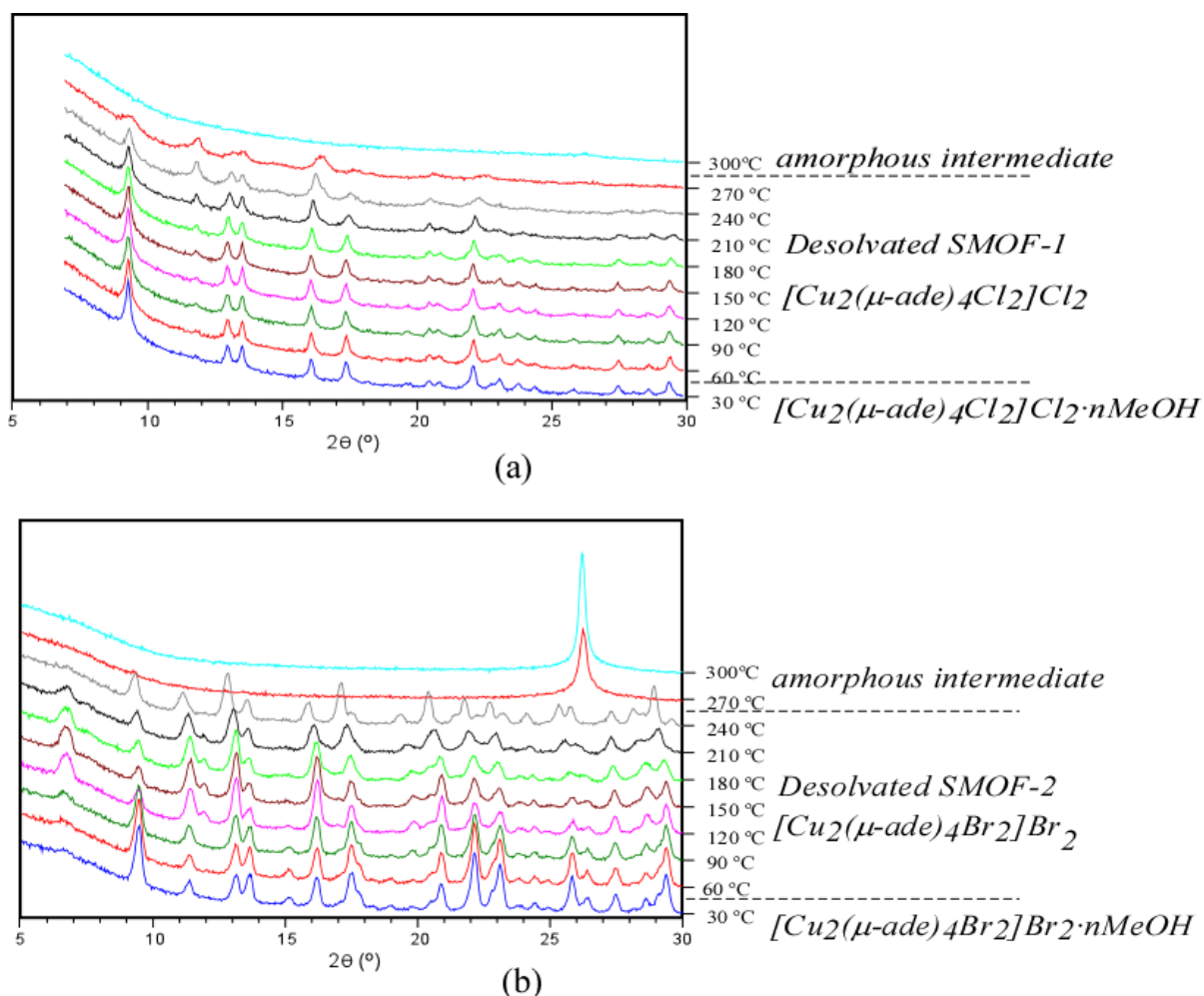
Figure 3.16 (a)

Figure 3.16: Thermodiffractometric plots of (**a**) *CUADECL–B (SMOF–1)* and (**b**) *CUADEBR–A (SMOF–2).*

3.3.2.2.2 Gas adsorption experiments on CUADECL–B (SMOF–1) and CUADEBR–A (SMOF–2).

Freshly synthesized single crystals of *CUADECL–B (SMOF–1) and CUADEBR–A (SMOF–2)* were used for gas adsorption experiments and they were activated under vacuum at temperatures ranging from 100 to 180ºC during 6–24 h to eliminate solvent guest molecules prior to measurements. Different outgassing conditions did not exert significant changes in N_2 uptake capacity. For clarity only the results of samples outgassed at 150 ºC during 12 h are shown in subsequent figures. The adsorption curve collected at 77 K exhibits features resulting from multilayer adsorption. The fitting of the adsorption area to BET equation lead to surface area values of 26 and 14 m^2/g, respectively. These values are substantially smaller than the accessible surface area calculated from the crystal structure (789

and 658 m^2/g) by a Monte Carlo integration technique, where a probe molecule with a diameter equal to the Lennard–Jones parameter for N$_2$ (3.681 Å) is "rolled" over the framework.[160] Thereafter, H$_2$ adsorption experiments were also carried out by collecting isotherms at 77 K. Similarly to N$_2$, a negligible adsorption is observed for both compounds. A common explanation for such difference between the experimental and expected porosity includes incomplete solvent removal, crystal collapse or a massive presence of impurities. However, the weight loss of the outgassed sample fits the one expected from the compound formula which suggests a quantitative removal of the solvent. The XRPD data confirms that the outgassed sample retains its crystallinity and therefore, its bulk porous framework. Finally, the comparison of XRPD, chemical analysis and scanning electron microscopy data on the fresh and outgassed samples allowed ruling out the presence of a substantial amount of impurities.

In a recent work, Matzger and coworkers explained the discrepancies between crystallographic porosity and experimental gas uptake for *Zn–HKUST–1* based on positron annihilation lifetime spectroscopy.[161] The authors state that the lack of gas uptake is due to the inherent surface instability after solvent removal which renders the material impermeable to molecular guests irrespective of the handling and activation methods used in the gas adsorption experiments. However, according to the later work, the surface collapse is overcome when the sample is immersed in a solvent and thus, the porous network is well accessible.

Nonetheless, preliminary experiments have shown that the desolvated product of ***CUADECL–B (SMOF–1)*** is able to adsorb in few minutes the humidity of the surrounding atmosphere to fill the empty channels with water molecules undergoing a weight increase of around 8% (*ca*. 4 water molecules per formula unit) and retaining the initial porous crystal structure without substantial changes in the X–ray diffraction powder pattern. Upon heating, the hydrated compound releases again the water molecules which are reabsorbed at room temperature. However, a suspension of the ***CUADECL–B (SMOF–1)*** in water affords an amorphous material after 24 hours. These facts suggest that the title compound is able to accept some amount of water molecules without any remarkable change in its crystal structure

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[160] Düren, T. et al. *J. Phys. Chem. C*, **2007**, *111*, 15350
[161] Feldblyum, J. I. et al. *J. Am. Chem. Soc.* **2011**, *133*, 18257.

but when the water is used as solvent, it acts as disruptor of the direct hydrogen bonds established between the adenine molecules and the crystal building collapses. With further experiments, the present compounds have shown to behave as an adsorbent not only for humidity but also when it was exposed to the vapours of methanol, acetone, dichloromethane, tetrachloromethane.[162] Thus it seems that the above described diffusion barrier resulting from the surface instability, it is not only overcame in solution but also when guest molecules in gas phase have enough interaction energy to pass through. In order to get further evidence on the later statement, we have carried out gas adsorption measurements at greater temperatures by collecting the isotherms for CO_2 at 273 K and CH_4 at 298 K (Figure 3.17).
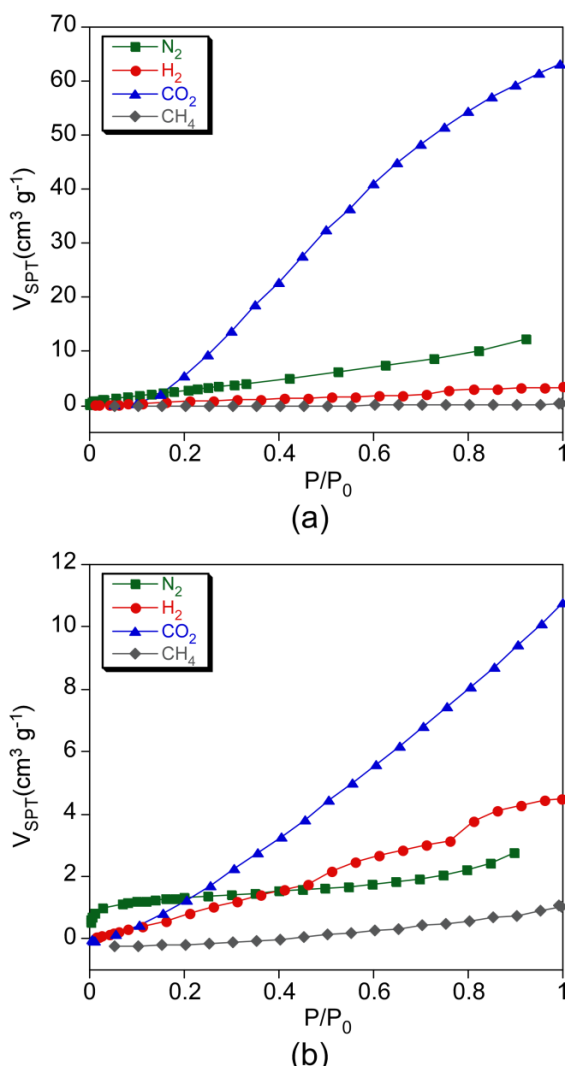
Figure 3.17: Adsorption isotherms for N_2 (77 K), H_2 (77 K), CO_2 (273 K), and CH_4 (298 K) for fresh samples of compounds *CUADECL–B (SMOF–1)* (a) and *CUADEBR–A (SMOF–2)* (b).

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[162] Thomas–Gipson, J. et al. *CrystEngComm.* **2011**, *13*, 3301.

Similar to the previous adsorbates, no methane adsorption is observed. However the CO_2 uptake shows a notable increase in both compounds. In fact while at pressures close to saturation, the N_2 uptake is of 0.54 and 0.12 mmol/g for compounds ***CUADECL–B (SMOF–1)*** and ***CUADEBR–A (SMOF–2)***, the CO_2 uptake increases about four times to reach values of 2.81 and 0.48 mmol/g, respectively. Considering the later results this behavior can be rationalized on the basis of the thermal energy and of the polar nature of the adsorbate. The apolar CH_4 lacks of quadrupole moment, while CO_2 presents a realtively strong quadrupole moment (-0.8908 e·Å^2), sustantially greater than that for N_2 or H_2 (-0.2946 and $+0.1288$ e·Å^2, respectively).[163] Methane has not been able to permeate the surface even with the increase of the adsorption temperature. Nonetheless, the greater measurement temperature and the stronger quadrupole moment of CO_2 confer the ability to diffuse through the surface barrier and permeate the porous network.

An additional proof that supports the surface instability of these compounds is obtained from the gas adsorption study of the sample ageing. In this regard, CO_2 measurements were carried out periodically during a month on samples of ***CUADECL–B (SMOF–1)*** stored at room conditions (Figure 3.18a). It becomes clear that the CO_2 uptake capacity decreases progressively as the sample becomes older, and after a month the uptake at P = 1 bar is depleted to a *ca.* 60% when compared to its initial value (V_{STP} = 63.3 and 24.4 cm^{3}g^{-1} for the initial and one month aged sample). A second phenomenon related with the sample ageing lies on the adsorption onset pressure calculated from the intersection between the tangents at the low pressure region and at the region of maximum slope of the adsorption branch (Table 3.10).

Table 3.10: Calculated onset point values for ***CUADECL–B (SMOF–1)***.

Sample	Aging (days)	Adsorption Temp. (K)	Onset value (bar)
SMOF–1	1	273	0.15
	21	273	0.35
	30	273	0.38
	21	298	0.31

[163] NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101. Release 16a, August 2013, Editor: Johnson, R. D. III. http://cccbdb.nist.gov/.
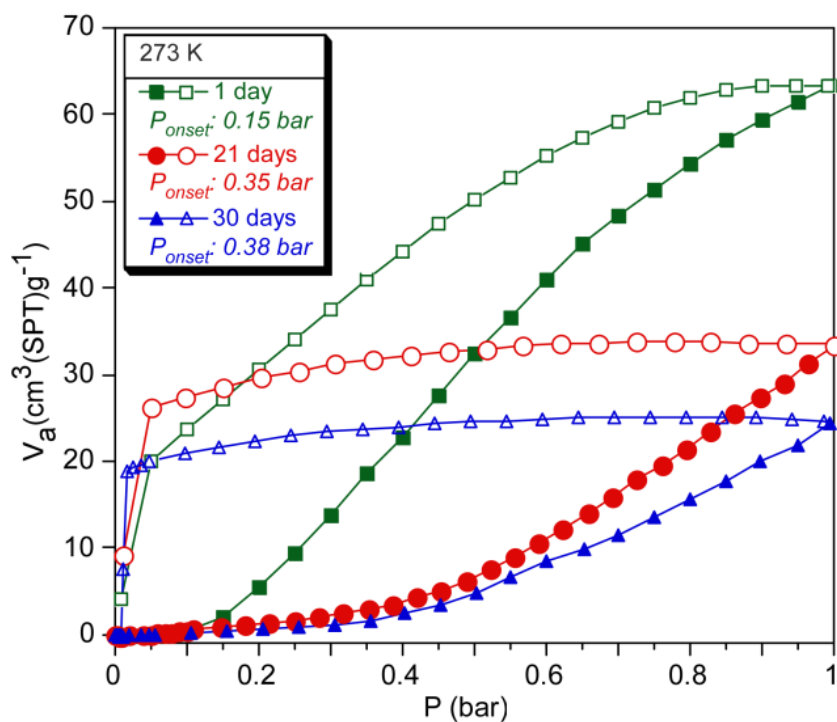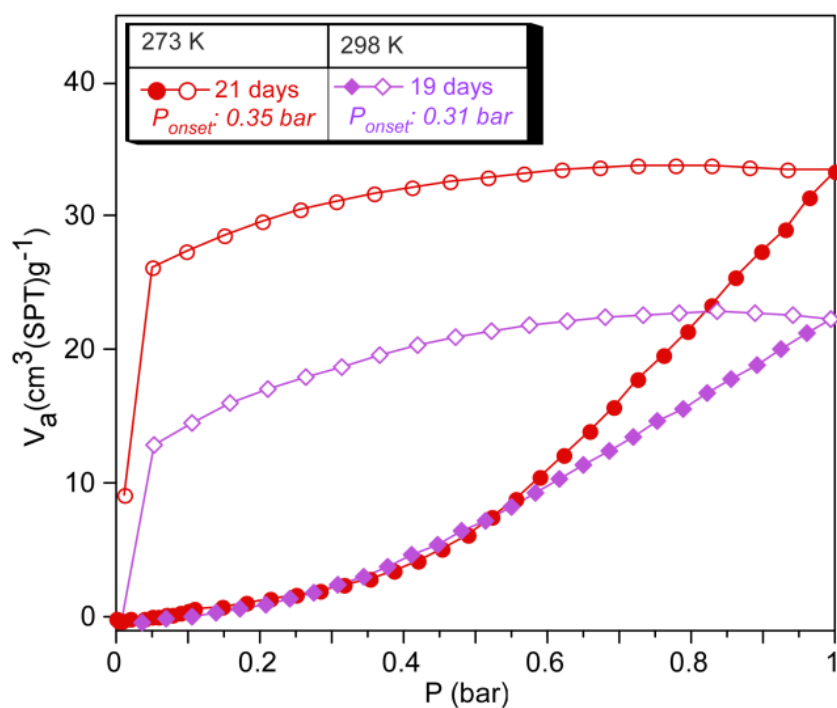
Figure 3.18: (a) CO_2 adsorption/desorption isotherms measured at 273 K showing the aging of ***CUADECL–B (SMOF–1)***. (b) CO_2 isotherms at 273 and 298 K. The onset pressure value is indicated for each case.

The adsorption of the initial sample shows a plateau with a negligible CO_2 uptake at pressures below 0.1 bar, and it requires a minimum breakthrough pressure (P_{onset}: 0.15 bar) to

permeate the surface and reach the porous network. Moreover, the breakthrough pressure has increased to higher values as the sample gets older, to reach an onset value of $P_{onset} = 0.38$ bar for the sample aged during 1 month. This progressive increase of the breakthrough pressure is related with an increase of the thickness of the collapsed surface which acts as a surface permeation barrier. Another feature that supports the presence of a surface barrier that hinders the diffusion of the molecules is related to the hysteresis cycle enclosed by desorption branch and its trend with the ageing of the sample (Figure 3.18a). It is noteworthy that despite different equilibration times were used the hysteresis cycle was not affected, and as a consequence, this hysteresis seems to be induced by structural features of the sample. In fact, the hysteresis becomes more acute as the sample is aged and its end–pressure is also delayed progressively (P_{end}: 0.05 and 0.02 bar for fresh and one month aged samples, respectively). This behavior is also congruent with an increasing thickness of the collapsed surface (or diffusion barrier) as the storage time goes on, which would also obstruct the release of the adsorbed molecules during the desorption process.

On the other hand, comparison between adsorption experiments carried out at 273 K and 298 K on similarly aged samples (Figure 3.18b), shows that the onset pressure (0.35 and 0.31 bar, respectively) is reduced with the increase of the experiment temperature, as the potential energy of the molecules to permeate the surface is increased.

In order to analyze the bulk crystal stability during CO_2 adsorption PXRD patterns were collected in a sample subjected to a CO_2 atmosphere with pressure ranging between 0.5 and 6 bar. Prior to the experiment the sample was outgassed at 150 ℃ during several hours. As it can be observed (Figure 3.19) all the experimental reflections match the ones corresponding to the simulated patterns of ***CUADECL–B (SMOF–1)***. ***CUADEBR–A (SMOF–2)***, and in any case no shift in 2θ positions is observed which stands for stability of the bulk crystallinity and for the bulk framework rigidity during the CO_2 adsorption process (i.e. reversible structural changes caused by CO_2 uptake can be disregarded, as for example, the so–called breathing effect.[164]

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[164] (a) Ramsahye, N. A. et al. *Chem. Commun.* **2007**, 3261. (b) Serre, C. et al. *Adv. Mater.* **2007**, *19*, 2246.
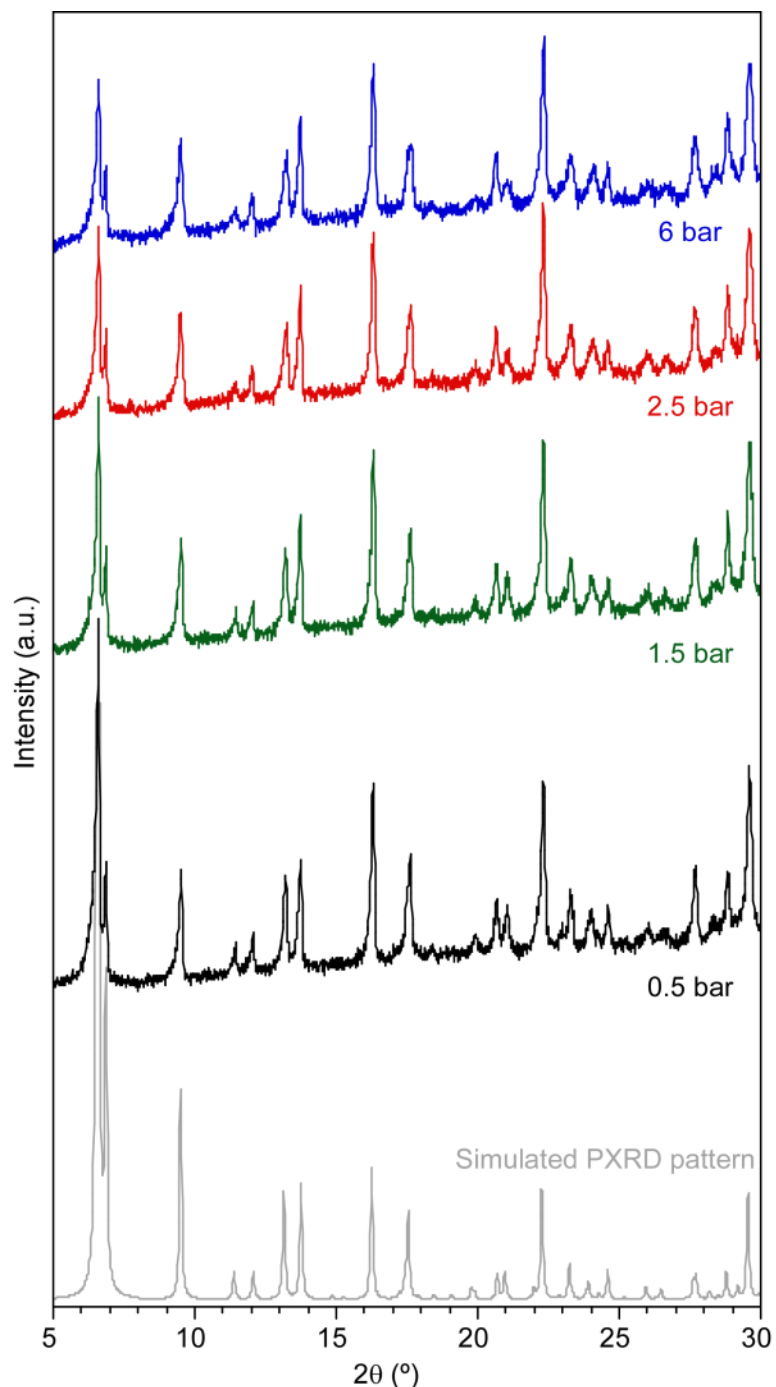
Figure 3.19: Comparison between experimental PXRD patterns collected at different CO_2 pressures and simulated PXRD pattern for the pristine crystal structure of ***CUADECL–B (SMOF–1).***

Regarding to the peak intensity, despite most of the peaks show no changes, the intensities of certain reflections are significantly affected. Figure 3.20a shows the trend of three reflections within the 6–10º 2θ range. As it can be observed [2 0 $\bar{1}$] reflection remains unvarying while the intensity of [2 $\bar{1}$ 0] and [1 0 1] decay continuously with the increasing CO_2 pressure, which seems to be related with the CO_2 uptake within the structural pores.
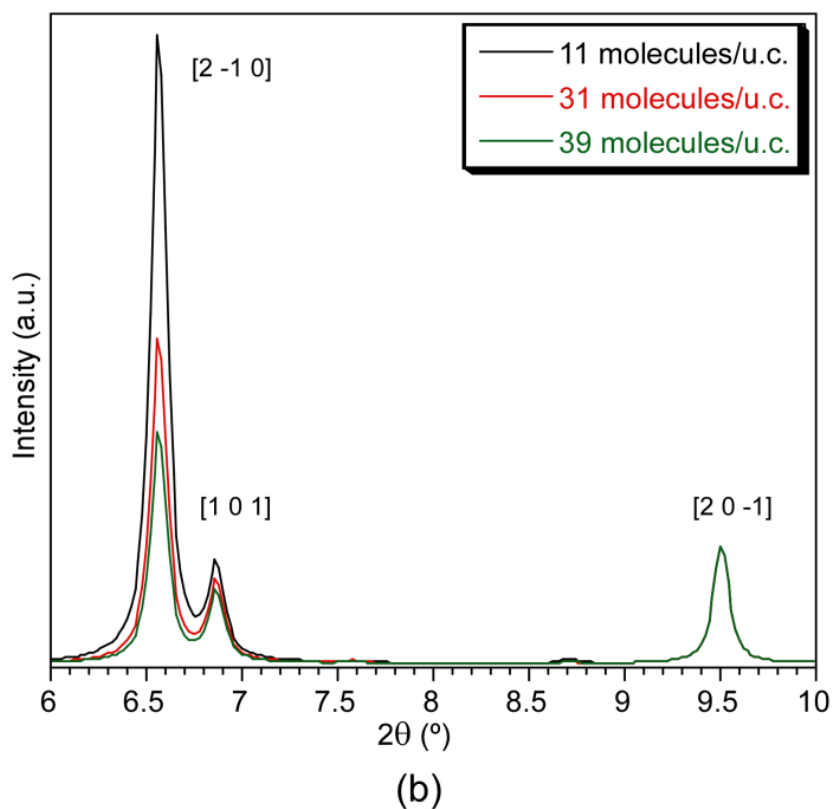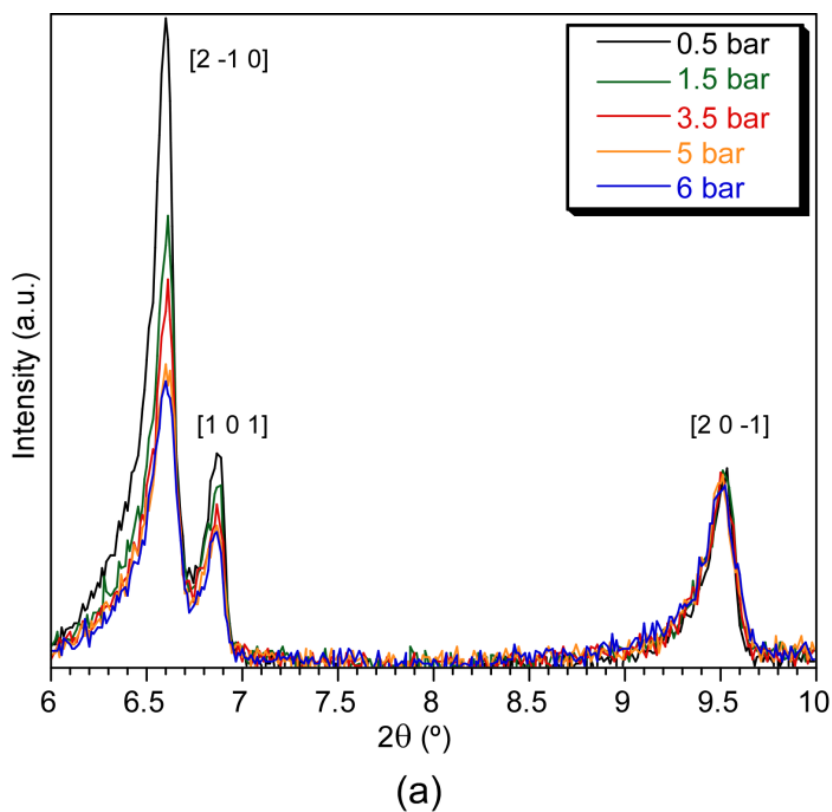
Figure 3.20: PXRD data for *CUADECL–B (SMOF–1)* within 6–10º: (a) experimental patterns with increasing CO_2 pressure. (b) Simulated PXRD patterns from GCMC low energy configurations with increasing CO_2 uptake per unit cell.

In order to confirm the later proposal, Grand Canonical Monte Carlo (GCMC) calculations were carried out in which the porous framework of **CUADECL–B (SMOF–1)** was loaded with different amounts of CO_2. Low energy configurations of the adsorbed molecules were used to model how the PXRD patterns are affected by the CO_2 (Figure 3.20b). The trend derived from the GCMC simulations matches the observed one for experimental PXRD patterns, which allows to state that intensity decay of the cited reflections ([2 $\bar{1}$ 0] and [1 0 1]) is due to the presence of CO_2 within the 1D pores. When coordinates of CO_2 molecules are considered non symmetry relation is found in any of the GCMC calculations. However, there is a periodicity of the preferential sites of adsorption (most sites derived from probability density distribution for the center of mass of CO_2 molecule) in which electron density coming from adsorbed gas is accumulated (Figure 3.21). As a consequence, the decay of the mentioned reflections can be attributed to this periodically distributed averaged electron density of the adsorbed molecules.
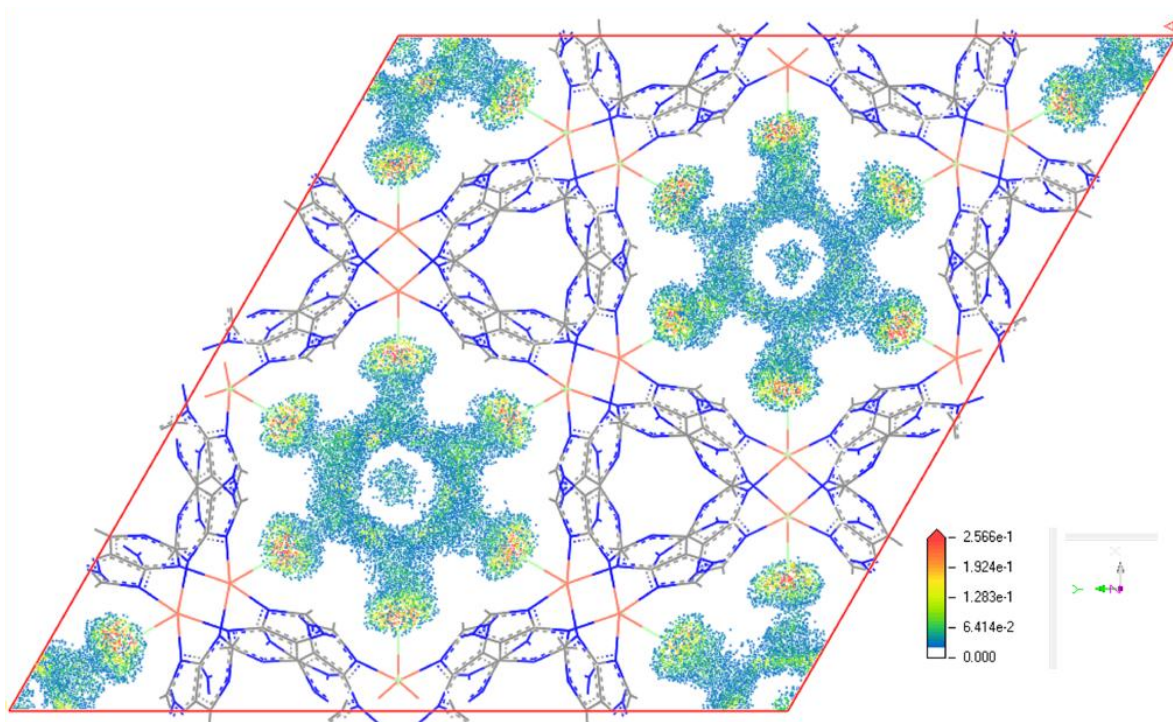
Figure 3.21: Average occupation profiles for CO_2 at 298 K in **CUADECL–B (SMOF–1)**.

3.3.2.3 Structural description of [Cu$_2$(μ–Hade)$_2$(μ–Cl)$_2$(Cl)$_2$]·2MeOH; *CUADECL– C (SMOF–3)* and [Cu$_2$(μ–Hade)$_2$(μ–Br)$_2$(Br)$_2$]·2PrOH; *CUADEBR–B*

Both compounds are comprised of neutral centrosymmetric dimeric [Cu$_2$(μ– adenine)$_2$(μ–X)$_2$(X)$_2$] entities (X: Cl⁻, Br⁻) (Figure 3.22). They present some resemblances with the previously described [Cu$_2$(μ–adenine)$_4$X$_2$]$^{2+}$ dimeric entity of **CUADECL–B**

(SMOF–1) and ***CUADEBR–A (SMOF–2).*** The overall paddle–wheel shape is retained but two opposite adenine ligands have been replaced by two bridging halido ligands giving rise to a neutral dimeric entity showing a UD conformation with regard to the adenine bridges and capped by two additional terminal halido ligands. The intradimeric Cu···Cu distances (2.942(1) and 2.902(1) Å, for chloride and bromide analogues) are slightly shorter than that of ***CUADECL–B (SMOF–1)*** and ***CUADEBR–A (SMOF–2)*** (3.064(1) and 3.082(1) Å). Each copper atom is penta–coordinated by a N_2X_3 donor set which resembles a compressed trigonal bipyramid. The equatorial plane consists of three halido ligands implying longer bond distances than the apical ones (Table 3.11) and X–Cu–X angles within the range of 106–144º and a deviation of *ca.* 0.05 Å for the Cu(II) centre. The apical positions are occupied by the N3 and N9 donor sites of two symmetry related adenine molecules with a N–Cu–N angle of *ca.* 165º and an angle between equatorial plane and Cu–N bond of 83–86º. The coordination bond distances of the bridging halide anions are slightly longer than those of the terminal ones as usually happens.[87]
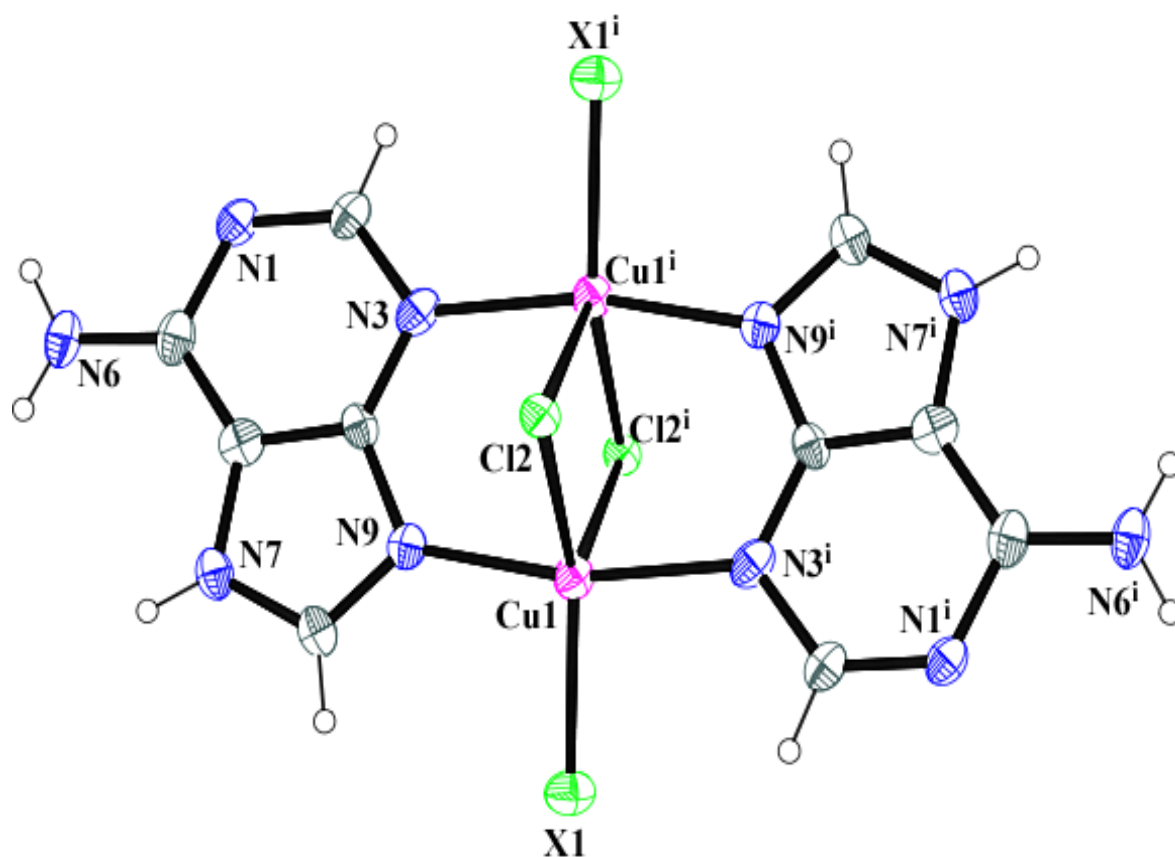
Figure 3.22: Ortep representation of the [$Cu_2(\mu–ade)_2(\mu–X)_2X_2$] units in ***CUADECL–C (SMOF–3)*** and ***CUADEBR–B***.

Table 3.11: Selected bond lengths (Å) and angles (°) for the coordination polyhedron of ***CUADECL–C (SMOF–3)*** and ***CUADEBR–B***.[a]

CUADECL–C		CUADEBR–B	
Cu–N3[i]	2.006(4)	Cu–N3[i]	1.963(5)
Cu–N9	1.983(4)	Cu–N9	1.962(5)
Cu–Cl1	2.241(1)	Cu–Br1	2.378(1)
Cu–Cl2	2.342(1)	Cu–Br2	2.540(1)
Cu–Cl2[i]	2.757(1)	Cu–Br2[i]	2.656(1)
Cu···Cu[i]	2.942(1)	Cu···Cu[i]	2.902(1)
N3[i]–Cu–N9	164.83(17)	N3[i]–Cu–N9	165.8(2)
N3[i]–Cu–Cl1	96.71(13)	N3[i]–Cu–Br1	98.02(14)
N3[i]–Cu–Cl2	87.19(14)	N3[i]–Cu–Br2	87.23(14)
N3[i]–Cu–Cl2[i]	83.77(13)	N3[i]–Cu–Br2[i]	86.58(13)
N9–Cu–Cl1	94.32(13)	N9–Cu–Br1	95.56(14)
N9–Cu–Cl2	87.19(14)	N9–Cu–Br2	86.78(14)
N9–Cu–Cl2[i]	83.21(13)	N9–Cu–Br2[i]	83.73(14)
Cl1–Cu–Cl2	144.00(6)	Br1–Cu–Br2	132.35(3)
Cl1–Cu–Cl2[i]	105.81(6)	Br1–Cu–Br[i]	115.45(3)
Cl2–Cu–Cl2[i]	110.07(4)	Br2–Cu–Br2[i]	112.12(3)

[a]Symmetry codes: (i) –x+1/2, –y+1/2, –z+1.

Obviously, in the case of ***CUADECL–C (SMOF–3)***, the coplanar arrangement and the lower amount of adenines in the dimeric [Cu$_2$(μ–ade)$_2$(μ–Cl)$_2$Cl$_2$] entity in comparison to the secondary building unit found in compounds ***CUADECL–B (SMOF–1)*** and ***CUADEBR–A (SMOF–2)***, does not preclude the polymerization through direct complementary hydrogen bonding interactions between the nucleobases. However, it reduces the dimensionality of the resulting supramolecular network polymerized through direct complementary hydrogen bonding interactions between the nucleobases. The hydrogen bonding parameters of ***CUADECL–C (SMOF–3)*** are given in Table 3.12. In fact, in the case of ***CUADECL–C (SMOF–3)***, the base pairing interaction between the Watson–Crick faces of [Cu$_2$(μ–ade)$_2$(μ–Cl)$_2$(Cl)$_2$] units gives rise to linear 1D supramolecular ribbons that spread along two different

crystallographic directions [1 1 0] and [1 $\bar{1}$ 0] as it can be observed in Figure 3.23. These supramolecular ribbons are further crosslinked by means of both the hydrogen–bonding interactions between the Hoogsteen face and the bridging chlorido ligands and π–π stacking interactions between adjacent adenines. The combination of the later two types of interactions leads also to a relatively rigid synthon that extends the connectivity towards a robust supramolecular 3D network and, at the same time, precludes an efficient occupation of the space. Considering both types of synthons (Watson–Crick base pairing and Hoogsteen···chlorido/π–π stacking) the supramolecular network can be described as a six–connected uninodal with ***rob*** topology and $(4^8.6^6.8)$ point symbol. This packing generates 1D channels along the crystallographic *c* axis with an elliptical cross–section of *ca*. 5.5x7.5 Å, that are filled by solvation methanol molecules that represent a 21% of the total volume. Again, the combination of rigid metal–nucleobase building unit and geometrically restricted supramolecular synthons leads to an ineffective space occupation providing accessible space within the crystal structure of this material. It is worthy to mention that the hydrogen bonding interaction between the Hoogsteen side of the adenine and the chlorido ligands is reinforced by an indirect hydrogen bond mediated by a solvation methanol molecule that will cause, as it is discussed later, a relatively significant unit cell change upon the removal of the solvent molecules.

Table 3.12: Supramolecular interactions (Å, °) in ***CUADECL–C*** (***SMOF–3***).

Hydrogen bonding interactions.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N6–H6B···O1	0.86	2.19	2.811(8)	128.7
N6–H6B···N1[i]	0.86	2.14	2.999(6)	175.0
N7–H7···Cl2[ii]	0.86	2.45	3.180(5)	143.5

π–π stacking interactions.[c]

Ring···Ring[d]	Angle	DC	α	DZ	DXY
Ring(1)···Ring(2)[iii]	2.1(3)	3.656(3)	26.93	3.298(2)	1.58
Ring(2)···Ring(1)[iv]	2	4.216(3)	37.52	3.260(2)	2.67

[a] Symmetry: (i) –x+1, –y, –z+1; (ii) –x+1/2, y–1/2, –z+1/2; (iii) x, –y, z+1/2; (iv) x, –y, z–1/2. [b] **D**: donor; **A**: acceptor. [c] Angle: Dihedral Angle between Planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] Ring 1: N7, C5, C4, N9, C8; Ring 2: N1, C2, N3, C4, N9, C6.
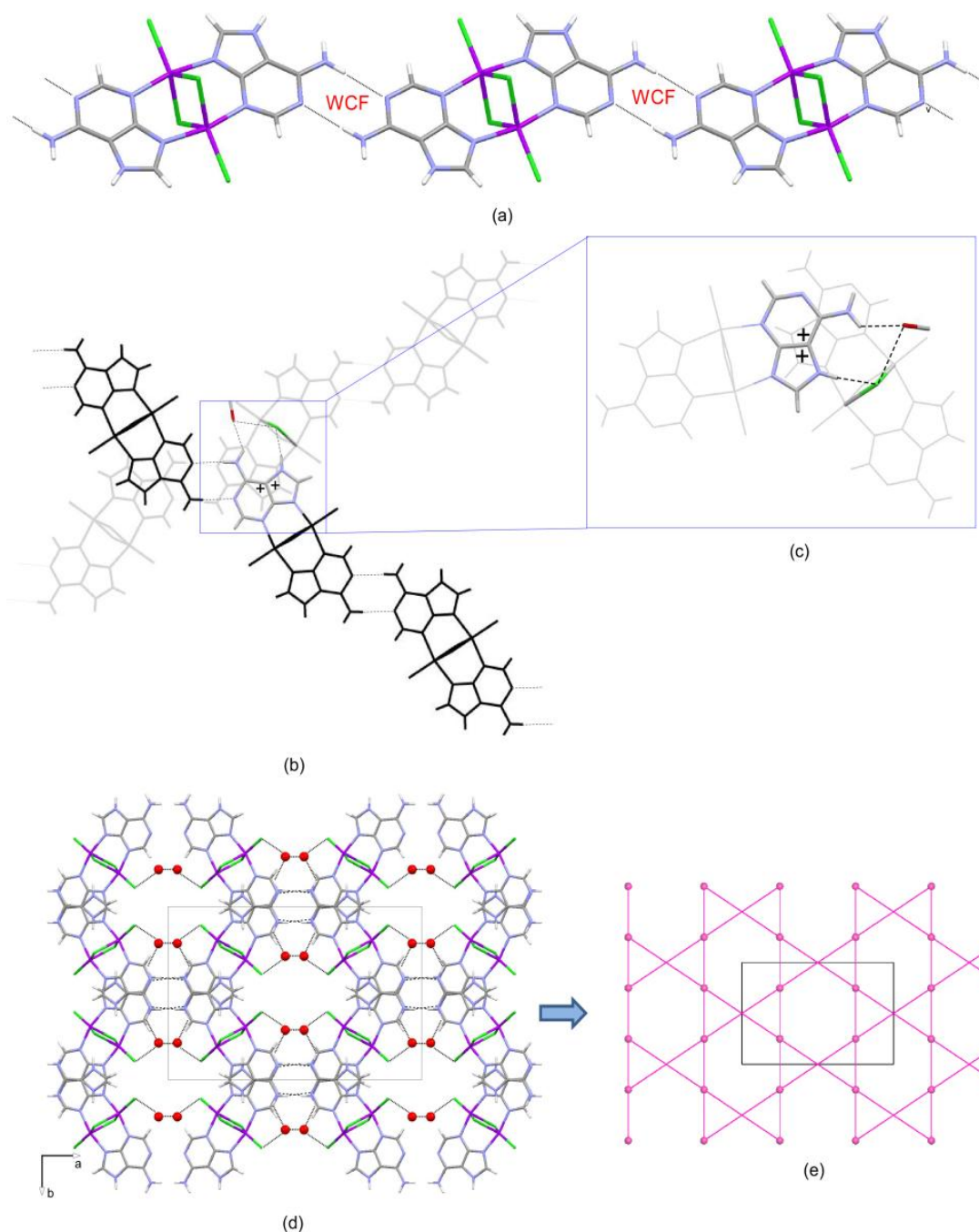
Figure 3.23: Crystal packing features in **CUADECL–C** (**SMOF–3**): (a) Strips of [Cu$_2$(μ–adenine)$_2$(μ–Cl)$_2$(Cl)$_2$] dinuclear complexes grown by Watson–Crick base pairing interactions. (b, c) Dinuclear entities interacting through Cl⋯Hoogsteen face and π–π interactions. (d, e) View of the crystal packing through [1 0 0] direction and overall supramolecular connectivity. Dashed lines indicate hydrogen bonds, while double plus signals represent π–π stacking interactions.

The weaker hydrogen bond accepting nature of the bromido ligand in comparison to chlorido makes the crystal packing features of **CUADEBR–B**, [Cu$_2$(μ–ade)$_2$(μ–Br)$_2$(Br)$_2$]·PrOH (Figure 3.24) to be essentially different from that of its chloride analogue **CUADECL–C** (**SMOF–3**). It does not present neither base pairing interactions nor any other

direct hydrogen bonding interactions between the adenine moieties and coordinated bromides. In fact, the dinuclear entities are held together by the hydrogen bonding interactions mediated through the entrapped propan–1–ol molecules with the Hoosgteen and Watson–Crick faces of adjacent paddle–wheel entities. The Hoogsteen face of the nucleobase is hydrogen bonded to the oxygen atom of the propan–1–ol molecule ($R_2^1(7)$ hydrogen bonded ring), while the Watson–Crick face of the adenine establishes a single hydrogen bond by means of the interaction of N1 with H atom of the alcohol group. The hydrogen bonding parameters are given in Table 3.13. The supramolecular network is further reinforced by halido···π type interactions established between the terminal Br1 atoms and C5 carbon of the (Br1···C5: 3.489(1) Å). The lack of direct hydrogen bonding interactions among the rigid adenine moieties and the solvent mediated disruption of the hydrogen bonding network results in a non–porous crystal structure which collapses at temperatures close to 50 ℃ rendering an amorphous product, according to the thermogravimetric and temperature variable XRPD measurements**.**

(b)
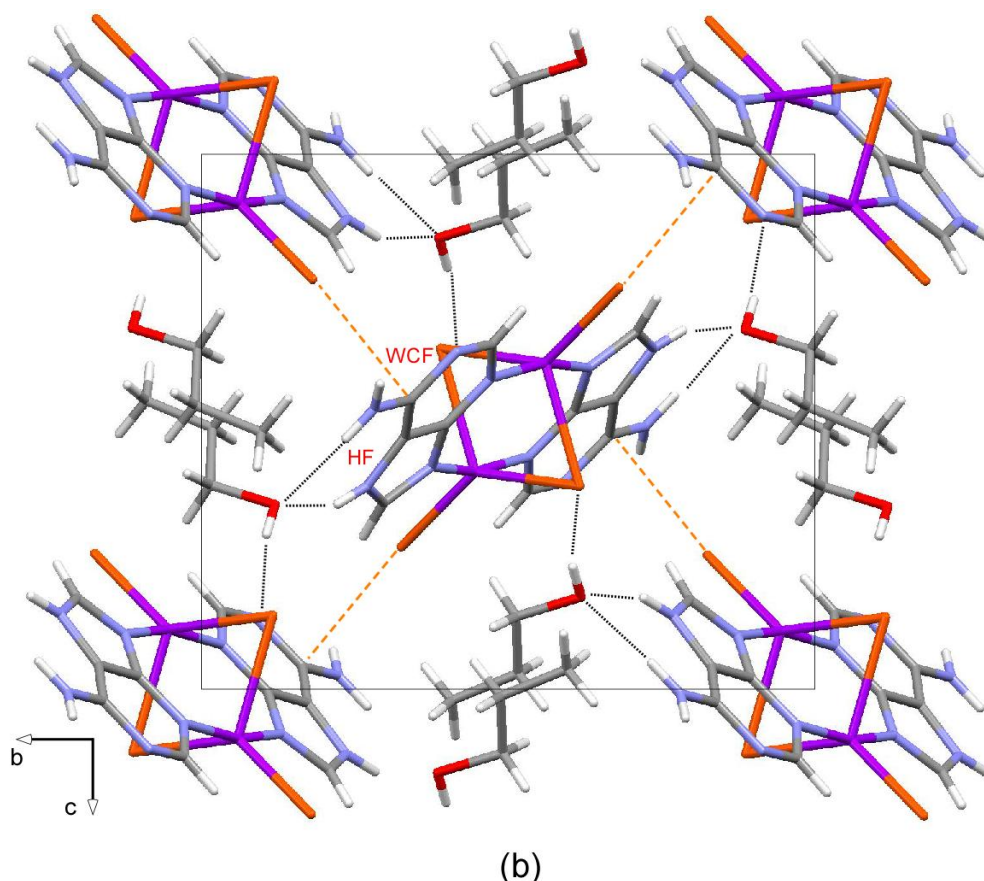
Figure 3.24: A view of the crystal packing through [1 0 0] direction in *CUADEBR–B*. Black dotted lines indicate hydrogen bonding interactions, while orange dashed lines indicate halido···π contacts.

Table 3.13: Hydrogen bonding interactions (Å, º) in the compound *CUADEBR–B*.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N6–H6A···Br2^{i}	0.86	2.63	3.424(5)	153.1
N6–H6B···O1^{ii}	0.86	2.10	2.931(6)	162.1
N7–H7···O1^{ii}	0.93(9)	1.89(9)	2.776(6)	159(8)
O1–H1···N1^{i}	0.77(10)	2.02(10)	2.775(6)	171(10)

[a] Symmetry codes: (i) –x+2, –y, –z+2; (ii) x, –y+1/2, z–1/2. [b] **D**: donor; **A**: acceptor.

3.3.2.3.1 *Thermogravimetric analysis of CUADECL–C (SMOF–3) and CUADEBR–B*

In order to assess the stability of the unsolvated *CUADECL–C* (*SMOF–3*) thermogravimetric (Figure 3.25 and Table 3.14) and temperature variable XRPD experiments were carried out (Figure 3.26). Thermogravimetric analysis shows that the solvent molecules are released easily at temperatures below 140 ºC. Afterwards, the TGA curve shows a stable plateau that extends up to 245 ºC. At higher temperatures the compound decomposes in successive exothermic steps to yield CuO as the final residue at temperatures above 500 ºC. The compound *CUADEBR–B* is also stable up to 200 ºC and then it decomposes to the final residue CuO above 600 ºC.

CUADECL-C (SMOF-3)   *CUADEBR-B*
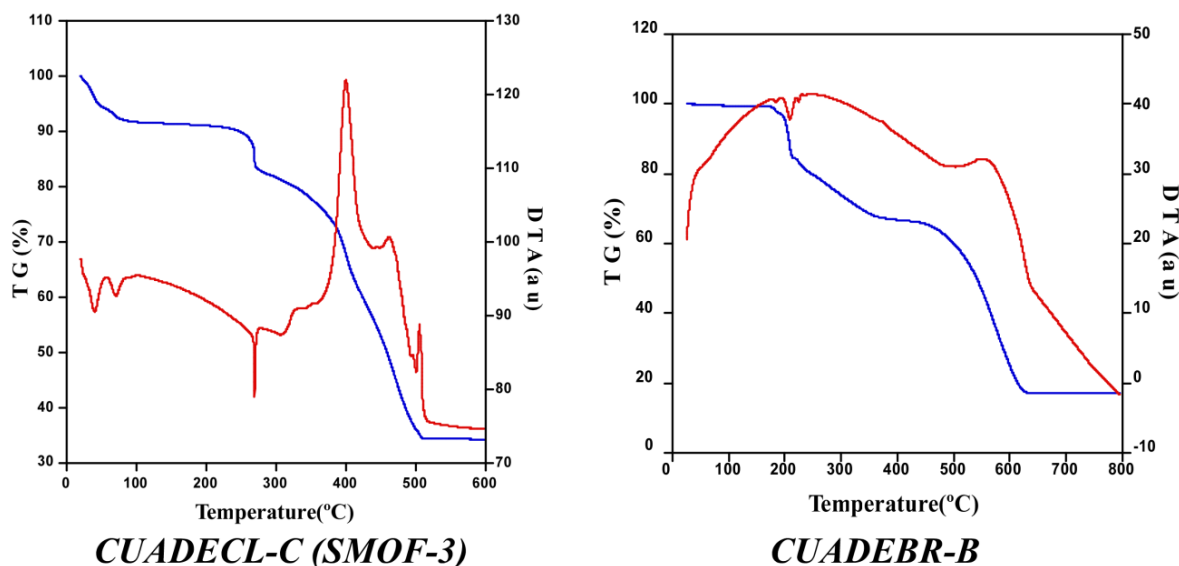
Figure 3.25: Thermogravimetric data for compounds *CUADECL–C* (*SMOF–3*) and *CUADEBR–B*

Table 3.14: Thermogravimetric data for compounds ***CUADECL–C*** (***SMOF–3***) and ***CUADEBR–B***[a,b]

Step	T_i	T_f	T_{peak}	$\Delta m(\%)$	ΔH	$\Sigma\Delta m(\%)$	$\Sigma\Delta m(\%)_{theor}$
CUADECL–C (SMOF–3)							
1	25	140	40/70	9.44	Endo	9.44	10.06(–2 CH$_3$OH)
2	245	320	270	7.37	Endo	16.81	16.10 (–HCl)
3	320	510	400/462/505	48.75	Exo	65.56	67.05 (2 CuO)
CUADEBR–B							
1	25	215	185/210	15.12	Endo	15.12	14.36 (–2 PrOH)
2	220	375	–	18.26	Exo	33.38	33.68 (–2 HBr)
4	430	630	555	49.48	Exo	82.86	81.00 (2 CuO)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released molecules/fragments and final residue per formula.

As it is evident from the Figure 3.26, the thermodiffractometric measurements of ***CUADECL–C*** (***SMOF–3***) show a significant difference between the diffractogram performed at 30 ℃ and those performed between 90–180 ℃. The cell parameters indexed for the PXRD pattern collected at 30 ℃ match the ones corresponding to the single crystal structure. However, the PXRD pattern change observed at temperatures above 60 ℃ lead to new unit cell parameters closely related to the previous ones but with a significant change in the unit cell transforming it to a non standard monoclinic setting with $\gamma \neq 90º$. This transformation is related to a rearrangement of the synthon established between the Hoogsteen face and the chloride anion once the methanol molecule is released.[165] A scheme of this rearrangement is given in the Figure 3.26. It indicates that although the supramolecular structure has suffered a moderate change, its overall supramolecular crystal structure remains essentially stable up to 180 ℃.

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[165] Thomas–Gipson, J. et al. *Cryst. Growth Des*. **2014**, *14(8)*, 4019.

T (°C)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)
30	22.962(1)	13.668(1)	7.184(1)	90	108.47(1)	90	2138.5(1)
60	21.657(1)	13.393(1)	7.096(1)	90	90	107.65(1)	1961.3(1)
90	21.643(1)	12.859(1)	7.391(1)	90	90	101.16(1)	2018.0(1)
120	21.631(1)	12.935(1)	7.440(1)	90	90	101.51(1)	2040.0(1)
150	21.559(1)	12.915(1)	7.135(1)	90	90	101.69(1)	1945.4(1)
180	21.639(1)	12.764(1)	7.725(1)	90	90	100.95(1)	2094.8(1)

Figure 3.26: Thermodiffractometric data of ***CUADECL–C*** (***SMOF–3***) and proposed rearrangement scheme for the structural phase transition**.**

3.3.2.3.2 *Gas Adsorption studies of CUADECL–C (SMOF–3)*

In order to assess the permanent porosity inferred from thermodiffractometric measurement, gas adsorption isotherms were measured on freshly synthesized sample of ***CUADECL–C*** (***SMOF–3)*** which was activated under vacuum at 140 °C during 12 h to eliminate solvent guest molecules. The results and conclusions derived from the study of the gas adsorption behavior of ***CUADECL–B*** (***SMOF–1)*** and ***CUADEBR–A (SMOF–2)***, suggest that the surface feebleness of this kind of supramolecular compounds can make routine nitrogen adsorption isotherms not suitable for the study of their porosity features. In fact, ***CUADECL–C*** (***SMOF–3)*** presents a computed surface area of 361 m^2g^{-1}, but the experimental N_2 adsorption isotherm corresponds to a non–porous material. ***CUADECL–C*** (***SMOF–3)*** adsorbs a significant amount of CO_2 as depicted by Figure 3.27, but comparatively smaller than ***CUADECL–B*** (***SMOF–1)*** and ***CUADEBR–A (SMOF–2)***, due to

the greater free volume and surface area of the later ones. Similar to the precedent supramolecular microporous compounds, ***CUADECL–C*** (***SMOF–3)*** presents a breakthrough pressure close to P = 0.31 bar.
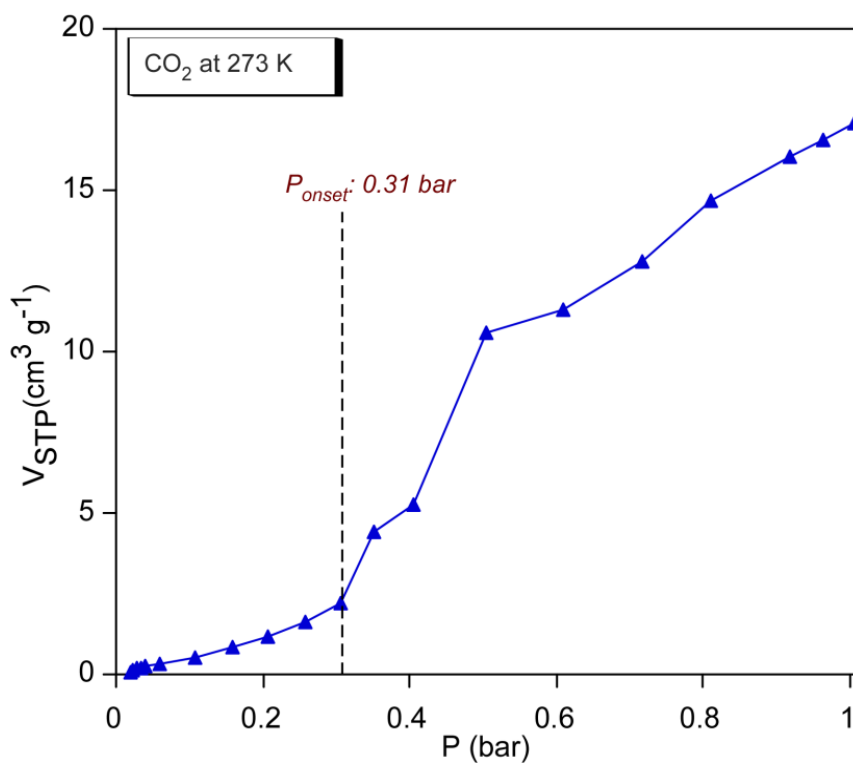
Figure 3.27: CO_2 adsorption isotherm ***CUADECL–C*** (***SMOF–3)*** at 273 K.

3.3.2.4 Structural description of $[Cu_2(\mu–ade)_3(\mu–OH)(H_2O)(CH_3OH)]_n \cdot n(solvent)$; ***CUADEOH*** (***SMOF–9***)

The basic structural unit of this compound consists of 1D infinite coordination polymers held together by complementary hydrogen bonding interactions in a 3D supramolecular porous structure. Table 3.15 and Table 3.16 display the most relevant coordination and hydrogen bonding structural parameters. The coordination polymer is composed of non– centrosymmetric dinuclear units (Figure 3.28) in which two Cu(II) centers are bridged by two adeninate moieties through the N3 and N9 nitrogen atoms and also by one oxygen atom of a hydroxyl group (Figure 3.29). One of the metal centers is also coordinated to a terminal water molecule while the other to the oxygen atom of a methanol molecule. These dinuclear units are connected by additional bridging adeninates that are coordinated to the Cu(II) centers through the N7 and N9 to provide a 1D coordination chain (Figue 3.29). An interesting structural feature is that the bridging adeninates inside the dinuclear units are tilted 22º, but they present wider tilt angle with respect to those connecting the dimeric units (56 and 78º,

respectively) in the polymeric chain. This fact together with the complementary hydrogen bonding interactions of the nucleobases promotes a three–dimensional propagation of the supramolecular structure sustained by the complementary hydrogen bonding interactions. The μ–$\kappa N3$:$\kappa N9$–adeninates are able to establish double WC$\cdots$WC and H$\cdots$H synthons leading to $R_2^2(8)$ and $R_2^2(10)$ hydrogen bonding rings, respectively. On the otherhand, the μ–$\kappa N7$:$\kappa N9$–adeninates are hydrogen bonded to the bridging hydroxide and the coordinated water molecule of an adjacent polymeric chain through N1 and N6 positions of the Watson–Crick face. The resulting supramolecular crystal structure shows the presence of large channels along the *b* axis with a calculated surface area of 295 m^2/g and 44% of void space.

Figure 3.28: Ortep representation of the the asymmetric unit of ***CUADEOH*** (***SMOF–9***) together with the numbering scheme.
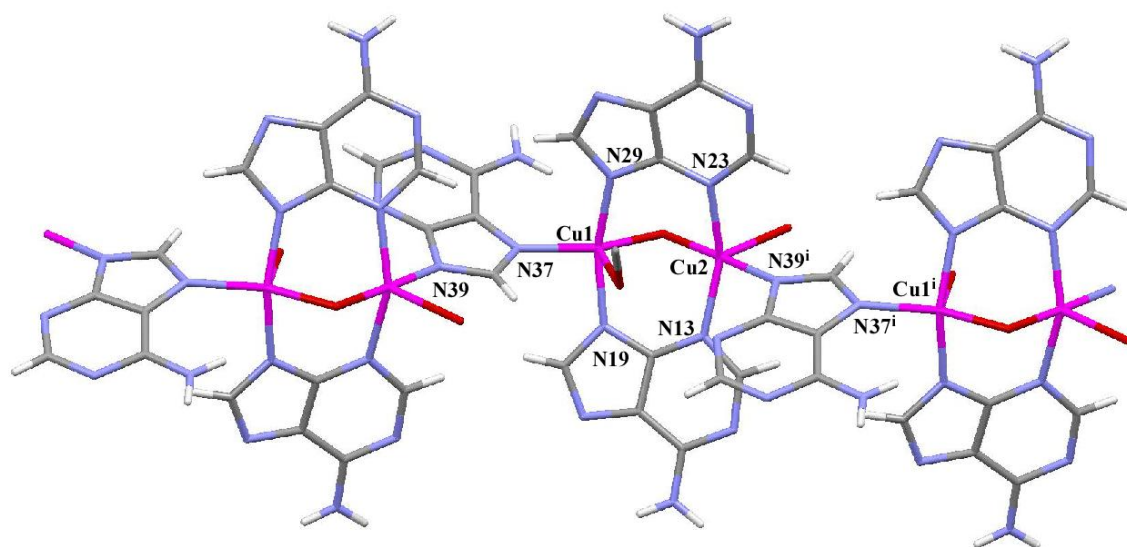
(a)
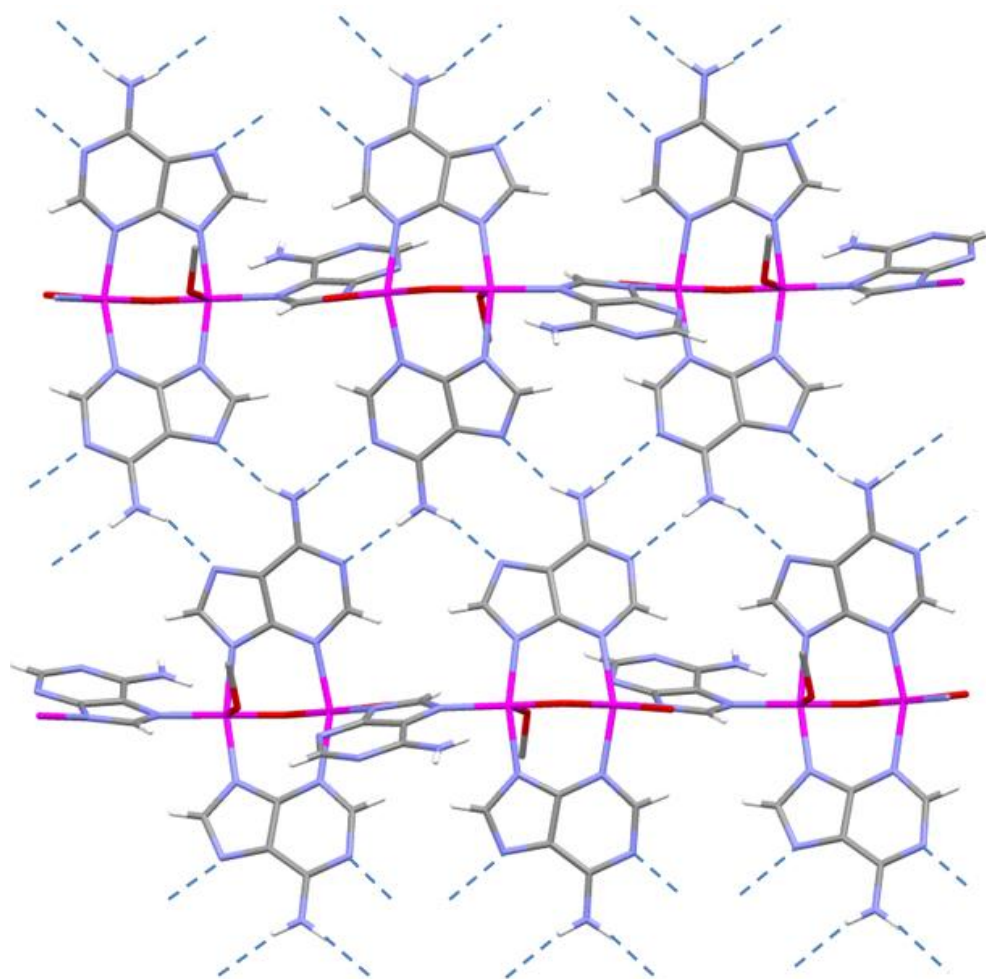
(b)

Figure 3.29: (a) The coordination polymeric chain and (b) supramolecular complementary base pairing interactions among the adeninate entities in compound ***CUADEOH*** (***SMOF–9***).

Table 3.15: Selected bond lengths (Å) and angles (°) of the coordination sphere of *CUADEOH* (*SMOF–9*).[a]

Cu1–N19	1.954(6)	N19–Cu1–N37	96.7(3)	N39[i]–Cu2–N13	91.1(3)
Cu1–N29	1.972(7)	O1–Cu1–N29	86.3(3)	N23–Cu2–N13	157.0(3)
Cu1–O1	1.940(6)	N19–Cu1–N29	161.2(3)	O1–Cu2–O2w	92.8(3)
Cu1–N37	1.969(8)	N37–Cu1–N29	95.2(3)	N39[i]–Cu2–O2w	89.6(3)
Cu2–N13	2.031(6)	O1–Cu1–Cu2	39.1(2)	N23–Cu2–O2w	95.9(3)
Cu2–N23	2.017(7)	N19–Cu1–Cu2	82.2(2)	N13–Cu2–O2w	106.8(3)
Cu2–O1	1.936(7)	N37–Cu1–Cu2	166.5(3)	O1–Cu2–Cu1	39.2(2)
Cu2–O2w	2.264(7)	N29–Cu–Cu2	82.8(2)	N39[i]–Cu2–Cu1	138.4(3)
Cu2–N39[i]	1.952(8)	O1–Cu2–N39[i]	177.6(3)	N23–Cu2–Cu1	80.7(2)
Cu1–Cu2	3.0046(18)	O1–Cu2–N23	86.9(3)	N13–Cu2–Cu1	81.5(2)
O1–Cu1–N19	89.1(3)	N39[i]–Cu2–N23	92.7(3)	O2W–Cu2–Cu1	131.80(19)
O1–Cu1–N37	154.3(4)	O1–Cu2–N13	88.4(3)		

[a] Symmetry codes: (i) –x+1/2, y+1/2, –z+1/2.

Table 3.16: Hydrogen bonding interactions (Å, °) in *CUADEOH* (*SMOF–9*).[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N16–H16A···N11[i]	0.86	2.23	3.075(10)	169.6
N26–H26A···N21[ii]	0.86	2.06	2.920(11)	179.2
N26–H26B···N17[iii]	0.86	2.08	2.904(11)	160.9
N36–H36B···O1[iv]	0.86	2.12	2.884(9)	148.1

[a] Symmetry codes: (i) –x+1, –y+2, –z+1; (ii) –x, –y+2, –z; (iii) x–1/2, –y+3/2, z–1/2; (iv)–x+1/2, –y+3/2, –z.
[b] **D**: donor; **A**: acceptor.

This compound is an interesting case because it is in between pure *MOFs* and *SMOFs* as it polymerizes into 1D through coordination bonds and further extends to supramolecular array through complementary hydrogen bonding interactions resulting in a 3D porous network (Figure 3.30).

(a)

(b)
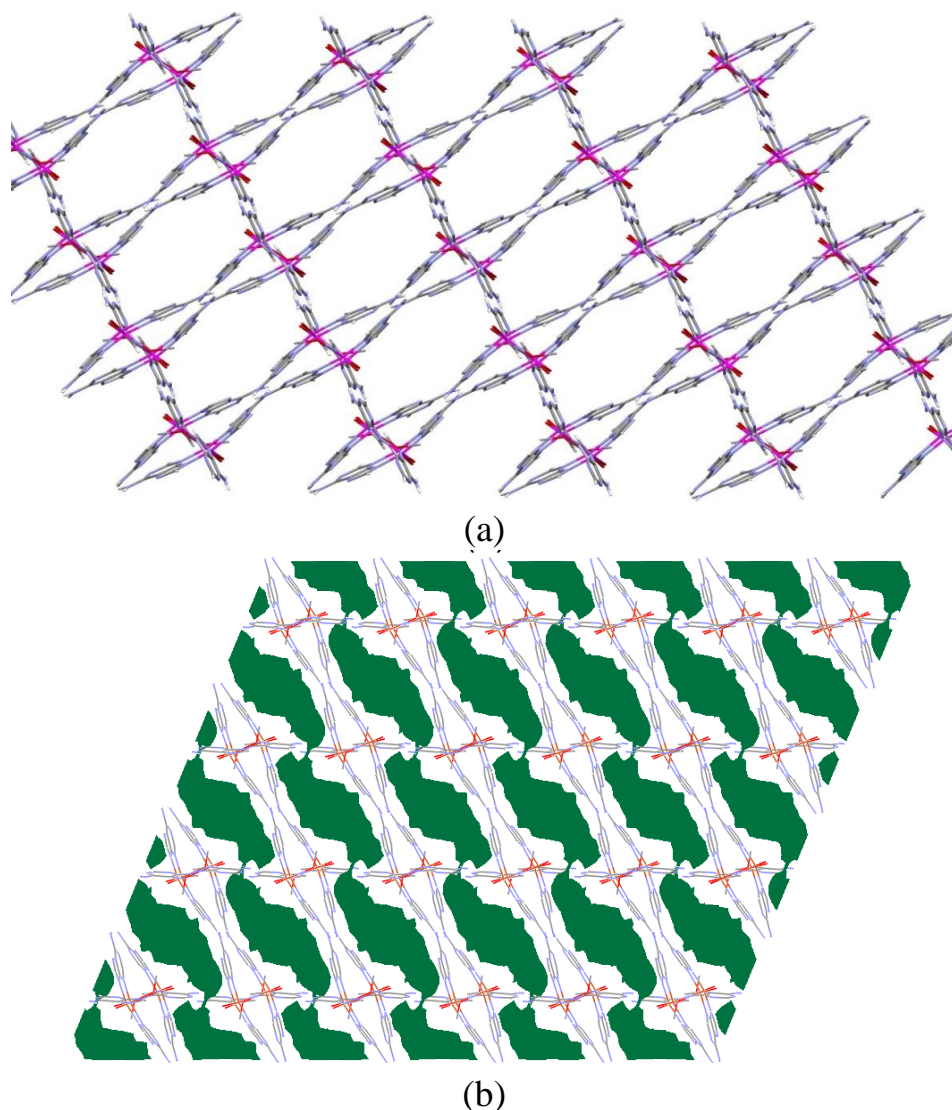
Figure 3.30: (a) Porous supramolecular architecture of ***CUADEOH*** (***SMOF–9***) (b) the available void space shown in green colour.

3.3.2.5 Structural   description   of $[Co_3(\mu–Hade)_2(\mu–Cl)_4Cl_2(H_2O)_4]\cdot 2H_2O$; (*CO3ADECL*)

The crystal structure consists of linear trinuclear units of formula $[Co_3(\mu–Hade)_2(\mu–Cl)_4Cl_2(H_2O)_4]$ and solvated water molecules. The metal centres are held together by two neutral 7H–adenines showing a $\mu–\kappa N3{:}\kappa N9$ coordination mode and four bridging μ–chloridos. Every cobalt(II) atom presents an octahedral coordination environment, with Cl_4N_2 atoms around the cobalt atom placed at the centre of the trimeric entity and $Cl_3N_1Ow_2$ atoms around the terminal cobalt centres. Figure 3.31 provides a structural representation of the trimeric entity of compound ***CO3ADECL***. The coordination bond lengths and angles are gathered in Table 3.17.

The 7H–tautomeric form of the adenine precludes the Hoogsteen side from establishing complementary hydrogen bond interactions because both N6 and N7 behaves as hydrogen bonding donor atoms but the Watson–Crick side remains available (N1: acceptor, N6: donor). However, the synthesis was performed in a water/methanol mixture and, as it happens in ***CUADECL–A***, the water molecules disrupt the direct hydrogen bonding interaction between the adenines. In fact, the trimeric units interact through hydrogen bonds between the N1 nitrogen of the adenines and the coordinated water molecules of the neighbouring units in a head to tail manner, leading to a 1D chain along the [0 1 0] direction (Figure 3.32). Additionally, the N6 and N1 donor positions of the Hoogsteen face are pointing towards a solvated water molecule that acts as acceptor of the two hydrogen bonds. This solvation water molecule is further hydrogen bonded as donor to a terminal chloride and a coordinated water molecule from adjacent trimers giving rise to a 3D non porous structure (Figure 3.33). Table 3.18 shows the hydrogen bonding interaction parameters.
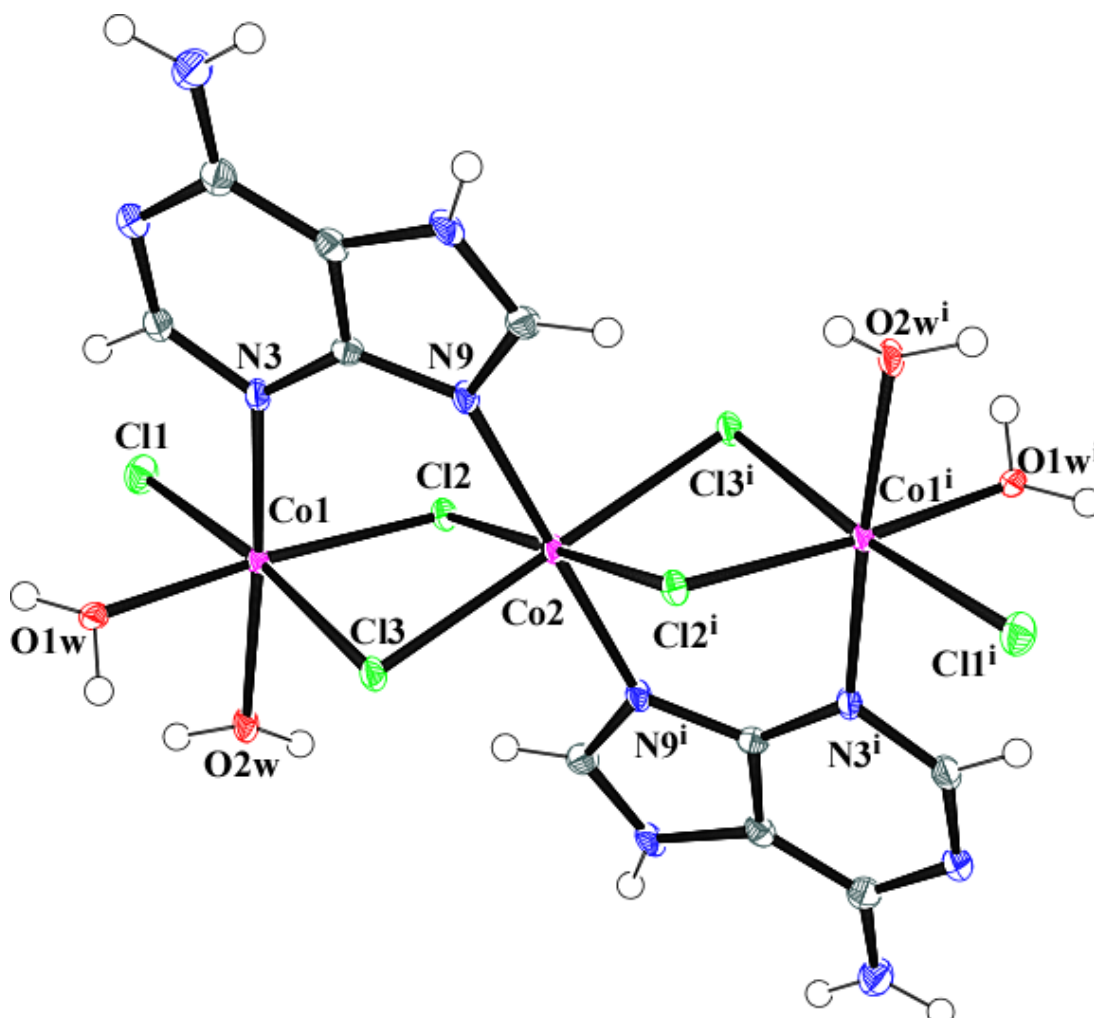
Figure 3.31: Ortep representation of $[Co_3(\mu–Hade)_2(\mu–Cl)_4Cl_2(H_2O)_4]$ trimeric unit in ***CO3ADECL***.

Table 3.17: Selected coordination bond lengths (Å) and angles (°) in **CO3ADECL**.[a]

Co1–N3	2.115(2)	N3–Co1–O1w	91.00(7)	Cl1–Co1–Cl3	174.15(2)
Co1–O1w	2.1217(16)	N3–Co1–O2w	175.45(6)	Cl2–Co1–Cl1	96.42(3)
Co1–O2w	2.1544(17)	N3–Co1–Cl1	90.92(6)	Cl2–Co1–Cl3	87.35(3)
Co1–Cl1	2.4356(11)	N3 Co1 Cl2	91.37(6)	N9–Co2–N9[i]	180.00(1)
Co1–Cl2	2.4106(10)	N3–Co1–Cl3	93.47(6)	N9–Co2–Cl2[i]	89.04(6)
Co1–Cl3	2.4823(11)	O1w–Co1–Cl1	87.79(5)	N9–Co2–Cl2	90.96(6)
Co2–N9	2.105(2)	O1w–Co1–Cl2	175.13(4)	N9–Co2–N9[i]	180.00(1)
Co2–Cl2	2.5108(11)	O1w–Co1–Cl3	88.26(5)	N9–Co2–Cl3[i]	93.01(5)
Co2–Cl3	2.4744(10)	O1w–Co1–O2w	84.45(6)	N9–Co2–Cl3[i]	86.99(5)
Co1⋯Co2	3.476(2)	O2w–Co1–Cl1	88.73(5)	Cl2–Co2–Cl2	180.00
		O2w–Co1–Cl2	93.18(5)	Cl3–Co2–Cl2[i]	94.65(3)
		O2w–Co1–Cl3	86.59(5)	Cl3–Co2–Cl2[i]	85.35(3)
				Cl3–Co2–Cl3[i]	180.00

[a] Symmetry code: (i) –x+2, –y, –z+2.

Table 3.18: Hydrogen bonding interactions (Å, °) in **CO3ADECL**.[a]

D–H⋯A[b]	D–H	H⋯A	D⋯A	D–H⋯A
N7–H7⋯O3w	0.86	1.92	2.731(3)	157.1
N6–H6A⋯Cl3[i]	0.86	2.70	3.435(2)	144.6
N6–H6B⋯O3w	0.86	2.23	3.054(3)	161.6
O1w–H11⋯N1[ii]	0.86	1.93	2.785(3)	176.4
O2w–H21⋯Cl1[iii]	0.87	2.20	3.055(2)	168.8
O1w–H12⋯O2w[iv]	0.84	2.08	2.859(2)	153.6
O3w–H31⋯O1w[v]	0.92	2.30	3.071(2)	141.4
O3w–H31⋯N3[v]	0.92	2.59	3.365(2)	142.0
O3w–H32⋯Cl1[vi]	0.93	2.24	3.1437(19)	163.5

[a] Symmetry code: (i) x, y–1,z; (ii)–x+2, –y–1,–z+3; (iii) –x+1, –y, –z+3 (iv); –x+2, –y, –z+3; (v) –x+3, –y–1, –z+2; (vi) –x+2, –y–1, –z+2. [b] **D**: donor; **A**: acceptor.
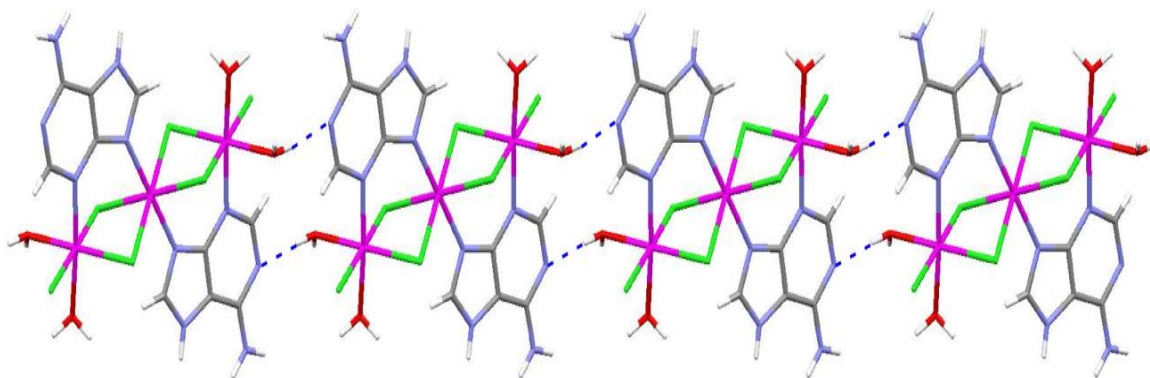
Figure 3.32: The head to tail hydrogen bonding interactions between the neighbouring trimeric units in *CO3ADECL.*

(a)

(b)

(c)
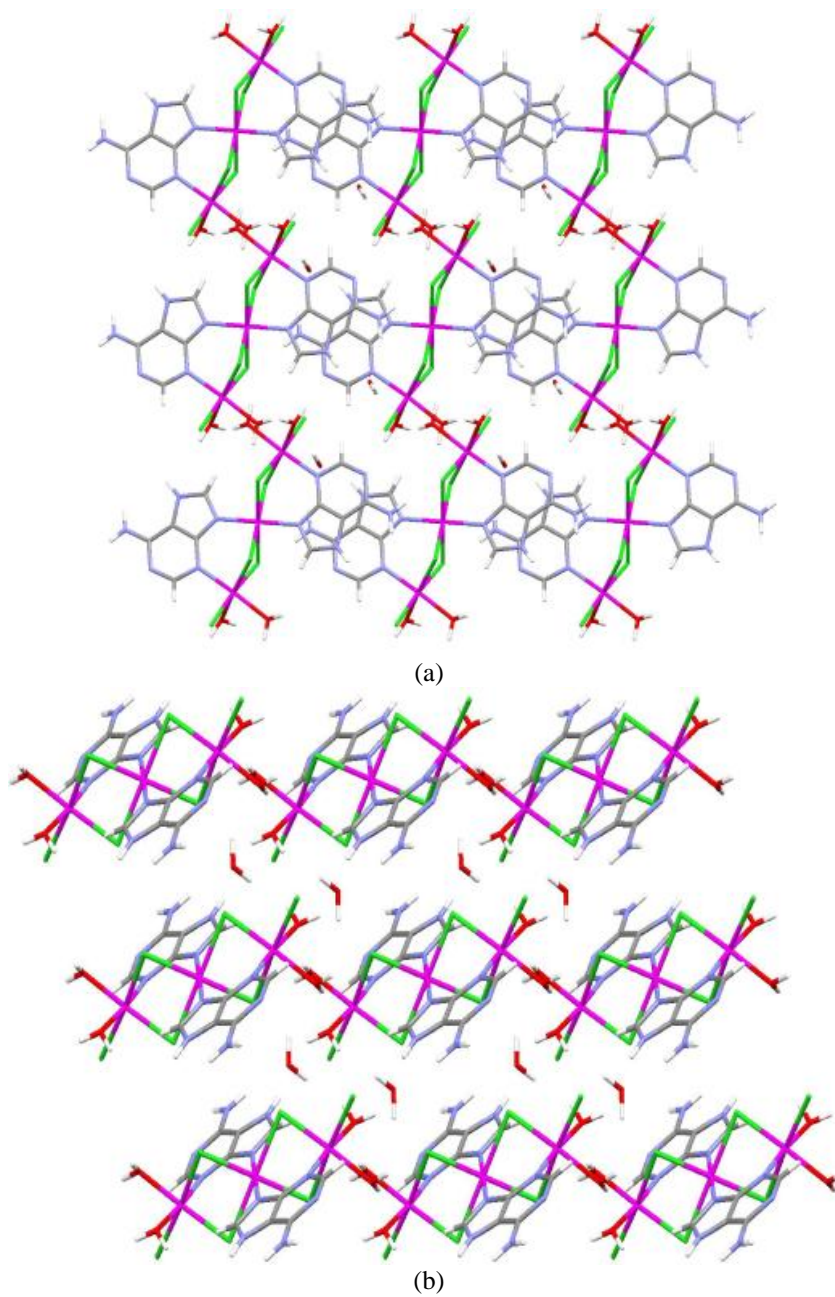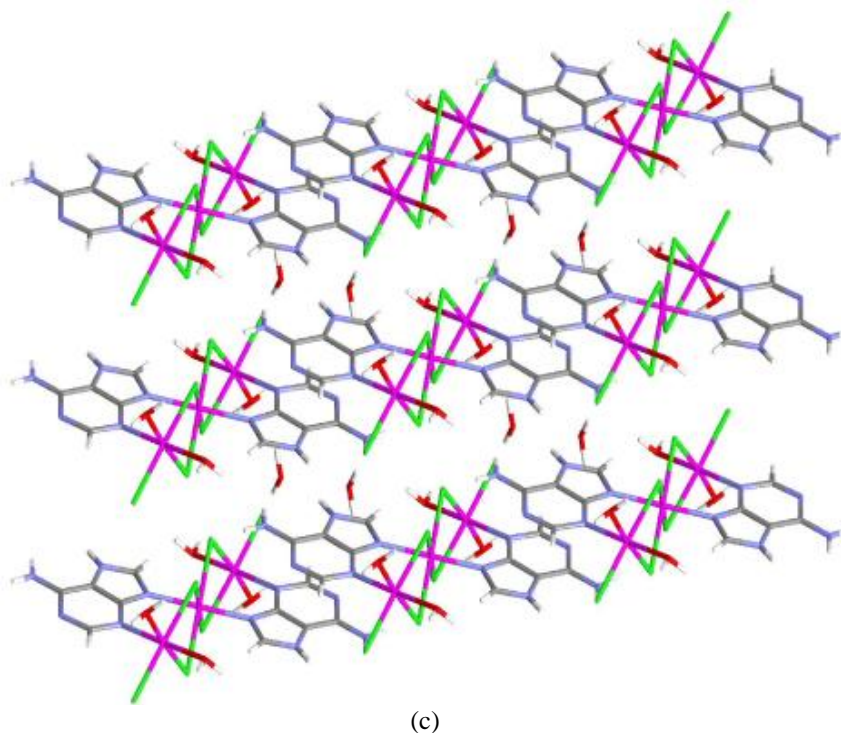
Figure 3.33: Projection of the crystal structure of compound ***CO3ADECL*** along the crystallographic *a* (a), *b* (b) and *c* (c) axes.

3.3.2.6 Structural description of compound [Cu₄(μ₃–ade)₂(μ₂–ade)₂(pentylNH₂)₂(CH₃OH)₂(CO₃)₂(H₂O)₂]·n(solvent) *CUADECO3* (*SMOF–8*)

Compound ***CUADECO3 (SMOF–8)*** is built up by tetranuclear units of [Cu₄(μ₃–ade)₂(μ₂–ade)₂(pentylNH₂)₂(CH₃OH)₂(CO₃)₂(H₂O)₂] in which coexist two types of neutral building units: a dimeric [Cu₂(μ–ade)₄(H₂O)₂] entity and two monomeric [Cu(pentylNH₂)(CH₃OH)(CO₃)] entities with a partial occupation factor of 0.775 (Figure 3.34). The presence of the carbonate has been attributed to the diffusion of CO_2 into the basic media of the reaction. In fact, this compound is obtained only if the reaction media is exposed to the open atmosphere. Similar behavior has been previously reported for some other compounds.[166]

The dimeric fragment is centrosymmetric and is made of two Cu(II) atoms bridged by four μ–*N3*:*N9*–adeninate anions in a paddle–wheel shaped arrangement. The apical position of the distorted square pyramidal coordination around Cu1 atom is completed with a water

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[166] (a) Sertucha, J. et al. *Inorg. Chem. Commun*. **1999**, *2*, 14. (b) Kitajima, N. et al. *J. Am. Chem. Soc*. **1993**, *115*, 5496. (c) Verdejo, B. et al. *Inorg. Chem*. **2006**, *45*, 3803.

molecule. Each dimeric entity is linked to two neighboring monomeric entities via the N7 imidazolic atoms of two adeninato ligands. Therefore, two adeninate anions behave as tridentate μ_3–*N3:N7:N9* bridging ligands, whereas the other two act as bidentate μ–*N3:N9*. Two oxygen atoms from a carbonato ligand, an oxygen atom of a methanol molecule and the nitrogen atom of a pentylamine molecule define the basal plane of the square pyramidal chromophore around Cu2 atom, whereas N7 atom of the adenine occupies the apical position with a slightly longer coordination bond distance.
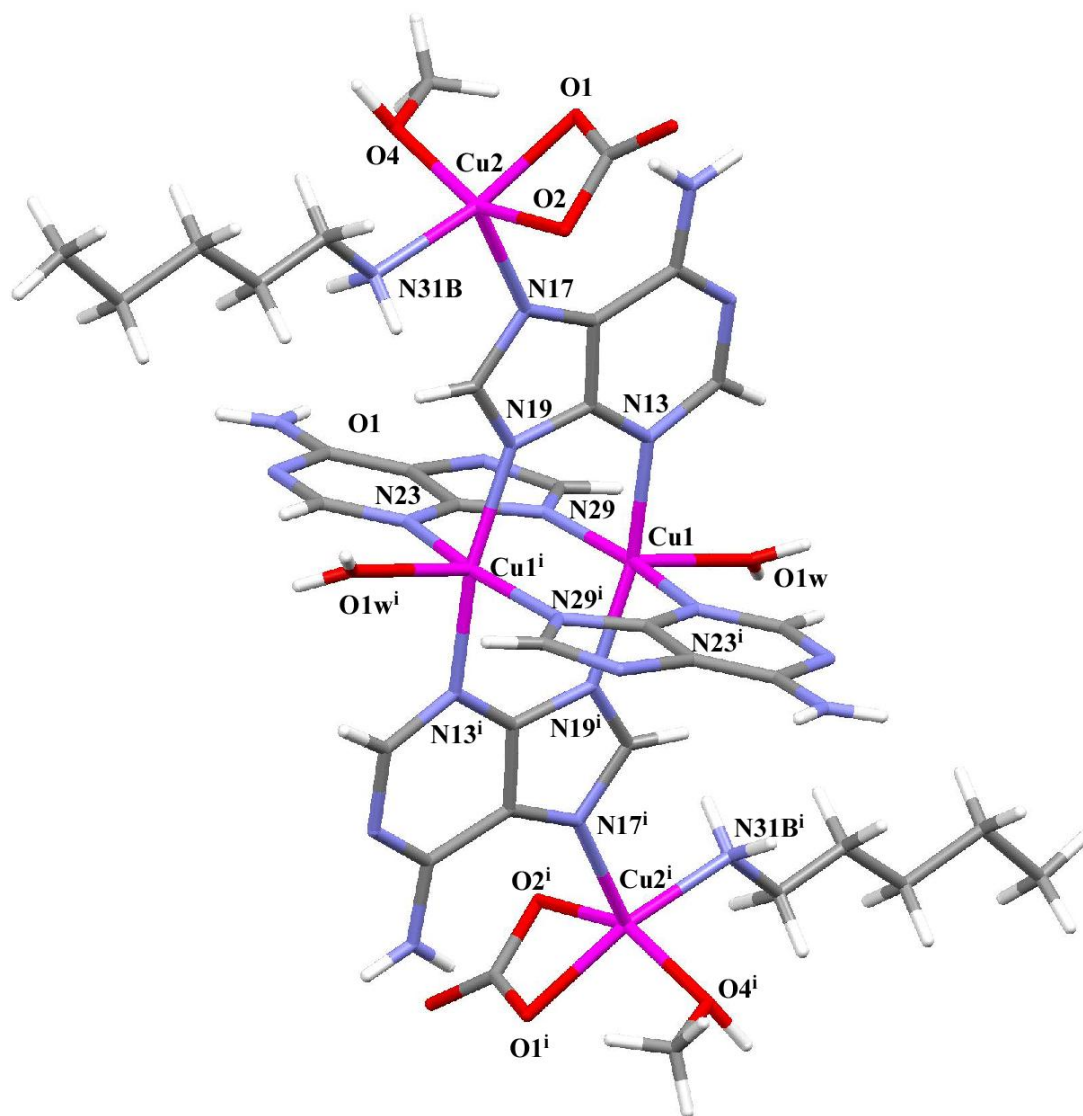
Figure 3.34: Structural unit of *CUADECO3 (SMOF–8)* with the atomic numbering scheme.

Each tetranuclear entity is linked to four adjacent ones via doubly N6–H···N1 hydrogen bonding interactions between the Watson–Crick faces of neighboring entities to give a $R_2^2(8)$ ring. The linkage of these tetrameric entities by the Watson–Crick faces gives rise to layers that can be described as a four–connected uninodal net with Shubnikov tetragonal **sql** topology and $(4^4.6^2)$ point symbol (Figure 3.35). The layers are further connected by means of

hydrogen bonding interactions involving the coordination water molecule, the carbonato ligand and the pentylamine molecule (Figure 3.36) leading to an α–Po **pcu** topology with a 42.9% of accessible volume (highlighted in green colour in Figure 3.36b). The selected coordination bond angles and bond lengths are given in Table 3.19 and the selected hydrogen bond lengths and angles are given in Table 3.20.

(a)

(b)
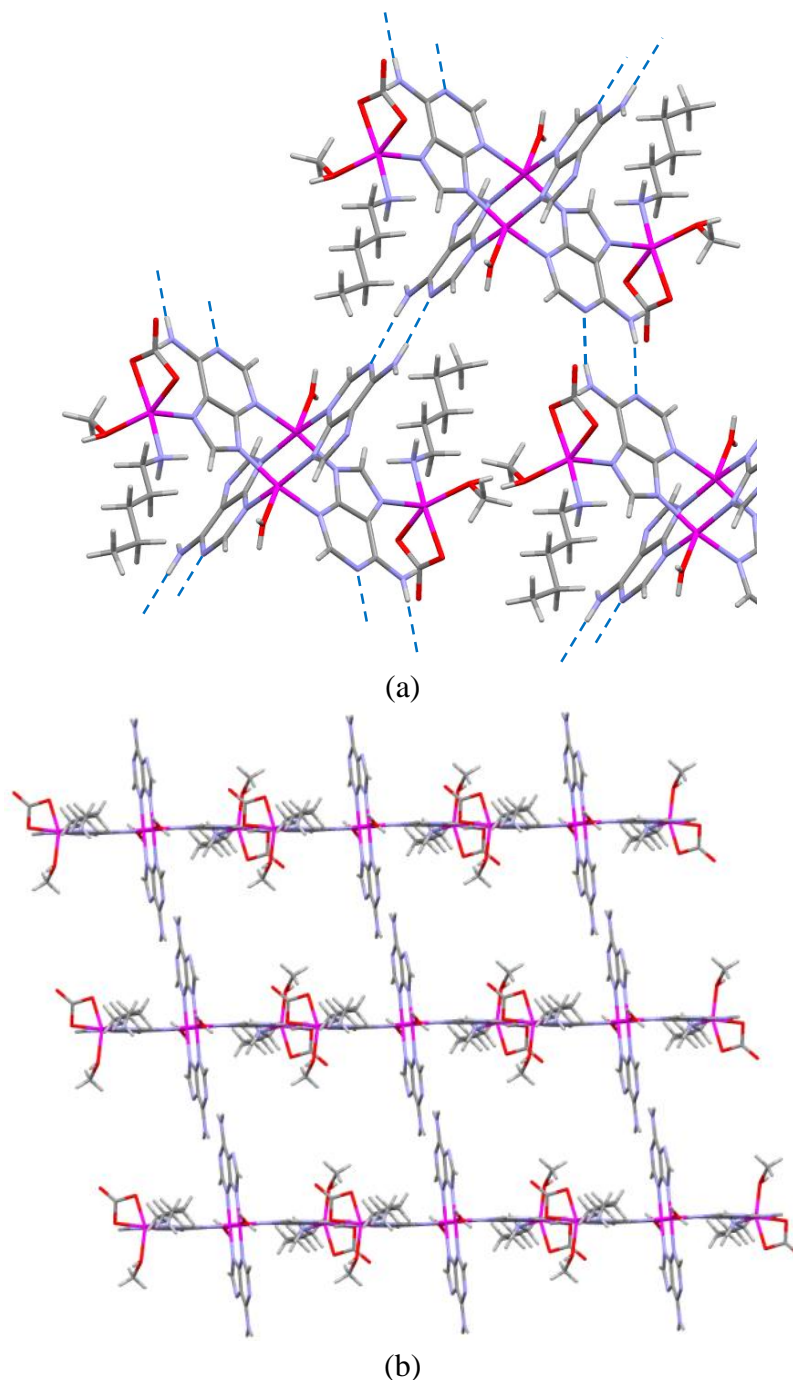
Figure 3.35: (a) Complementary hydrogen bonding interaction through the Watson–Crick faces of the adenines. (b) Supramolecular sheets sustained through Watson–Crick faces interaction *CUADECO3 (SMOF–8)*.

(a)

(b)
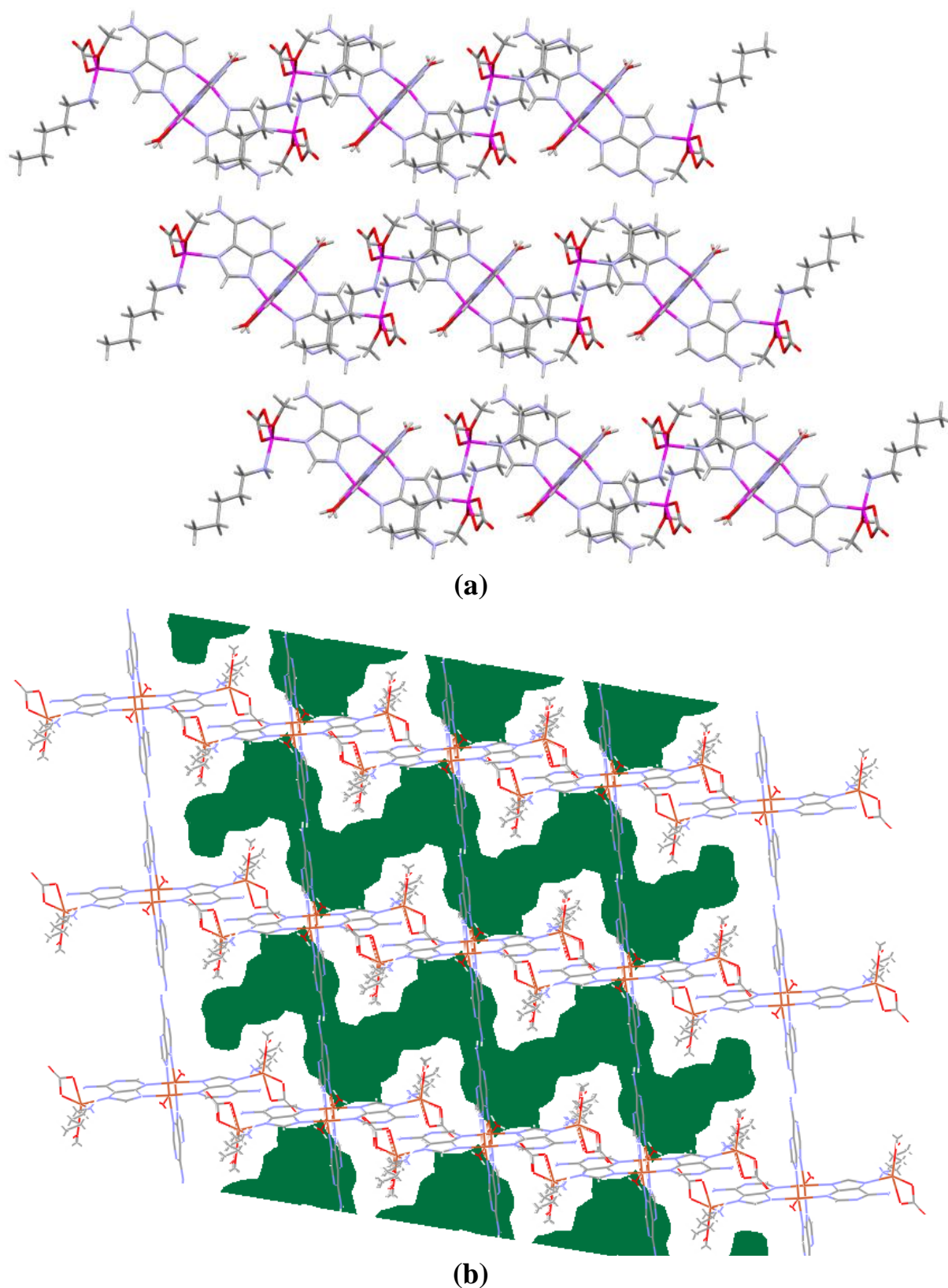
Figure 3.36: (a) Projection of the crystal structure of compound ***CUADECO3 (SMOF–8)*** along the crystallographic *c* axis and (b) green coloured regions representing the solvent accessible void.

Table 3.19: The coordination bond lengths (Å) and angles (°) for ***CUADECO3*** (***SMOF–8***).[a]

Cu1–N29	1.952(10)	N29–Cu1–N19 [i]	90.0(3)	N13–Cu1–Cu1 [i]	84.5(2)
Cu1–N23 [i]	1.989(9)	N23 [i]–Cu1–N19 [i]	89.5(3)	O1w–Cu1–Cu1 [i]	176.69(19)
Cu1–N19 [i]	1.993(7)	N29–Cu1–N13	89.6(3)	O2–Cu2–O1	66.4(3)
Cu1–N13	2.010(7)	N23 [i]–Cu1–N13	87.2(3)	O2–Cu2–N31	94.9(5)
Cu1–O1w	2.235(7)	N19 [i]–Cu1–N13	165.2(3)	O1–Cu2–N31	149.5(4)
Cu1···Cu1 [i]	2.945(3)	N29–Cu1–O1w	97.2(3)	O2–Cu2–O4	156.2(6)
Cu2–O2	1.953(14)	N23 [i]–Cu1–O1w	97.2(4)	O1–Cu2–O4	94.6(6)
Cu2–O1	1.997(9)	N19 [i]–Cu1–O1w	96.5(3)	N31–Cu2–O4	95.6(7)
Cu2–N31	2.057(12)	N13–Cu1–O1w	98.2(3)	O2–Cu2–N17	96.3(6)
Cu2–O4	2.08(2)	N29–Cu1–Cu1 [i]	80.9(3)	O1–Cu2–N17	105.2(4)
Cu2–N17	2.185(10)	N23 [i]–Cu1–Cu1 [i]	84.8(3)	N31–Cu2–N17	100.4(4)
N29–Cu1–N23 [i]	165.5(4)	N19 [i]–Cu1–Cu1 [i]	80.8(3)	O4–Cu2–N17	102.8(6)

[a] Symmetry codes: (i) –x+2. –y, –z+1.

Table 3.20: Hydrogen bonding interactions (Å, °) in ***CUADECO3*** (***SMOF–8***).[a]

D–H···A [b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N16–H16A···N11 [i]	0.86	2.13	2.978(11)	167.1
N16–H16B···O1	0.86	2.11	2.965(13)	174.7 .
N26–H26B···N21 [ii]	0.86	2.08	2.935(17)	172.4
O1W–H12W···O3 [iii]	0.86	1.94	2.790(13)	169.0
N31–H31A···O2 [iv]	0.90	1.94	2.843(18)	176.1

[a] Symmetry codes: (i) –x+2, –y+1, –z+1; (ii) –x+2, –y, –z; (iii) x–1, y, z; (iv) –x+3, –y, –z+1. [b] **D**: donor; **A**: acceptor.

3.3.2.7 Structural description of [Co(Hade)₂Cl₂] *COADECL (SMOF–5)* and [Co(Hade)₂Br₂] *COADEBR (SMOF–6)*

Both compounds are isostructural (Figure 3.37) but only single crystals of ***COADECL*** were obtained. Its crystal structure is comprised of neutral monomeric [Co(Hade)$_2$Cl$_2$] building units (Figure 3.38a). In this compound 9H–adenine acts as a monodentate ligand and it is coordinated to the Co(II) metal centre through the N7 position. This N7 coordination is very common in the case of unsubstituted adenine moieties, but it requires a second anchoring position of the nucleobase to be stiff enough for our requirements. It is achieved by the

presence of intramolecular hydrogen bonding interactions between the amino hydrogen and chlorido ligand. Most relevant coordination bond lengths and angles are given in Table 3.21.

Space group	C 2/c
a (Å)	11.247(3)
b (Å)	6.981(1)
c (Å)	19.268(4)
β (°)	97.99(19
V (Å^3)	1498.2(6)
R_f	1.38
R_b	2.26
R_p	15.4
R_{wp}	19.9
χ^2	1.95
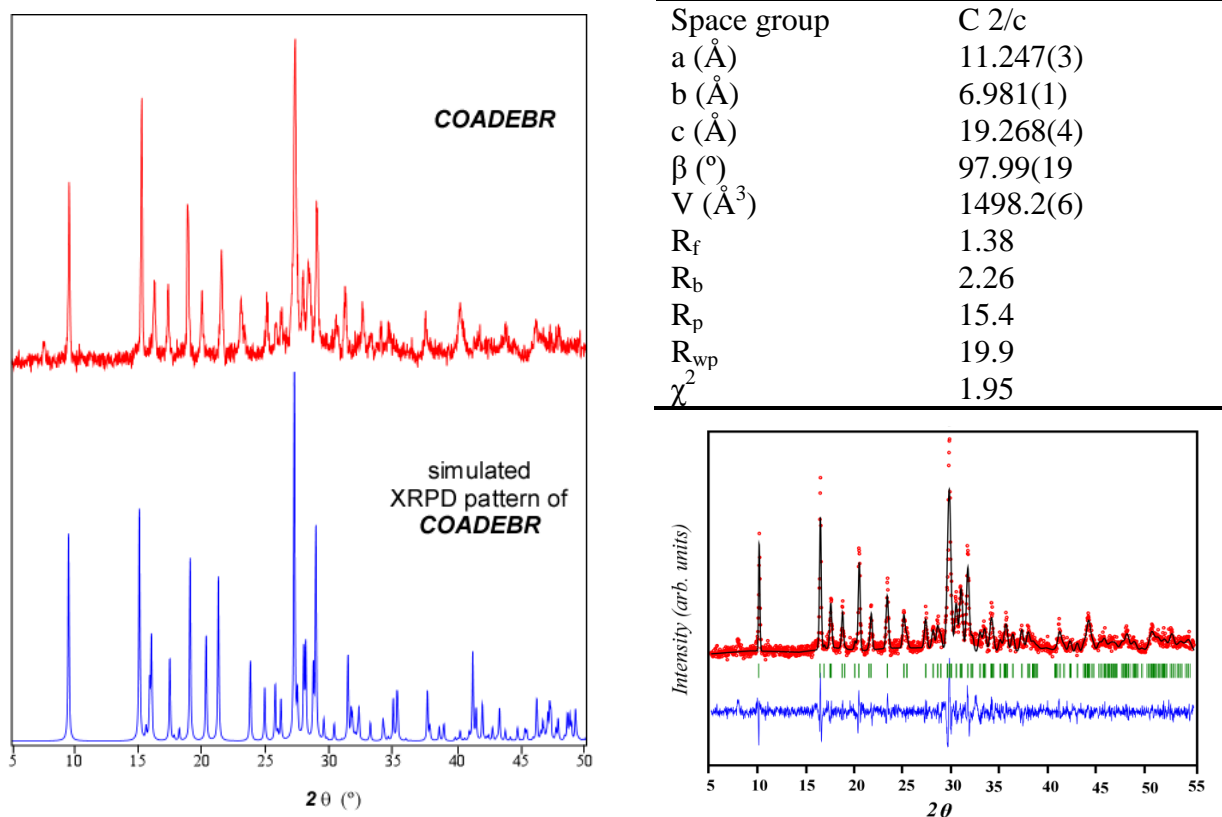
Figure 3.37: X–ray powder diffractograms of ***COADEBR (SMOF–6)*** and simulated pattern resulting from the replacement of chloride by bromide in the crystal structure of ***COADECL (SMOF–5)***.

Table 3.21: Coordination bond lengths (Å) and angles (°) in ***COADECL–A (SMOF–5)***.[a]

Co1–N7	2.047	N7–Co1–Cl1	106.85(11)
Co1–Cl1	2.2560(13)	N7–Co1–Cl1	115.77(12)
N7–Co1–N7	104.2(2)	Cl1–Co1–Cl1	107.75(8)

[a].Symmetry codes: (i) –x, y, –z+1/2.

The adenine exposes its Watson–Crick and sugar–edges to establish intermolecular complementary hydrogen bonding interactions with other adenine molecules (Figure 3.38). It gives rise to two rigid synthons involving WC···WC and sugar···sugar edges that build up a four–connected uninodal supramolecular net with **dia** topology and (6^6) point symbol. This supramolecular framework would represent a new porous material with an estimated internal surface area of 3600 m^2/g and 66.7 % of void space (Figure 3.39a). The structural parameters for hydrogen bonding are given in the Table 3.22.

(a)   (b)
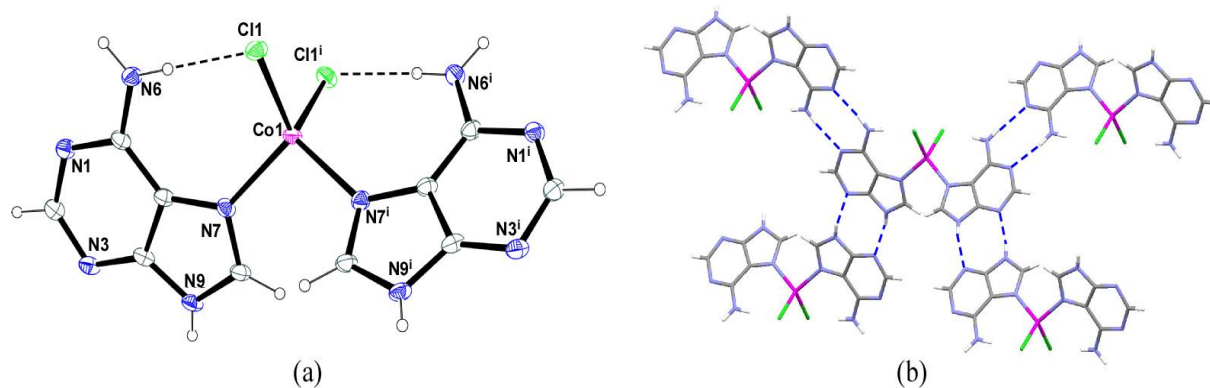
Figure 3.38: (**a**) Ortep representation of the monomeric entity [Co(Hade)$_2$Cl$_2$] together with the labelling scheme and (**b**) Complementary hydrogen bonding interactions taking place between the [Co(Hade)$_2$Cl$_2$] units.

Table 3.22: Hydrogen bonding interactions (Å, º) in ***COADECL (SMOF–5)***.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N6–H6A···N1^i	0.86	2.06	2.912(6)	173.3
N6–H6B···Cl1	0.86	2.39	3.237(4)	167.3
N9–H9···N3	0.74(7)	2.11(7)	2.833(6)	165(6)

[a] Symmetry codes: (i)–x+1/2, –y+1/2, –z+1; (ii) –x, –y–1, –z+1. [b] **D**: donor; **A**: acceptor.

Nevertheless, it would contain so huge channels that the real crystal structure involves three fold interpenetrated networks that occupy all the available space providing a non–porous material. This entanglement problem is also common in MOFs.[167] Huge pore sizes usually give rise to a fundamental complication, namely called interpenetration that consist on the inclusion of additional sublattices occupying the void space left by the first one. This interpenetration greatly reduces the pore size and thus the available space[168] and is a challenge in designing compounds with potential porosities. Porous materials try to minimize the systematic energy through optimal filling of void space, but structural interpenetration may occur only if the pore space of an individual net is sufficiently large to accommodate an additional net. Moreover, various weak supramolecular forces such as H–bonding, π–π aromatic stacking interactions, and van der Waals forces are believed to play vital roles in the formation of interpenetrated structures. ***COADECL (SMOF–5)*** follows the same pattern,

[167] (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Alexandrov, E. V. et al. *Acta Crystallogr. Sect. A*, **2012**, 484.

[168] Shekhah, O. et al. *Nat. Mater.* **2009**, *8,* 481.

provided that it contains comparatively bigger voids. Thus the resulting structure can be described as a 3–fold interpenetrated network as shown in Figure 3.39b.

(a)

(b)
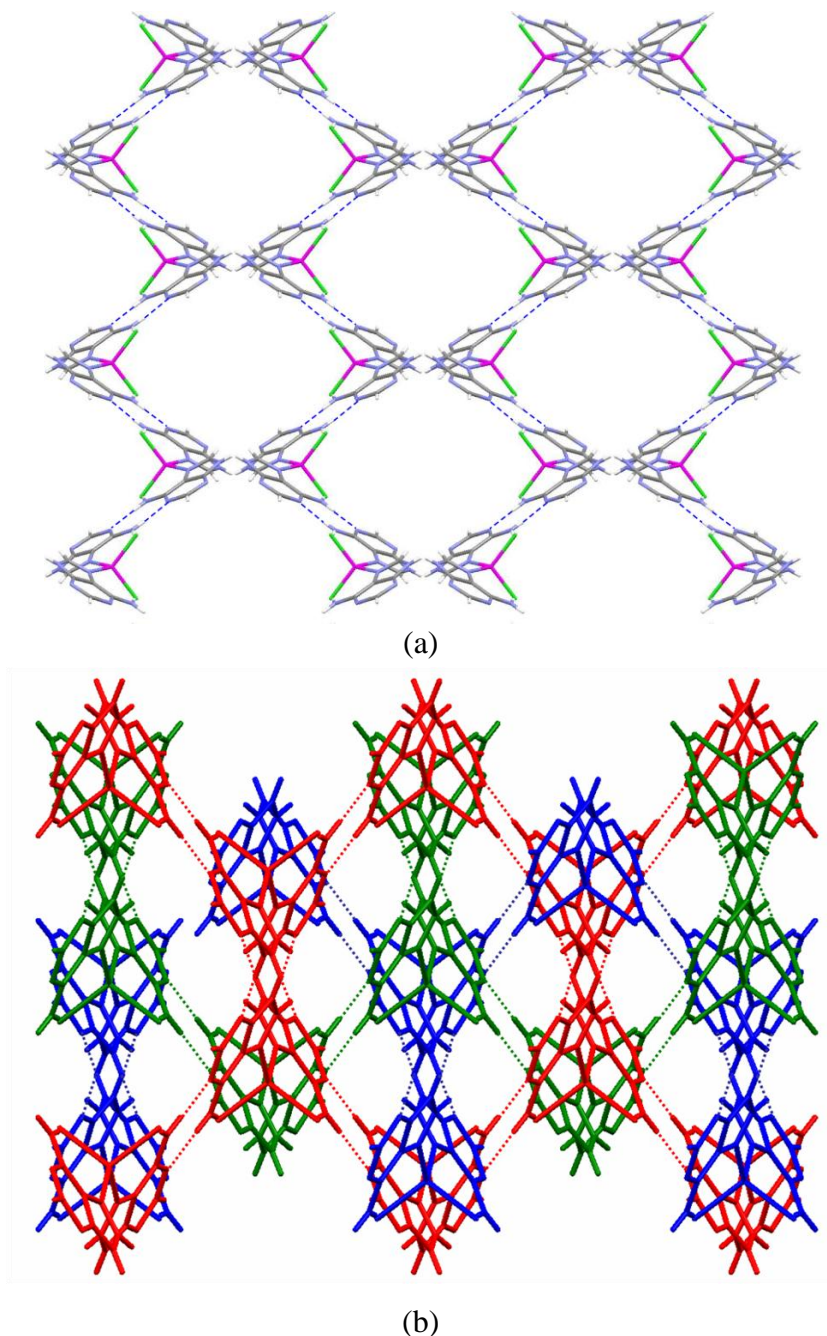
Figure 3.39: (a) Crystal structure of an individual supramolecular subnet of ***COADECL (SMOF–5)*** and (b) real crystal structure resulting from the interpenetration of three individual subnets depicted using different colours.

The stability of ***COADECL (SMOF–5)*** and ***COADEBR (SMOF–6)*** has been measured using thermogravimetric techniques (TG/DTA) under synthetic air (Figure 3.40 and Table 3.23). The ***COADECL*** remains stable up to 260 ℃ and then undergoes a mass loss that ends at 390 ℃ by a strong endothermic process. The intermediate is not stable and decomposes in several consecutive exothermic processes to afford Co_3O_4 at 620 ℃. The results obtained

from ***COADEBR (SMOF–6)*** show a small mass loss below 100ºC, that could be attributed to humidity but we believe that it could imply a small portion of the non–interpenetrated phase. Around 300 ºC the compound suffers a second endothermic mass loss that agrees with the release of HBr acid. The intermediate remains relatively stable up to 425 ºC after which it suffers several consecutive exothermic processes to afford Co_3O_4 at 590 ºC.

(**a**)   (**b**)
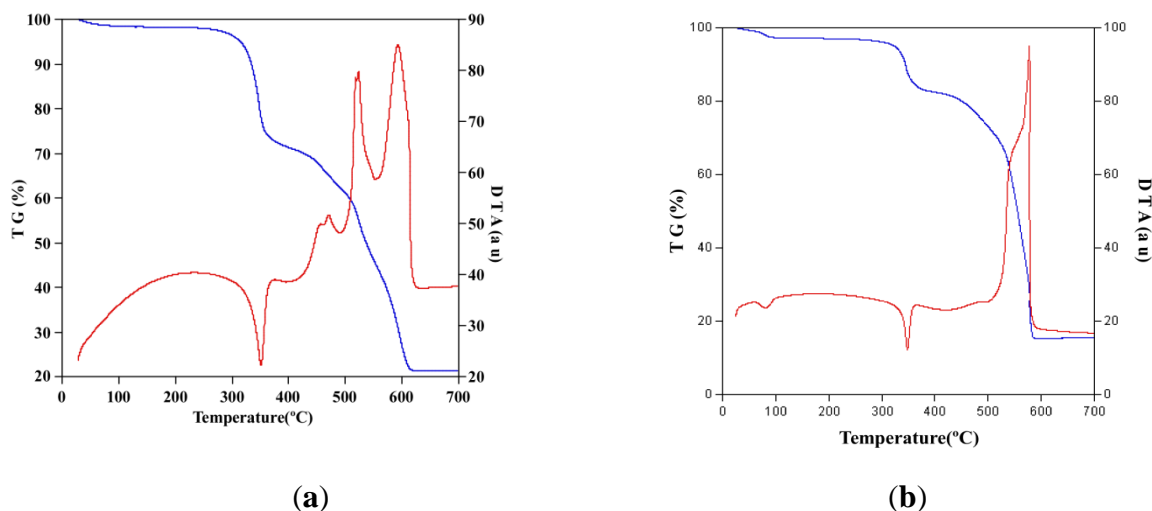
Figure 3.40: TG and DTA curves of the ***COADECL (SMOF–5)*** and ***COADEBR (SMOF–6)*** under synthetic air atmosphere.

Table 3.23: Thermogravimetric data for ***COADECL (SMOF–5)*** and ***COADEBR (SMOF–6)***.[a,b]

Step	T_i	T_f	T_{peak}	$\Delta m(\%)$	ΔH	$\Sigma\Delta m(\%)$	$\Sigma\Delta m_{theor}$[b]
COADECL (SMOF–5)							
1	25	390	352	28.32	Endo	28.32	–
3	390	620	524,590	50.40	Exo	78.72	79.93 (1/3 Co_3O_4)
COADEBR (SMOF–6)							
1	25	95	82	2.8	Endo	2.8	2.9 (–0.8 H_2O)
2	270	395	347	14.72	Endo	17.52	16.54 (–1 HBr)
3	425	590	577	66.95	Exo	84.47	83.57 (1/3 Co_3O_4)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released fragments and final residue per formula.

Although interpenetration usually provides robustness to the MOFs, it negatively affects the porosity of open frameworks by reducing the size of open pores and hence posses low surface area and high density which negatively affects the potential applications of such

materials because high surface area and porosity are generally most desired in porous material.[169] Therefore it is important to find some methods to avoid interpenetration. Many new strategies have been developed to suppress the interpenetration in order to construct highly porous MOFs with high surface area and some of them are explained below in detail. In this work we have adopted many of such strategies to avoid the interpenetration of compounds ***COADECL (SMOF–5)*** and ***COADEBR (SMOF–6)***.

Reaction parameters such as temperature and concentration play vital role in the determination of framework interpenetration of MOFs. For example, in the case of IRMOFs (isoreticular MOF) longer organic linkers leads to 2–fold interpenetrated networks but lowering the concentration of reaction solution has been found effective in affording non–interpenetrated MOFs with larger pores[23] and specific surface areas ranging from 570 to 3800 m^2/g.[169] To better understand the effect of concentration on the interpenetration, it is convenient to consider this phenomena as two or more crystals growing in the same point of the space. At lower concentration, the chances for several crystals growing at the same place is smaller than when using higher concentration of the reagents. Therefore, diluting the reaction media hinders the interpenetration phenomena. On the other hand, the [Cd(4,4'–bpy)(bdc)] system showed that not only the concentration but also the temperature plays a relevant role in determining the presence of interpenetration. The interpenetrated isomer was preferentially produced at elevated temperatures and hence temperature control was the key factor in obtaining the non–interpenetrated form of this compound together with concentration control.[170] To better understand this fact, we must consider a hypothetical equilibrium reaction between the non–interpenetrated and interpenetrated forms of a compound (equation 1). It is easy to understand that due to entropic effects, reaction (1) would be displaced towards the interpenetrated form at high temperatures, being more probable to isolate the non–interpenetrated one at lower temperatures.

$$MOF \cdot nSolv + MOF \cdot nSolv \rightarrow MOF_2 \text{ (interpenetrated)} + 2nSolv \qquad (1)$$
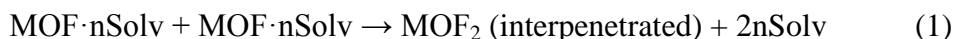
The use of templates has been widely used for the construction of porous materials. It is also reasonable to introduce a template in order to construct non–interpenetrated MOFs with larger pores on assuming that the MOF will grow around the surface of the template and thus

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[169] Jiang, H.–L. et al. *Coord. Chem. Rev*. **2013**, *257*, 2232.
[170] Zhang, J. et al. *J. Am. Chem. Soc*. **2009**, *131*, 17040.

prevent the interpenetration of multiple nets.[169] The Zhou research group with the synthesis of non interpenetrated PCN–6' has proven that in this specific case only template control could determine the presence or absence of interpenetration where temperature and concentration controls were not fruitful.[171] The template effect can be also exerted by the solvent molecules.[172] A relatively similar approach consist of modifying/designing the ligand to incorporate bulky subtituents, although they do not occupy the total accessible volume of the MOF, avoids the interpenetration of additional nets.[169]

Finally, layer–by–layer assembly–liquid phase epitaxy provides another way to achieve the interpenetration suppression. It is done through liquid–phase epitaxy on an organic monolayer modified surface followed by a layer–by–layer growth approach.[168] The surface is modified with functional groups able to anchor the metal centers. Later on, using a dip coating strategy the MOFs are grown by consecutive immersion in a solution containing only the bridging ligand or metal. This strategy completely avoids the interpenetration phenomena as the presence of a second net is completely precluded.

However, although we have made great efforts to avoid the interpenetration of compounds ***COADECL (SMOF–5)*** and ***COADEBR (SMOF–6)***, it has been unsuccessful. Probably because the hydrogen–bonding nature of the connections established between the building units makes this issue more difficult to overcome.

3.3.2.8 Structural Description of [Co(9–MeAde)$_2$(H$_2$O)$_4$]Cl$_2$·2H$_2$O; *CO–9–MEADECL*

After exploring the possibilities that adenine offers as a ligand and a hydrogen–bond donor/acceptor molecule, we tried to analyze the effects on the resulting crystal structures by methylating this nucleobase. The 9–methyladenine was selected for this purpose because it somehow mimics the behaviour of the adenosine/deoxyadenosine where the adenine is bonded through N9 to a ribose or deoxyribose, respectively. The alkylation of adenine at N9 position prevents N3,N9–bidentate coordination mode which was essential for it to act as a bridging ligand in forming windmill shaped dimeric entities. A search in the CSD database of transition metal complexes of 9–methyladenine shows the prevalence of N7 coordination mode, because of the steric hindrance imparted by the methyl group on the neighbouring N3

[171] Sun, D. et al. *J. Am. Chem. Soc.* **2006**, *128*, 3896.
[172] Ma, L.; Lin, W. *J. Am. Chem. Soc*. **2008**, *130*, 13834.

nitrogen atom makes its coordination difficult. The different coordination modes of 9–methyl adenine are shown in Figure 3.41 with the frequency of their appearance as found in the CSD data base.
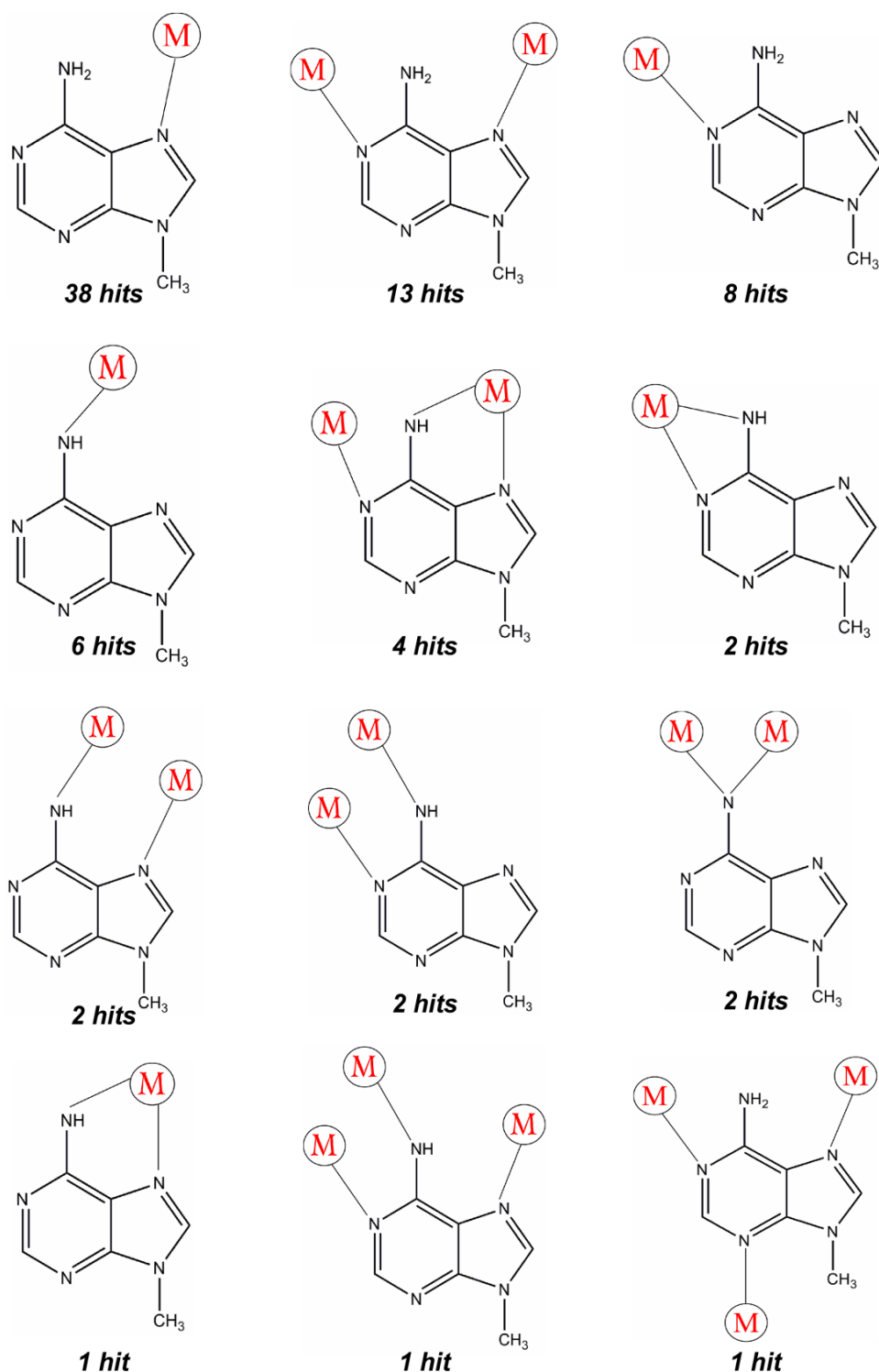
Figure 3.41: Coordination modes of 9–methyladenine and their appearance frequency.

The crystal structure of the compound resulting from the reaction of two equivalents of 9–methyladenine with one equivalent of $CoCl_2 \cdot 6H_2O$ in methanol consist of complex

monomeric $[Co(9–MeAde)_2(H_2O)_4]^{2+}$ cations, chloride counterions and crystallization water molecules. The cobalt(II) centre is octahedrally coordinated to four water molecules in the equatorial plane and to two 9–methyladenine molecules occupying the axial positions (Figure 3.42). The methylated nucleobase is anchored to the metal centre through N7 providing a distorted octahedral environment around the metal centre with slightly longer coordination bond distances for Co–N bonds than for Co–O ones (Table 3.24).
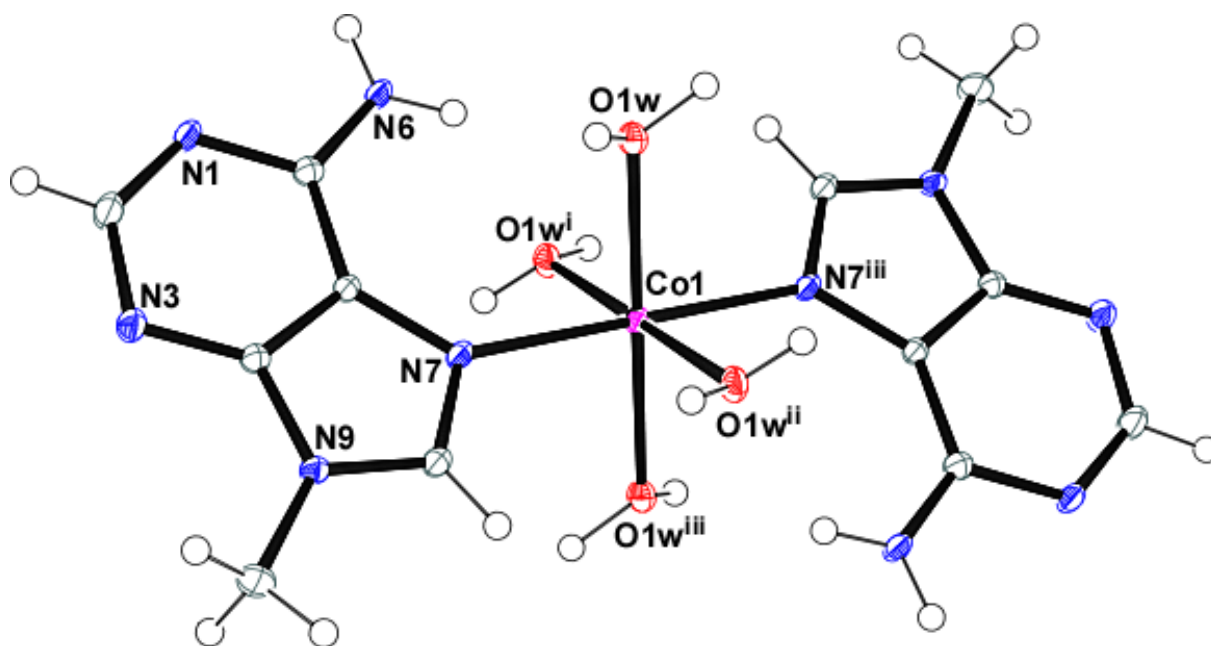
Figure 3.42: Ortep view of the complex cation present in compound *CO–9–MEADECL*.

Table 3.24: Coordination bond lengths (Å) and angles (º) for compound *CO–9–MEADECL*.[a]

Co1–O1w	2.0912(11)	O1w^{i}–Co1–O1w^{iii}	89.06(6)
Co1–N7	2.1488(18)	O1w^{i}–Co1–N7	91.09(4)
N7–Co1–N7^{iii}	180.000(1)	O1w^{i}–Co1–N7^{iii}	88.91(4)
O1w–Co1–N7	88.91(4)	O1w^{ii}–Co1–1w^{iii}	90.94(6)
O1w–Co1–N7^{iii}	91.09(4)	O1w^{ii}–Co1–N7^{iii}	91.09(4)
O1w–Co1–O1w^{i}	90.94(6)	O1w^{ii}–Co1–N7	88.91(4)
O1w–Co1–O1w^{iii}	180.0	O1w^{iii}–Co1–N7	88.91(4)
O1w–Co1–O1w^{ii}	89.06(6)	O1w^{iii}–Co1–N7	91.09(4)
O1w^{i}–Co1–O1w^{ii}	180.0		

[a] Symmetry codes: (i) −x+2, y, −z; (ii) x, −y+1, z; (iii) −x+2, −y+1, −z+1.

The crystal architecture is dominated by the hydrogen–bonding complementary interactions taking place between the Watson–Crick faces that connect the cationic complex

entities in supramolecular 1D chains (Figure 3.43 and Table 3.25). The N6–H of each 9–methyladenine moieties further establishes intramolecular hydrogen bonds with coordinated water molecules. The supramolecular chains are held together not only by the electrostatic interactions taking place between the cationic complex and the choride counterions but also by a complex network of hydrogen bonding interactions between the water molecules, the N3 position of the 9–methyladenine and the chloride counterions. There are also some structural evidences of weak π–π stacking interactions between the pyrimidine rings of the 9–methyladenines with a perpendicular distance of 3.365 Å between the mean planes and a slippage of 2.07 Å.
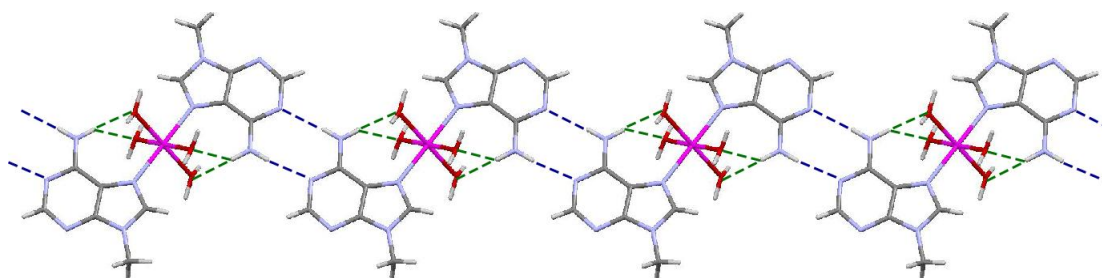
Figure 3.43: Supramolecular chain of $[Co(9–MeAde)_2(H_2O)_4]^{2+}$ complex cations.

Table 3.25: Supramolecular interactions (Å, °) in *CO–9–MEADECL*.

Hydrogen bonding interactions.[a]				
D–H···A[b]	***D–H***	***H···A***	***D···A***	***D–H···A***
N6–H6A···N1[i]	0.86	2.12	2.974(3)	175.6
N6–H6B···O1w	0.86	2.31	2.980(2)	135.3
N6–H6B···O1w[ii]	0.86	2.31	2.980(2)	135.3
O1w–H1A···Cl1[iii]	0.96	2.13	3.073(1)	167.2
O1w–H1B···O2w	0.85	1.93	2.771(2)	171.2
O2w–H2A···N3[iv]	0.91	2.06	2.920(2)	156.6
O2w–H2B···Cl1	0.87	2.35	3.209(2)	171.4

π–π stacking interactions.[c]					
Ring···Ring[d]	Angle	DC	α	DZ	DXY
Ring(1)···Ring(1)[v]	0	3.9521(8)	31.62	3.3654(1)	2.072

[a] Symmetry: (i) –x+1,–y+1,–z+1; (ii) x,–y+1,z; (iii)–x+2,–y+1,–z+1; (iv) –x+3/2,–y+3/2,–z+3/2; (v) –x+3/2, y–1/2, –z+3/2. [b] **D**: donor; **A**: acceptor. [c] Angle: Dihedral Angle between Planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] Ring 1: N1, C2, N3, C4, N9, C6.

As it was expected, the methyl group at N9 position reduces the capacity of the adenine to both coordinate and to establish hydrogen–bond interactions. The adenine molecule could provide three faces able to establish complementary hydrogen bonding interactions (Figure 3.44): Watson–Crick face (N1/N6), Hoogsteen side (N6/N7) and sugar edge (N3/N9). The methylation at N9 precludes the sugar–edge for this purpose and the coordination at N7 does the same for the Hoogsteen side. Therefore only the Watson–Crick face is available to establish complementary hydrogen bonding interaction. Taking into account that there are only two nucleobases per cobalt(II) center, the generation of supramolecular 1D chains though double hydrogen–bond interactions would be expected, as it has been the case.
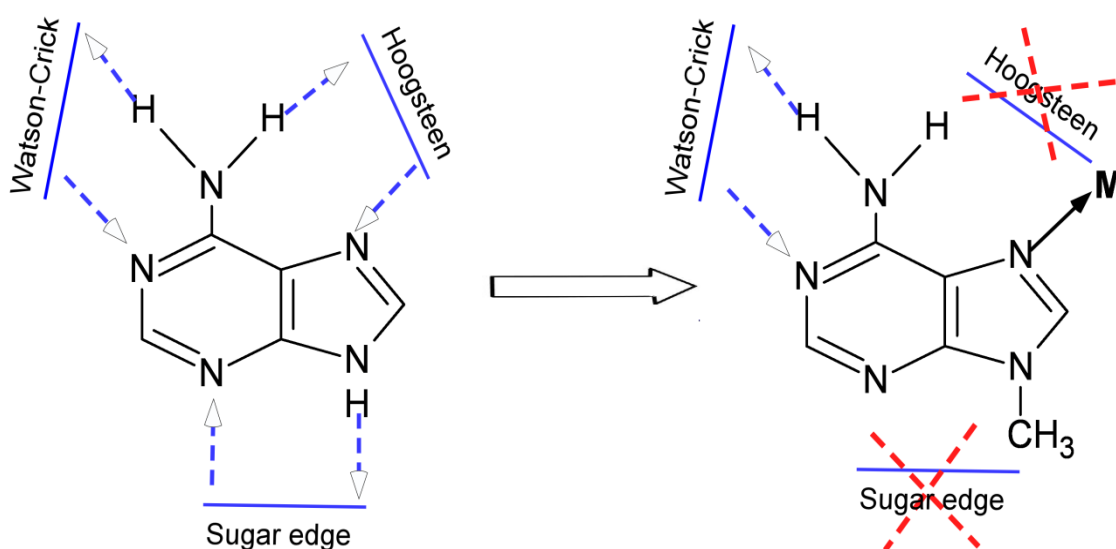
Figure 3.44: The availability of hydrogen bonding faces for free adenine and *N7*–coordinated 9–methyladenine.

Details of the thermogravimetric studies are given in Figure 3.45 and Table 3.26. According to the thermogravimetric analysis, the first mass loss occurs below 55 ºC. Then the compound remains stable upto 75 ºC. After that it undergoes consecutive decomposition to the final residue Co_3O_4 above 630 ºC.
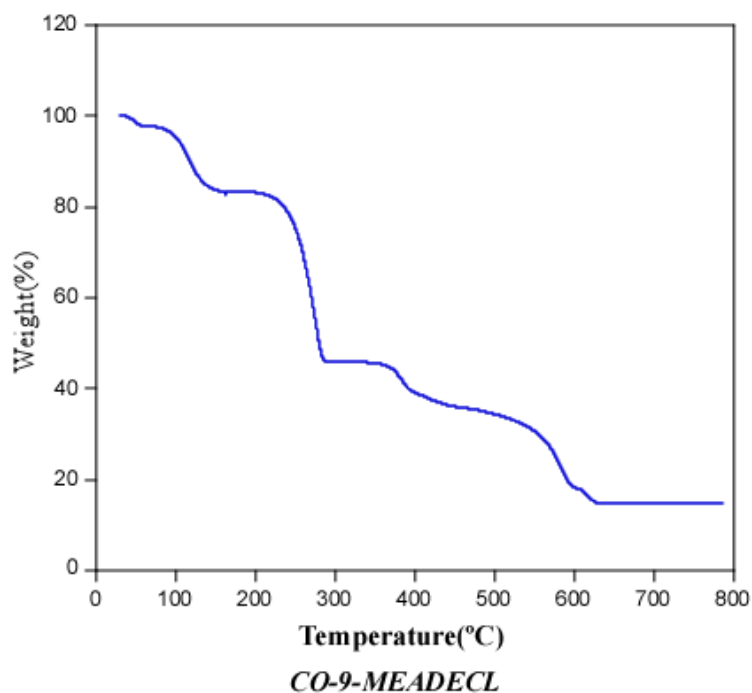
CO-9-MEADECL

Figure 3.45: Thermogravimetric analysis of *CO–9–MEADECL*.

Table 3.26: The thermogravimeric data of *CO–9–MEADECL*.[a,b]

Step	T_i	T_f	$\Delta m(\%)$	$\Sigma \Delta m(\%)$	$\Sigma \Delta m(\%)_{theor}$
CO–9–MEADECL					
1	25	55	2.16	2.16	3.36 (–1 H_2O)
2	75	155	14.32	16.48	16.78 (–4 H_2O)
3	205	285	37.4	53.88	–
4	330	630	31.17	85.05	85.03 (1/3 Co_3O_4)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma \Delta m(\%)$ = total mass loss percentage; $\Sigma \Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released molecules and final residue per formula.

3.3.2.9 Structural Description of $[Cu_2(\mu–CH_3COO)_4(\mu–9–MeAde)]_n \cdot nCH_3OH$; *CU–9–MEADEACE*

The reaction between 9–methyladenine and $Cu(OOCCH_3)_2 \cdot H_2O$ in methanol at room temperature provided a green compound that retains the usual $[Cu_2(\mu–OOCCH_3)_4]$ paddle–wheel shaped entities but bridged by μ–9–methyladenine–$\kappa N1$:$\kappa N7$ molecules that are anchored to the apical positions of the dimeric entities (Figure 3.46a). This coordination mode is the second most probable one for the 9–methyladenine and it is reinforced by the intramolecular hydrogen bonding interactions implying the exocyclic amino group as donor

and the oxygen atoms from two acetates as acceptors (Figure 3.46b). The copper(II) coordination environment can be described as an elongated square pyramid with the apical bond distances (Cu–N) longer that the equatorial ones (Cu–O). The coordination bond network extends into *zig–zag* infinite chains that propagates along the [0 1 1] direction with acetate anions and 9–methyladenine moieties bridging alternatively the copper(II) atoms. The metal⋯metal distances are shorter through the four–fold acetate bridge (2.64 and 2.66 Å) than through the μ–9–methyladenine–κ*N1*:κ*N7* molecule (7.08 Å). Table 3.27 list the most relevant coordination bond distances and angles.

The μ–κ*N1*:κ*N7* coordination mode of the 9–methyladenine precludes any possible complementary hydrogen–bonding interaction along either its Watson–Crick or Hoogsteen sides. Therefore, the supramolecular crystal structure is dominated by weak van der Waals interactions and the hydrogen–bonding interactions between the methanol solvatation molecules and the oxygen atoms of the carboxylato ligands that does not provide any accessible void (Figure 3.47 and Table 3.28). No structural evidence of π–π interactions has been observed. An interesting result coming from this compound is that the 9–methyladenine does not coordinate strong enough to the metal center as to displace the carboxylato ligands from the paddle–wheel shaped building unit, instead being only able to occupy the more labile apical positions.
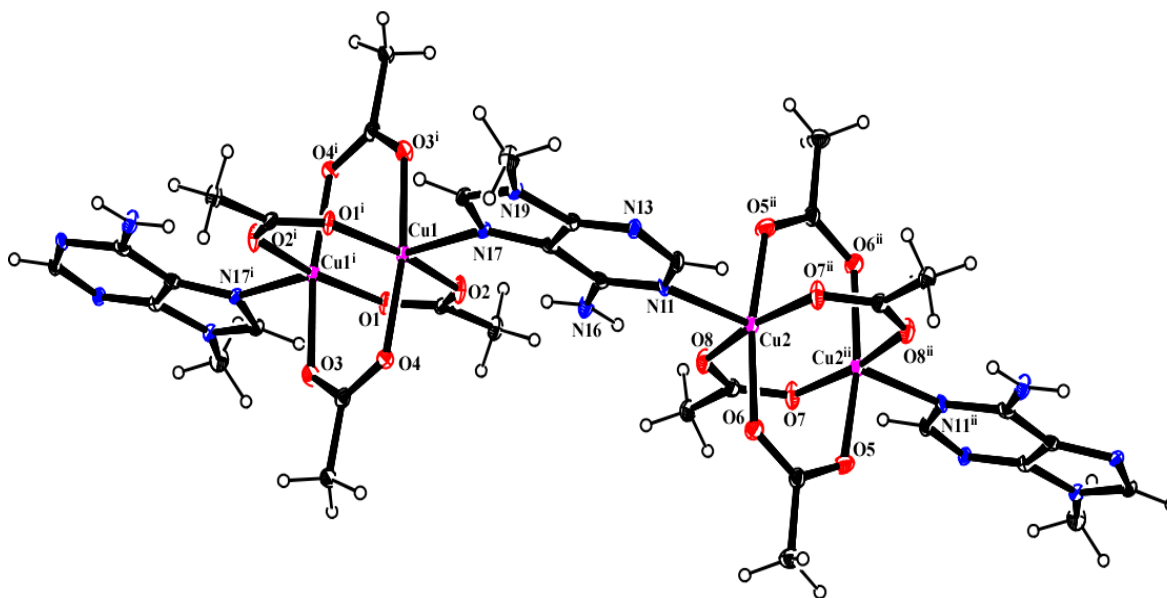
(a)
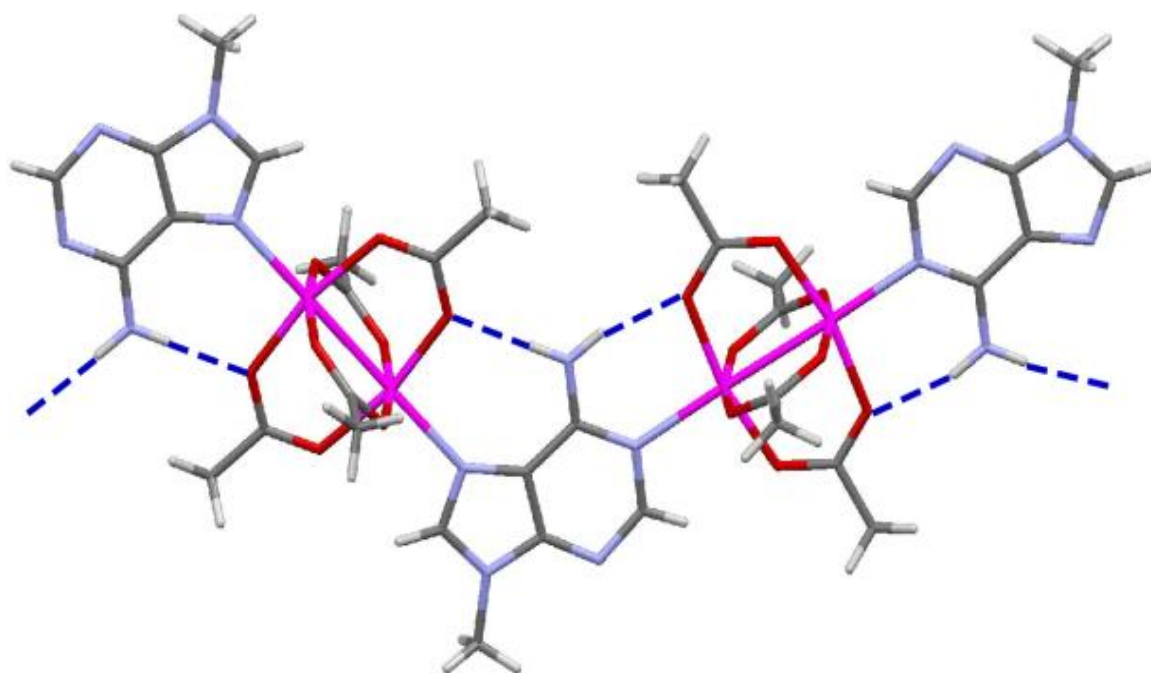
(b)

Figure 3.46: (a) A fragment of the polymeric chain of ***CU–9–MEADEACE*** (b) and the intramolecular hydrogen bond between N6–H and oxygen atoms of the carboxylate anions**.**

Table 3.27: Selected bond lengths (Å) and angles (º) of compound ***CU–9–MEADEACE***.[a]

Cu1–O2[i]	1.952(4)	O1–Cu1–O3	90.48(17)	O5–Cu2–O7	89.33(18)
Cu1–O1	1.955(4)	O1–Cu1–O4[i]	89.73(17)	O5–Cu2–Cu2[ii]	83.96(12)
Cu1–O3	1.967(4)	O1–Cu1–N17	94.12(17)	O5–Cu2–O7	89.33(18)
Cu1–O4[i]	1.977(4)	O2–Cu1–O1[i]	168.08(16)	O6–Cu2–O7[ii]	88.79(19)
Cu1–N17	2.211(5)	O2–Cu1–O3[i]	89.38(17)	O6–Cu2–N11[ii]	96.13(17)
Cu2–O5	1.957(4) .	O2–Cu1–O4[i]	87.91(16)	O6–Cu2–Cu2[ii]	83.31(13)
Cu2–O8[ii]	1.959(4)	O2–Cu1–N17[i]	97.69(16)	O7–Cu2–N11	99.25(17)
Cu2–O6[ii]	1.962(4)	O3–Cu1–O4[i]	167.79(17)	O7–Cu2–Cu2[ii]	82.13(12)
Cu2–O7	1.982(4)	O3–Cu1–N17	98.19(17)	O8–Cu2–N11[ii]	93.61(17)
Cu2–N11	2.211(5)	O4–Cu1–N17[i]	93.97(16)	O8–Cu2–O7[ii]	167.13(16)
Cu1···Cu1[i]	2.6434(14)	O5–Cu2–O8[ii]	89.32(19)	O8–Cu2–Cu2[ii]	85.00(12)
Cu1···Cu2	7.0797(11)	O5–Cu2–O6[ii]	167.27(17)	O8–Cu2–O6[ii]	89.7(2)
Cu2···Cu2[ii]	2.6616(14)	O5–Cu2–N11	96.60(17)	O8–Cu2–O6[ii]	89.7(2)

[a] Symmetry codes: (i) –x+1, –y, –z; (ii) –x+1, –y+1, –z+1.
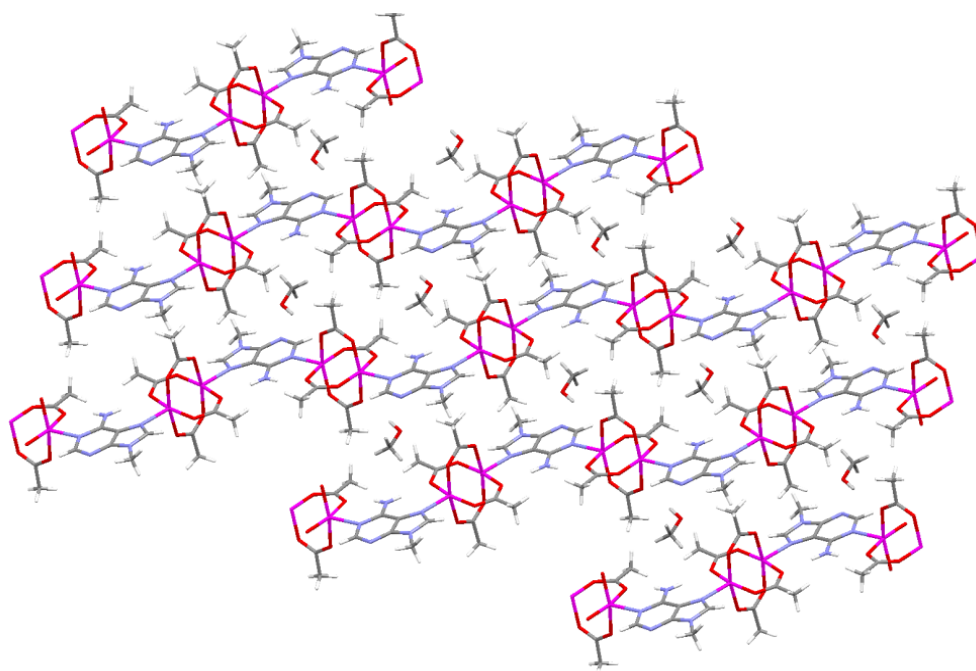
Figure 3.47: Crystal packing of *CU–9–MEADEACE* viewed along the crystallographic *b* axis.

Table 3.28: Hydrogen bonding interactions (Å, º) in *CU–9–MEADEACE*.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
N16–H16A···O7	0.86	1.96	2.793(6)	162.3
N16–H16B···O3	0.86	1.94	2.801(6)	178.1
O9–H9···O5[i]	0.82	2.04	2.835(6)	161.8

[a] Symmetry code: (i) –x+1, –y+1, –z+1. [b] **D**: donor; **A**: acceptor.

The thermogravimetric analysis of the compound *CU–9–MEADEACE* (Figure 3.48 and Table 3.29) shows that the solvent removal occurs below 135 ºC, then the compound remains stable up to 185 ºC and further decomposes in different steps to CuO as final residue, above 475 ºC.
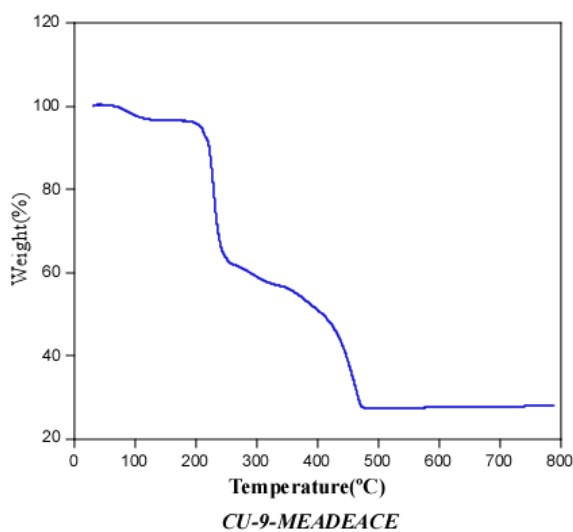
CU-9-MEADEACE

Figure 3.48: Thermogravimetric analysis of *CU–9–MEADEACE*.

Table 3.29: Thermogravimetric data of *CU–9–MEADEACE*.[a,b]

Step	T_i	T_f	$\Delta m(\%)$	$\Sigma\Delta m(\%)$	$\Sigma\Delta m(\%)_{theor}$
CO–9–MEADEACE					
1	25	135	3.4	3.4	3.31 (–1 H_2O)
2	185	260	34.54	37.94	–
3	260	475	34.61	72.35	70.8 (2 CuO)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released water molecules and final residue per formula.

3.3.2.10 Structural description of [Cu$_2$(Hgua)$_2$(H$_2$gua)$_2$(µ–Cl)$_2$Cl$_2$(H$_2$O)][CuCl$_4$]; *CUGUACL*

There are few examples of unsubstituted guanines coordinated to a metal centre because it is highly insoluble in most solvents. Herein, a very acidic media has been employed in order to promote its solubility and reaction with the copper(II) metal centres. *CUGUACL* compound contains two disordered copper(II) cationic dimeric entities and $[CuCl_4]^{2-}$ counterions. The centrosymmetric dimeric entities are based on double chloride bridged copper(II) metal centers that complete their coordination sphere with two *1H,3H,7H*–guaninium/*1H,7H*–guanine in *trans*–arrangement and coordinated through N9. Crystallographically there is no way to distinguish between the guaninium and guanine ligand because the hydrogen atom placed at N3 position is disordered over the two ligands with 50% occupation factor. The coordination of a cationic molecule to a metal centre is not usual but there have been some reported examples.[173] The difference between the two dimeric entities relays on the orientation of the Jahn–Teller effect and the presence of a coordination water molecule (Figure 3.49). The $[Cu_2(C_5H_5N_5O)_2(C_5H_6N_5O)_2(µ–Cl)_2Cl_2]^{2+}$ entity, with an occupation factor of 50%, presents a square–pyramidal coordination geometry around the metal centers, whereas $[Cu_2(C_5H_5N_5O)_2(C_5H_6N_5O)_2(µ–Cl)_2Cl_2(OH_2)]^{2+}$ dimer (occupation factor: 50%) provides a tetragonally elongated octahedral geometry. The N3 nitrogens of all guaninium cations are held additionally through an intramolecular hydrogen bonding with the coordinated water molecule. Table 3.30 lists the coordination bond lengths and angles.

[173] (a) Turel, I. et al. *J. Inorg. Biochem.* **2004**, *98*, 393. (b) Gaballa, A. S. et al. *Inorg. Chim. Acta* **2008**, *361*, 2070. (c) Sundaralingam, M.; Carrabine J. A. *J. Mol. Biol.* **1971**, *61*, 287. (d) Declercq, J. P. et al. *Bull. Soc. Chim. Belg*. **1971**, *80*, 527.

The copper(II) dimeric entities are linked together through direct nucleobase–nucleobase base pairing interactions involving the Hoogsteen face to provide a double–ladder like supramolecular structure, as shown in Figure 3.50. It becomes clear that the protonation of the guanine does not preclude the formation of complementary hydrogen–bonding interacterions among these nucleobases (Table 3.31). In fact, a detailed inspection of the hydrogen–bond donor/acceptor position at the 1H,7H–guaninium molecule indicate that both O6/N1 (Watson–Crick face) and O6/N7 (Hoogsteen face) are available for this purpose. However, the parallel arrangement of the coordinated nucleobases precludes their supramolecular polymerization into a 3D structure.
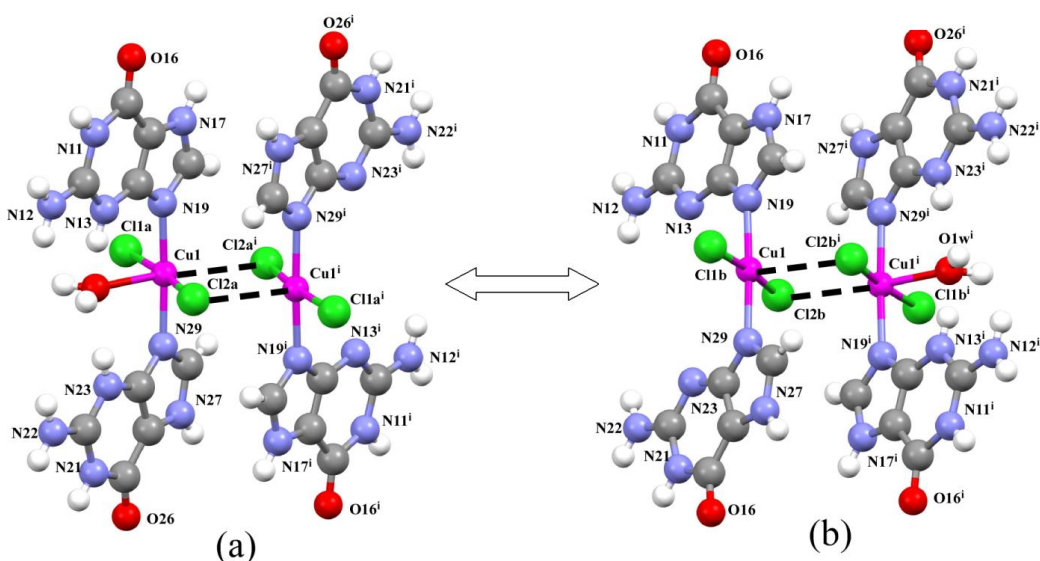
Figure 3.49: Disordered dimeric $[Cu_2(Hgua)_2(H_2gua)_2(\mu–Cl)_2Cl_2]^{2+}$ and $[Cu_2(Hgua)_2(H_2gua)_2(\mu–Cl)_2Cl_2(H_2O)]^{2+}$ cations of compound ***CUGUACL***.

Table 3.30: Coordination bond lengths (Å) and angles (°) of ***CUGUACL***.[a]

Cu1–N29	1.987(4)	N19–Cu1–O1w	88.38(17)
Cu1–N19	1.991(5)	N29–Cu1–Cl2B[i]	92.59(15)
Cu1–O1w	2.134(5)	N19–Cu1–Cl2B[i]	91.34(16)
Cu1–Cl2A	2.242(3)	O1w–Cu1–Cl2B[i]	179.48(17)
Cu1–Cl1A	2.350(3)	N29–Cu1–Cl2A	88.13(16)
Cu1–Cl2B[i]	2.260(4)	N19–Cu1–Cl2A	88.88(18)
Cu1···Cu1	3.658(4)	N29–Cu1–Cl1A	89.94(16)
N29–Cu1–N19	175.50(2)	N19–Cu1–Cl1A	92.72(18)
N29–Cu1–O1w	87.70(16)	Cl2A–Cu1–Cl1A	174.17(12)

[a] Symmetry code: (i) –x+1, –y, –z+1.
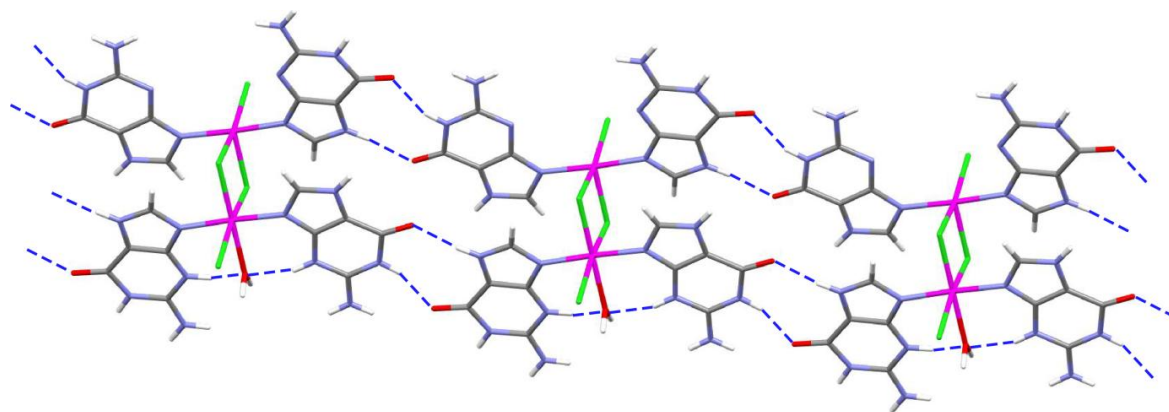
Figure 3.50: Hydrogen bonding interaction in the crystal structure of **CUGUACL**. Only the water coordinated dimeric entities are depicted here for clarity purposes.

Table 3.31: Hydrogen bonding interactions (Å, °) for compound **CUGUACL**.[a]

D–H···A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
O1w–H2w ··Cl1B[i]	0.94	1.92	2.786(10)	153.9
N13–H13 ··O1w	0.86	1.86	2.576(6)	139.4
N23–H23·· O1w	0.86	1.93	2.604(6)	133.9
N13–H13·· Cl1B[i]	0.86	2.66	3.389(6)	143.8
N23–H23 ··Cl1B[i]	0.86	2.68	3.393(6)	141.8
N11–H11 ··O26[ii]	0.86	1.90	2.723(6)	161.1
N12–H12A ··Cl1A[i]	0.86	2.60	3.421(6)	161.1
N12–H12A ··Cl1B[i]	0.86	2.37	3.182(6)	158.4
N12–H12B ··O26[ii]	0.86	2.42	3.105(6)	137.5
N17–H17 ··Cl4[iii]	0.86	2.27	3.118(5)	170.0
N21–H21···Cl3[iv]	0.86	2.31	3.123(5)	156.8
N22–H22A···Cl1A[i]	0.86	2.62	3.429(7)	156.4
N22–H22A···Cl1B[i]	0.86	2.36	3.172(7)	156.7
N22–H22B···Cl3[iv]	0.86	2.52	3.274(6)	147.5
N27–H27···O16[v]	0.86	1.90	2.754(6)	174.7

[a] Symmert code: (i) –x+1, –y+1, –z+1; (ii) x, y, z+1; (iii) x+1, y, z+1; (iv) x, y+1, z; (v) x, y, z–1. [b] **D**: donor; **A**: acceptor.

The supramolecular structure further extends into a 3D network through hydrogen–bonding interactions involving the Watson–Crick faces of the nucleobases, the coordinated chlorido ligands of the [CuCl$_4$]$^{2-}$ counterions and adjacent cationic dimers resulting in a compact crystal packing (Figure 3.51).
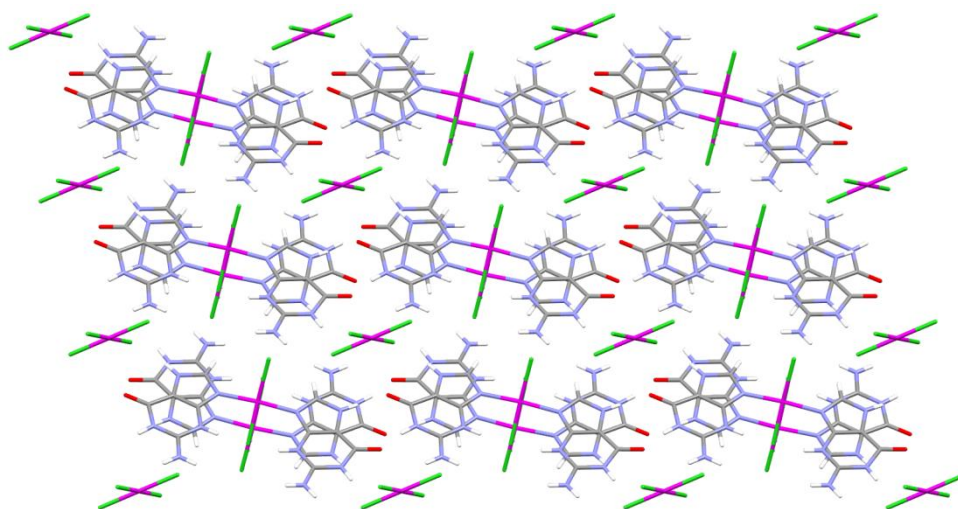
Figure 3.51: Packing of compound ***CUGUACL.***

3.3.2.11 Structural description of [Co(6–ClPur)₂(H₂O)₄]·4H₂O; *CO–6–CLPUR*

We have also tried to obtain supramolecular porous materials using non–natural nucleobases such as 6–chloropurine by its reaction with $Co(NO_3)_2·6H_2O$ in a pentylamine containing aqueous media. The presence of pentylamine in the reaction media promotes the deprotonation of the nucleobase increasing the options of obtaining a neutral complex entity but it also could play a templating effect on the resulting crystal structure. The crystal structure of ***CO–6–CLPUR*** consist of $[Co(6–ClPur)_2(H_2O)_4]$ monomeric entities (6–ClPur being 6–chloropurinate) and crystallization water molecules (Figure 3.52). The cobalt centers are coordinated to two 6–chloropurinato ligands through N9 positions occupying axial positions and the equatorial positions are coordinated by four water molecules forming an octahedral environment (Table 3.32).

The coordination of the 6–chloropurinato ligands is reinforced by the presence of an intramolecular hydrogen bond between a coordinated water molecule as donor and N3 position of the nucleobase as acceptor. It is worthy to denote that, as far as we know, this is the first example of this coordination mode for the 6–chloropurine/6–chloropurinato ligand (Figure 3.53).[174] The deprotonation of the chloropurine ligands leads to a situation that avoids any chance to promote a robust supramolecular structure by means of complementary hydrogen bond interactions between the nucleobases as it only contains donor groups. In fact

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[174](a) Dalby, C. et al. *Angew. Chem. Int. Ed.* **1993**, *32*, 1696. (b) Cepeda, J. et al. *Eur. J. Inorg. Chem.* **2009**, 2344.

the supramolecular structure seems to be dominated by the π–π stacking interactions between the nucleobases to provide a corrugated supramolecular sheet of monomeric complexes. There are also many hydrogen bond interactions involving the coordination and crystallization water molecules that reinforce the supramolecular sheet and also provide cohesion between adjacent sheets giving rise to a non porous structure (Figure 3.54 and Table 3.33).
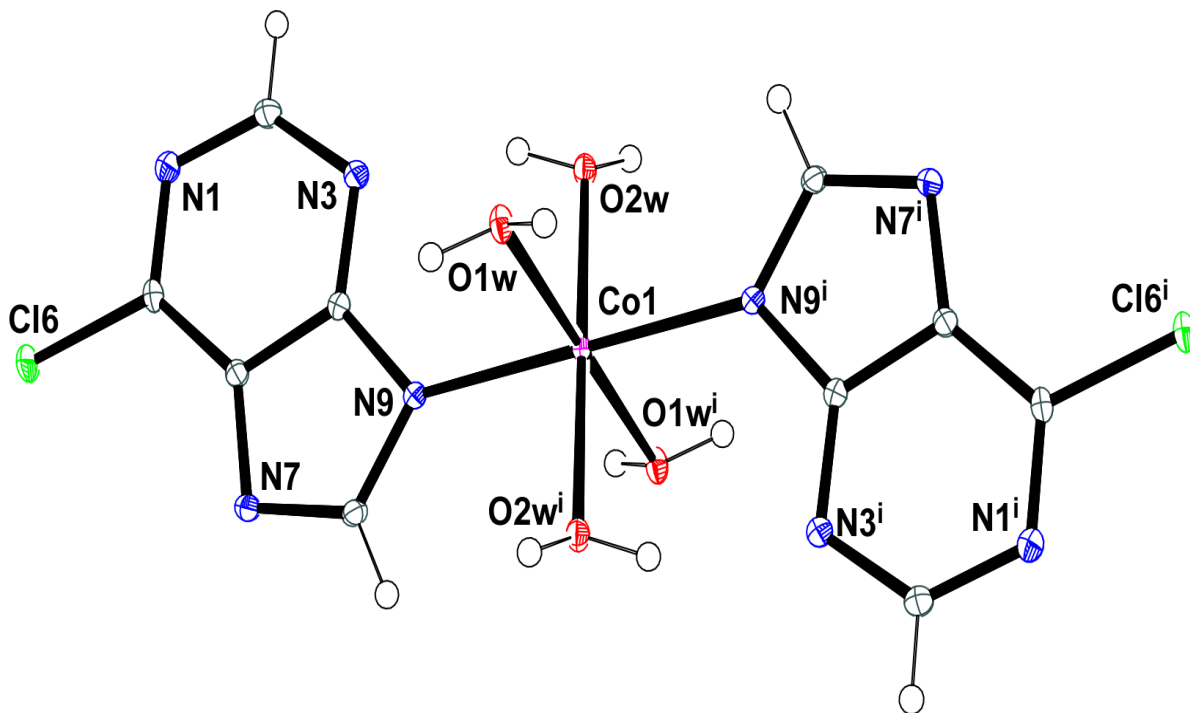
Figure 3.52: The monomeric entity of *CO–6–CLPUR*.

Table 3.32: Selected coordination bond lengths (Å) and angles (º) for compound *CO–6–CLPUR*.[a]

Co1–O2w[i]	2.0860(11)	O2w–Co1–O1w[i]	94.74(4)	O1w–Co1–N9	88.16(4)
Co1–O2w	2.0860(11)	O2w–Co1–O1w[i]	85.26(4)	O2w–Co1–N9[i]	88.33(5)
Co1–O1w[i]	2.1215(11)	O2w–Co1–O1w	94.74(4)	O2w–Co1–N9[i]	91.67(5)
Co1–O1w	2.1215(11)	O1w–Co1–O1w[i]	180.0	O1w–Co1–N9[i]	88.16(4)
Co1–N9	2.1284(13)	O2w–Co1–N9[i]	91.67(5)	O1w–Co1–N9[i]	91.84(4)
Co1–N9[i]	2.1284(13)	O2w–Co1–N9	88.33(5)	N9–Co1–N9[i]	180.0
O2w–Co1–O2w[i]	180.0	O1w–Co1–N9[i]	91.84(4)		

[a] Symmetry code: (i) –x+2, –y+1, –z+1.
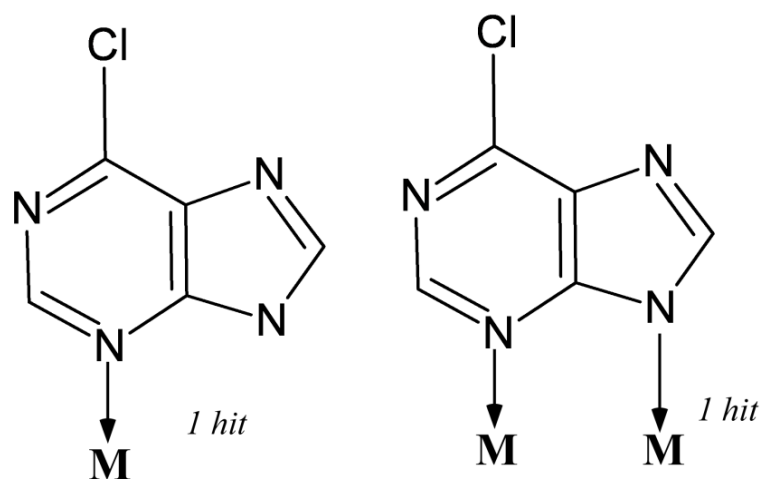
Figure 3.53: Coordination modes of 6–chloropurine/6–chloropurinate as found in the CSD data base.

(a)

(b)
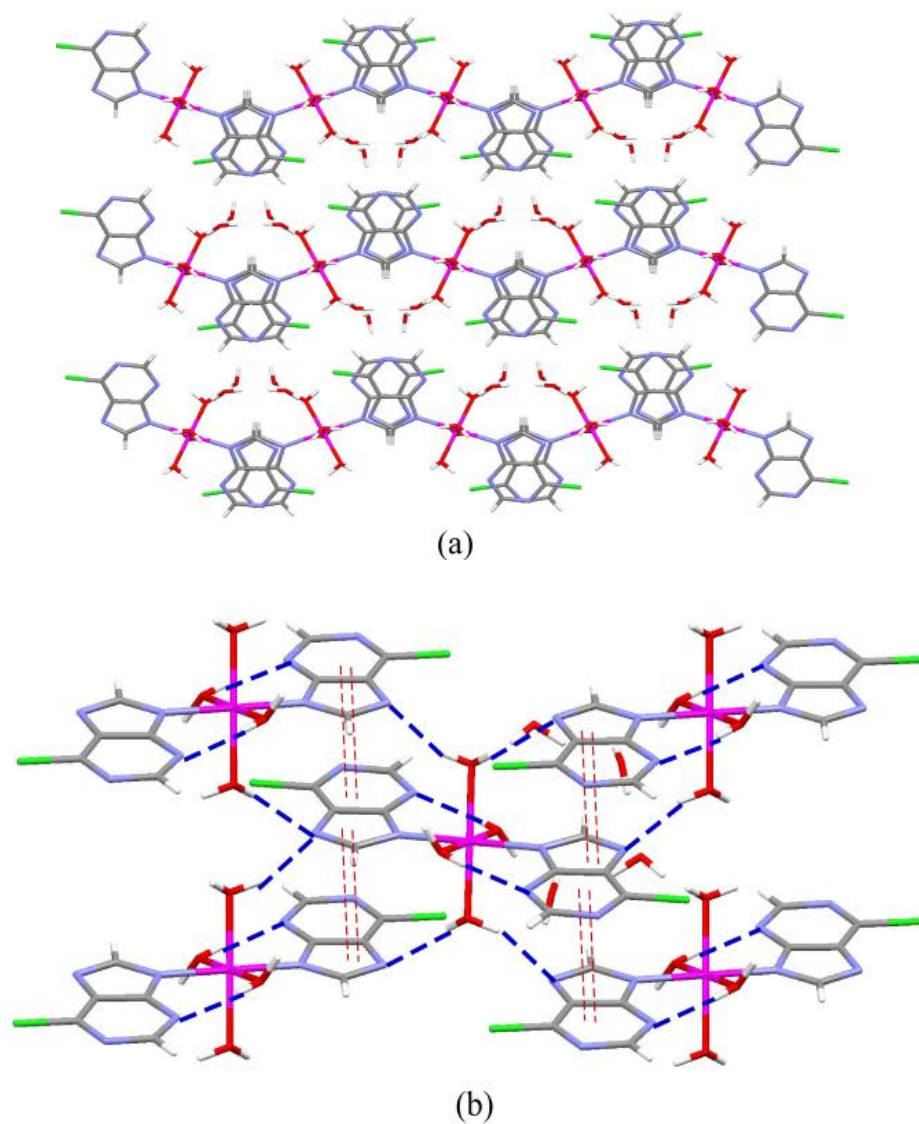
Figure 3.54: (a) Packing of compound ***CO–6–CLPUR*** and (b) hydrogen bonding (blue dashed lines) and π–π stacking interactions (red double dashed lines).

Table 3.33: Supramolecular interactions (Å, °) in ***CO–6–CLPUR***.

Hydrogen bonding interactions.[a]

D–H·· A[b]	*D–H*	*H···A*	*D···A*	*D–H···A*
O1w–H11···N7[i]	0.87	2.24	3.020(2)	149.8
O1w–H12···N7[ii]	0.87	2.11	2.902(2)	151.1
O2w–H21···N3[iii]	0.86	1.94	2.737(2)	153.4
O2w–H22···O4w[iv]	0.91	1.81	2.709(2)	169.4
O3w–H31···O1w	0.85	2.19	2.979(2)	153.7
O4w–H41···N1	0.95	1.90	2.827(2)	164.0
O4w–H42···O3w[v]	0.85	1.82	2.673(2)	175.5

π–π stacking interactions.[c]

Ring···Ring [d]	Angle	DC	α	DZ	DXY
Ring1–Ring1[vi]	2	3.6908(9)	19.22	3.4987(6)	1.1752
Ring1–Ring1[vii]	2	3.6908(9)	18.56	3.4851(6)	1.2149
Ring1–Ring2[vi]	1.79(8)	3.6505(8)	18.26	3.4958(6)	1.1434
Ring2–Ring1[vii]	1.79(8)	3.6506(8)	16.74	3.4668(6)	1.1438
Ring2–Ring2[vi]	1	3.7471(8)	22.24	3.4857(6)	1.3750
Ring2–Ring2[vii]	1	3.7472(8)	21.53	3.4684(6)	1.4183

[a] Symmetry: (i) –x+2, y–1/2, –z+3/2; (ii) x, –y+3/2, z+1/2; (iii) –x+2, –y+1, –z+1; (iv) x+1, –y+3/2, z+1/2; (v) –x+1, y+1/2, –z+3/2; (vi) x, 3/2–y,–1/2+z; (vii) x, 3/2–y, 1/2+z; [b] **D**: donor; **A**: acceptor. [c] Angle: Dihedral Angle between Planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] Ring1: N7, C5, C4, N9, C8; Ring 2: N1, C2, N3, C4, C5, C6.

The thermogravimetric analysis of the compound ***CO–6–CLPUR*** (Figure 3.55 and Table 3.34) shows that the solvent removal occurs in two steps at moderately low temperatures, below 80 ºC. Then the compound remains stable up to 370 ºC and further decomposes to Co_3O_4 as final residue above 610 ºC.
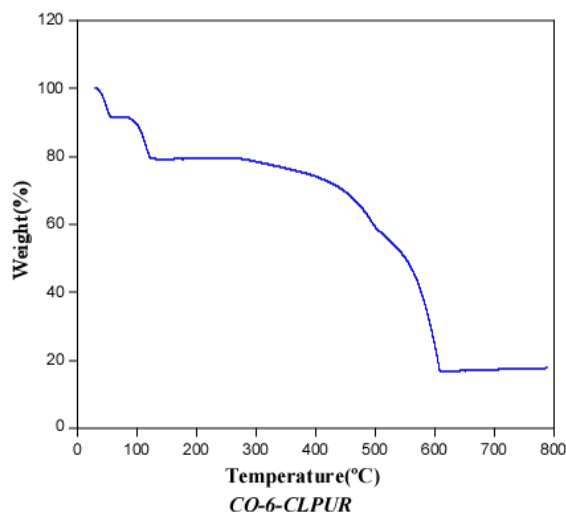
CO-6-CLPUR

Figure 3.55: Thermogravimetric studies of ***CO–6–CLPUR***.

Table 3.34: Thermogravimetric data of ***CO–6–CLPUR***.[a,b]

Step	T_i	T_f	$\Delta m(\%)$	$\Sigma\Delta m(\%)$	$\Sigma\Delta m(\%)_{theor}$
CO–6–CLPUR					
1	25	60	8. 35	8.35	7.05 ($-2\ H_2O$)
2	80	130	12.39	20.74	21.16 ($-4\ H_2O$)
3	370	610	62.63	83.37	84.27 ($1/3\ Co_3O_4$)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; $\Delta m(\%)$ = mass loss percentage for each process; ΔH = process type in the basis of DTA; $\Sigma\Delta m(\%)$ = total mass loss percentage; $\Sigma\Delta m(\%)_{theor}$ = theoretical total mass loss percentage. [b] Released water molecules and final residue per formula.

3.3.2.12 Structural description of [Co(ThioG)$_3$]·nH$_2$O; *CO–6–THIOG (SMOF–4)*

The analysis of the previous compounds enabled us to select a more appropriate ligand which even when deprotonated can promote complementary hydrogen–bonding interactions. The selected non–natural nucleobase was 6–thioguanine. There are not many examples of transition metal coordination complexes of 6–thioguanine in the literature but the preferred coordination mode seems to involve the chelation through 6–thione and N7 as it is found in the Ru, Rh and Ir complexes of 6–thioguanine.[175] There are also examples of 6–thioguanine acting as bridging ligands to provide 1D chains using a μ–κ*N7*,κ*S6*:κ*S6* coordination mode.[176] Figure 3.56 represents the possible complementary hydrogen bonding scheme for the different tautomers of the anionic form of this molecule when chelating a metal centre through S6 and N7 positions.

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[175] Yamanari, K. et al. *Inorg. Chem.* **2002**, *41*, 6824.
[176] Amo–Ochoa, P. et al. *Inorg. Chem.* **2013**, *52*, 5290.
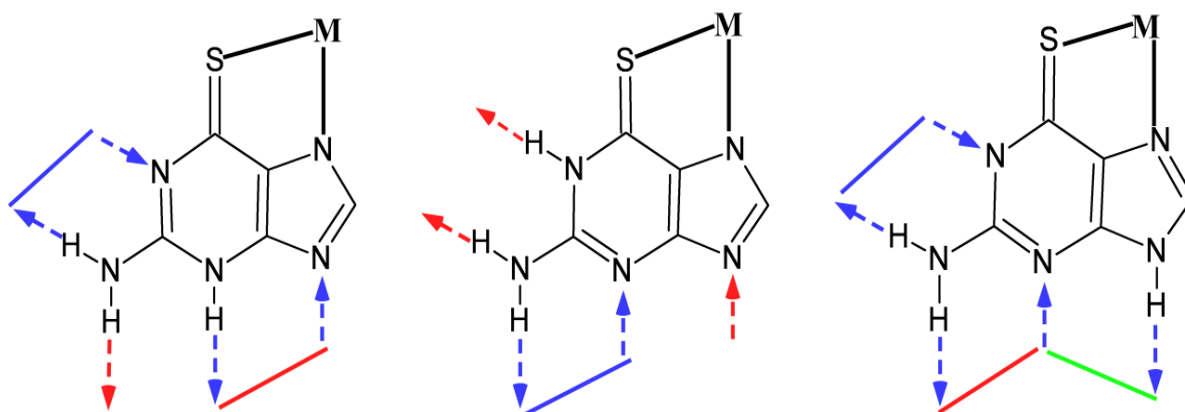
Figure 3.56: 6–thiopurinate sides available for complementary hydrogen bonding interaction when chelating to a metal centre through S6 and N7.

The reaction between 6–thioguanine and $Co(NO_3)_2 \cdot 6H_2O$ in a basic media of pentylamine containing aqueous solution favoured the oxidation to Co(III), as assured by its diamagnetic nature, gave rise to neutral monomeric $[Co(ThioG)_3]$ entities (Figure 3.57). Three thioguaninato ligands, in its *9H*–tautomeric form, are coordinated in a bidentate chelating mode to the Co(III) metal centers by their N7 and S6 atoms affording an octahedral coordination environment (Table 3.35).

Table 3.35: Selected bond lengths (Å) and angles (º) for ***CO–6–THIOG (SMOF–4)***.[a]

Co1–N17	1.950(3)	N17–Co1–N17[i,ii]	90.01(14)	N17–Co1–S16[ii]	92.12(10)
Co1–N17[i]	1.950(3)	N17–Co1–N17[ii]	90.01(14)	S16–Co1–S16[i]	88.73(5)
Co1–N17[ii]	1.950(3)	N17–Co1–S16[i]	89.17(10)	N17–Co1–S16[i,ii]	92.12(10)
Co1– S16	2.2979(12)	N17–Co1–S16[i]	92.12(10)	N17–Co1–S16[ii]	177.72(10)
Co1–S16[i]	2.2979(12)	N17–Co1–S16[i,ii]	177.72(10)	N17–Co1–S16[ii]	89.17(10)
Co1–S16[ii]	2.2979(12)	N17–Co1–S16[i]	177.72(10)	S16–Co1–S16[i,ii]	88.73(5)
N17–Co1–N17[i]	90.01(14)	N17–Co1–S16	89.17(10)	S16–Co1– S16[ii]	88.73(5)

[a] Symmetry codes: (i) –x+y, –x+1, z; (ii) –y+1, x–+1, z.
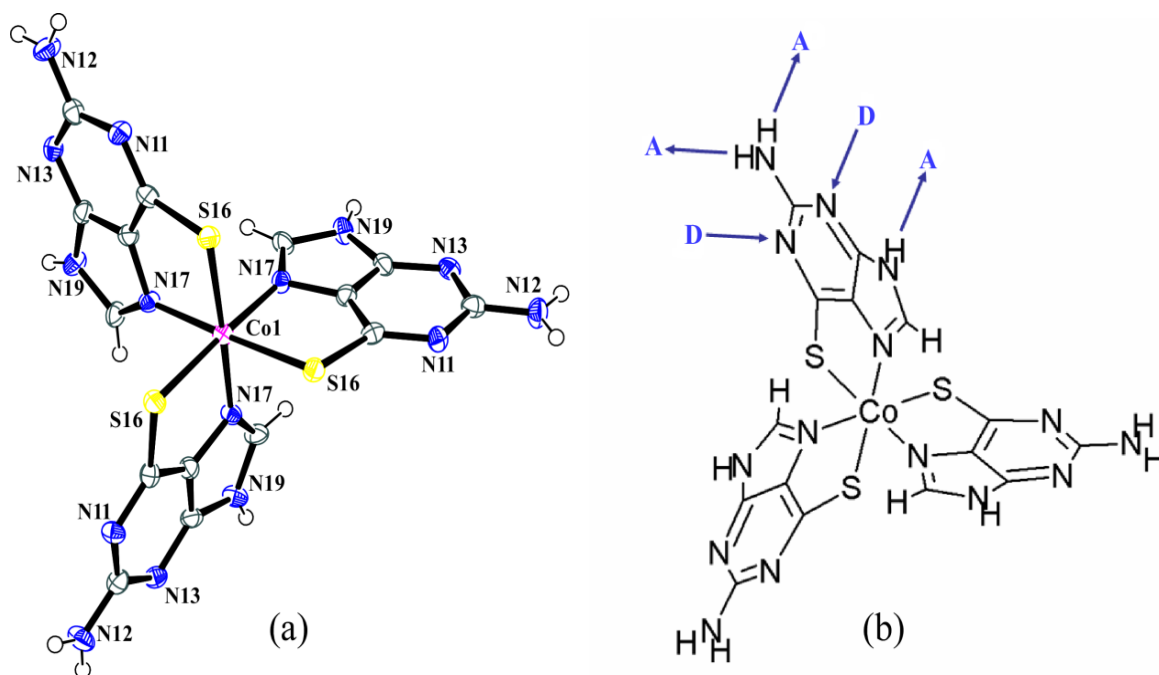
Figure 3.57: [Co(ThioG)$_3$] entity (a) of ***CO–6–THIOG (SMOF–4)*** and (b) available supramolecular hydrogen bonding scheme.

The coordination mode of the nucleobase analogue renders a rigid metal complex, and, at the same time, exposes its Watson–Crick (N1, N2) and sugar edges (N3, N9) that are both able to establish complementary hydrogen bonding interactions in non–coplanar directions. Therefore, this discrete complex entity seems to fulfill the requirements for the successful development of a supramolecular porous material.[90] In fact, there is a previous result based on similar discrete entities but using 6–thioguanosine that provides a complementary hydrogen bonding interaction involving only the Watson–Crick face (N1, N2) as the sugar edge is blocked by the sugar residue. It affords a supramolecular assembly containing great voids that are occupied by the sugar residue of the thioguanosine.[176] In compound ***CO–6–THIOG (SMOF–4)*** both sides of the 6–thioguaninato ligands are available to contribute to the supramolecular assembly. The sugar edge (N3, N9) of the nucleobases establish a double hydrogen bonding interaction with the nucleobases of three neighboring entities to give a $R_2^2(8)$ ring (Figure 3.58 and Table 3.36). This rigid synthon, based on direct thioguaninato⋯thioguaninato pairing interactions, leads to layers in the *ab* plane in which Δ and Λ isomers of the trischelate complex are sequentially arranged similarly to what happens

in layered $[M(ox)_3]^{n-}$ compounds.[177] The resulting arrangement corresponds to the Shubnikov hexagonal **hcb** topology with a (6^3) point symbol (Figure 3.59).[178]
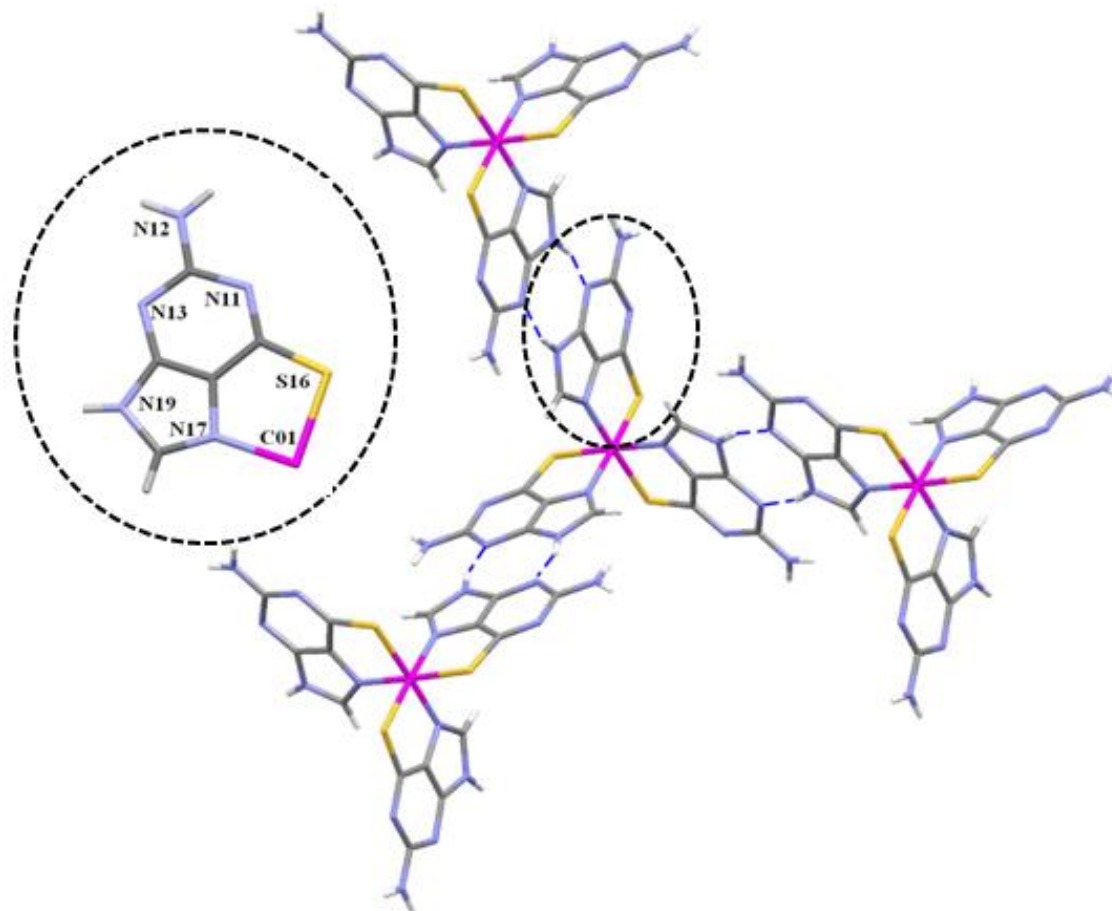
Figure 3.58: Nucleobase···nucleobase base pairing interactions.

Table 3.36: Supramolecular interactions (Å, °) in *CO–6–THIOG (SMOF–4)*.

Hydrogen bonding interactions.[a]

$D–H···A$[b]	$D–H$	$H···A$	$D···A$	$D–H···A$
N19–H19···N13[i]	0.86	2.03	2.875(5)	167
N12–H12···S16[ii]	0.86	2.69	3.467(4)	151
C18–H18···S16[iii]	0.86	2.67	3.415(4)	138

[a] Symmetry Code: (i) –x, –y+1, –z+2; (ii) x–y, x, –z+1; (iii) –x+y, –x+1, z+1. [b] **D**: donor; **A**: acceptor.

[177] (a) García–Couceiro, U. et al. *Inorg. Chem.* **2010**, *49*, 11346. (b) Coronado, E. et al. *Nature* **2000**, *408*, 447.
[178] (a) Blatov, V. A. *IUCR CompComm. Newletter* **2006**, 7, 4, (accessed Apr. 2014), TOPOS Main Page. http://www.topos.ssu.samara.ru. (b) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 675.

π–π interactions.[c]

Ring···Ring[d]	Angle	DC	α	DZ	DXY
Ring1···Ring2[iv]	0.0	3.46	18.5	3.28	1.10

[a] Symmetry: (i) –x, –y+1, –z+2; (ii) x–y, x, –z+1; (iii) –x+y, –x+1, z+1; (iv) –x,1–y,1–z.[b] **D**: donor; **A**: acceptor. [c] Angle: Dihedral Angle between Planes I and J (°), DC: Distance between ring centroids (Å), α: Angle Cg(I)—>Cg(J) vector and normal to plane I (°), DZ: Perpendicular distance of Cg(I) on ring J (Å), DXY: Slippage. [d] Ring 1: N17, C15, C14, N19, C18; Ring 2: N11, C12, N13, C14, N19, C16.
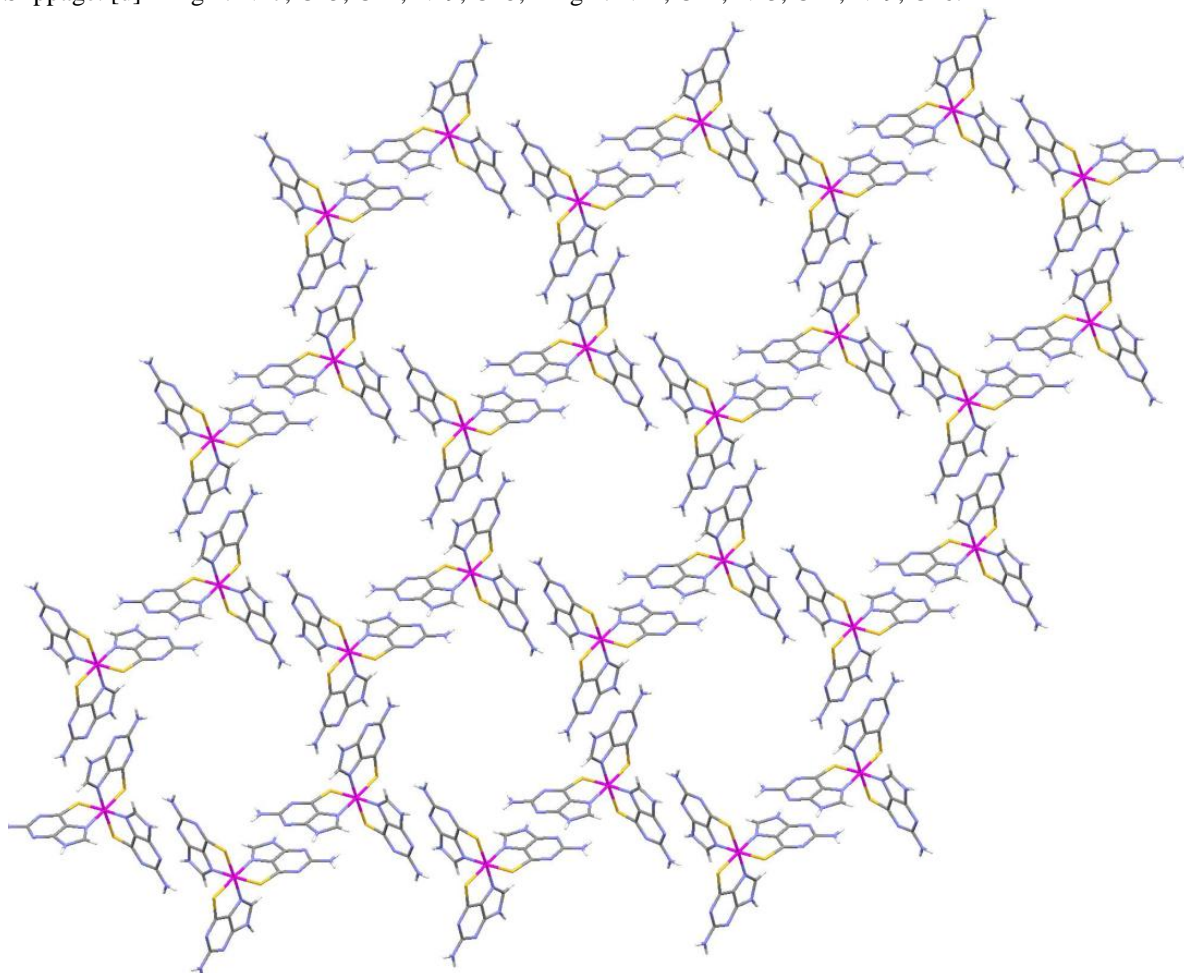
Figure 3.59: 2D supramolecular sheet assembled by means of base pairing interactions among the 6–thioguanine nucleobases with a Shubnikov hexagonal **hcb** topology in ***CO–6–THIOG (SMOF–4).***

The interactions among the three–connected uninodal two–dimensional (2D) nets are linked via weaker hydrogen bonds (N2–H···S6 and C8–H···S6) and reinforced with π–π interactions, (Table 3.36) leading to an **acs** topology and $(4^9.6^6)$ point symbol that corresponds to a porous crystal structure with an estimated surface area of 887 m^2/g and 43% of void space

based on theoretical calculations.[179] The resulting porous structure consists of 1D channels that run along the crystallographic *c* axis with a diameter of 8.2–9.4 Å (Figure 3.60).
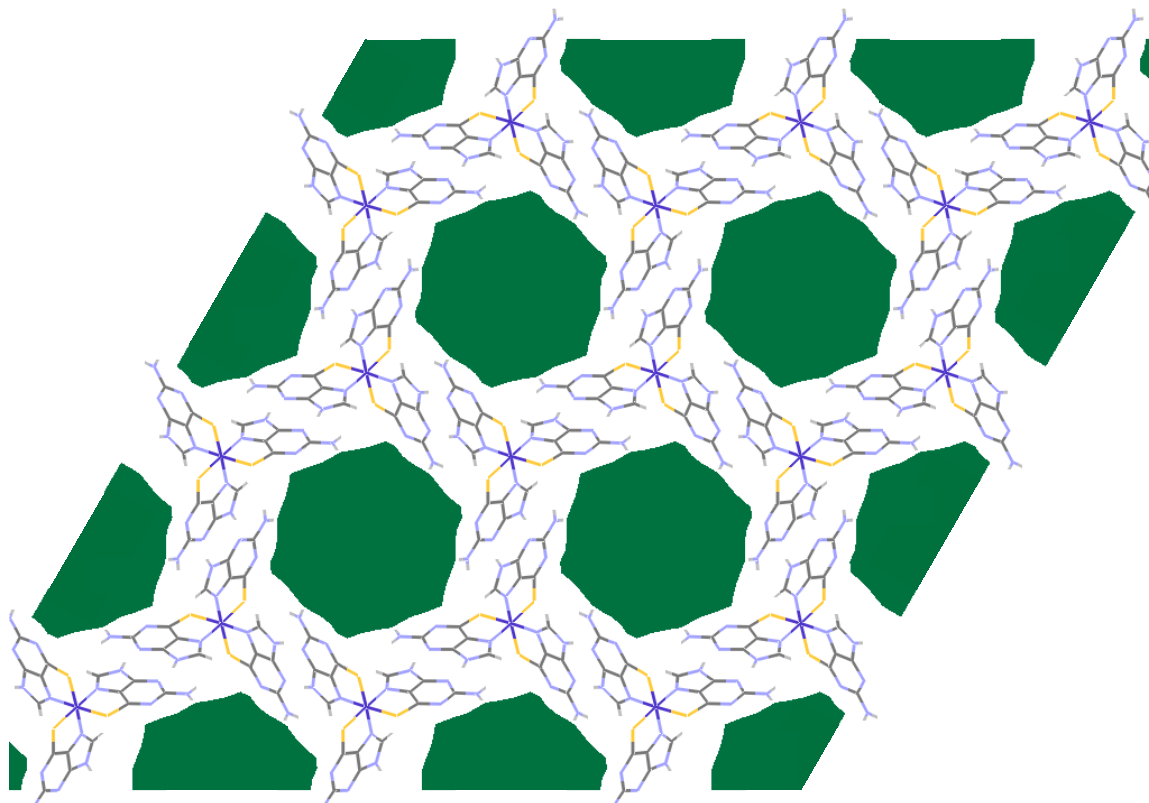
Figure 3.60: Projection of the crystal packing of ***SMOF–4*** along the crystallographic *c* axis. Green coloured regions represent the solvent accessible void.

It is worth to mention the template effect exerted by pentylamine. This molecule provides the basic media that this reaction requires and, at the same time, the tendency of the aliphatic tails to form aggregates in water promotes the growth of the supramolecular structure around them. In fact, the same synthesis but using different amines with shorter aliphatic tails does not provide this compound.

The thermogravimetric analysis (Figure 3.61 and Table 3.37) shows that, the solvent molecules are released below 100 ºC. After the solvent removal, the compound remains stable up to almost 280 ºC and then get decomposed in different exothermic steps to the final residue Co_3O_4 above 545 ºC.

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[179] (a) Sarkisov, L.; Harrison, A. *Mol. Simul.* **2011**, *37*, 1248. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
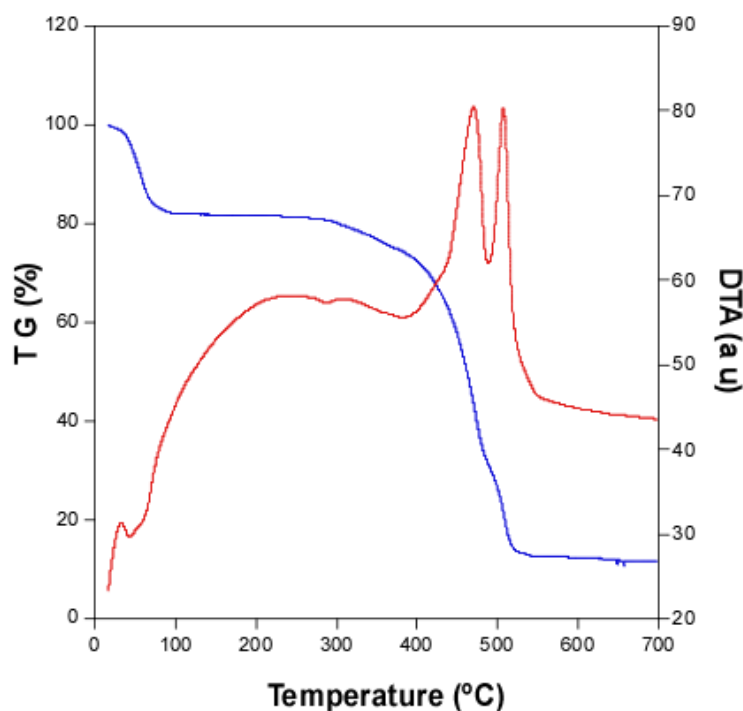
Figure 3.61: Thermogravimetric studies of *CO–6–THIOG (SMOF–4).*

Table 3.37: Thermogravimetric data of *CO–6–THIOG (SMOF–4).*

Step	Ti	Tf	Tpeak	Δm(%)	ΔH	ΣΔm(%)	ΣΔm(%)theor
CO–6–THIOG							
1	25	100	43	18.25	Endo	18.25	19.37 ($-6H_2O$)
2	280	545	470, 507	69.12	Exo	87.37	85.60 ($1/3Co_3O_4$)

[a] T_i = initial temperature; T_f = final temperature; T_{peak} = DTA peak temperature; Δm(%) = mass loss percentage for each process; ΔH = process type in the basis of DTA; ΣΔm(%) = total mass loss percentage; ΣΔm(%)$_{theor}$ = theoretical total mass loss percentage. [b] Released water molecules and final residue per formula.

3.3.2.12.1 *Adsorption* **studies of CO–6–THIOG (SMOF–4)**

According to N_2 (77 K) and CO_2 (273 K) adsorption studies this compound is highly selective towards CO_2 adsorption (Figure 3.62). The N_2 adsorption curve exhibits features of a non–porous material and, accordingly, the fitting of the adsorption area to BET equation leads to a negligible value. However, it shows a significant CO_2 uptake with a non–saturating curve reaching a value of 1.4 mmol/g at 1 bar. This behaviour has been described in the introduction section for *CUADECL–B* (*SMOF–1)*, *CUADEBR–A* (*SMOF–2)*, and *CUADECL–C (SMOF–3)* and its explanation for *CO–6–THIOG (SMOF–4)* probably would also be related to a crystal surface instability.
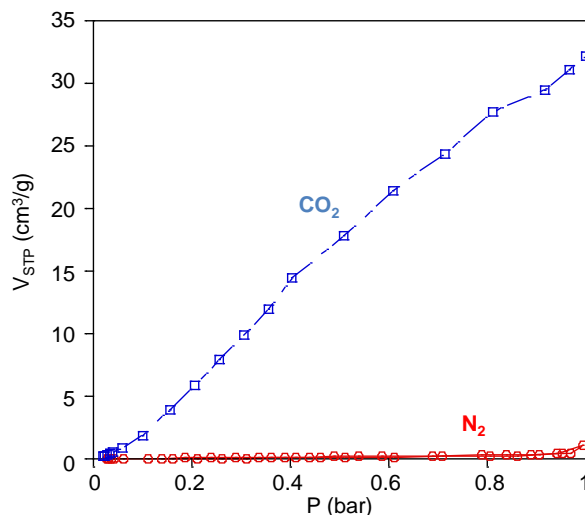
Figure 3.62: Adsorption isotherms for N_2 (77 K) and CO_2 (273 K), of a fresh sample of *CO–6–THIOG (SMOF–4)*.

3.4   CONCLUSIONS

On examining the above discussed structures, it becomes clear how a combination of rigid tectons with rigid synthons spreading at least in three non–coplanar directions is a well suited route to obtain porous supramolecular networks. In this context, the metal–nucleobase complexes can be good candidates to fulfill both requirements when the nucleobase is anchored to the discrete entity by at least two positions to provide a rigid building unit. This anchoring and the aromatic nature of the nucleobase provide rigid supramolecular building units. On the other hand, the well known complementary hydrogen bonding established between the nucleobases ensures the necessary rigidity of these synthons. Therefore, as it has been proved here the chances to obtain 3D supramolecular metal–organic frameworks based on metal–nucleobase systems are high. However, it is necessary to take care of the synthetic conditions in order to ensure the presence of the required direct hydrogen bonding interactions between the nucleobases. Related to this later issue, the presence of water molecules can disrupt these direct adenine···adenine hydrogen bonding interactions, leading to non porous materials as evidenced by the crystal structure of $[Cu_2(\mu–adenine)_4Cl_2]Cl_2·8H_2O$ (*CUADECL–A*). The direct hydrogen bonding disrupting capacity of the water molecule seems also to be responsible of the surface instability observed in *CUADECL–B (SMOF–1)*, *CUADEBR–A (SMOF–2)*, *CUADECL–C (SMOF–3)* and *CO–6–THIOG (SMOF–4)*.

Chapter 4

Conclusions and future perspectives

4.1 Conclusiones

4.2 Future perspectives

4.1 CONCLUSIONS

Taking into account the great potential of MOFs, we have explored a related type of material, in which the coordination bonds are replaced with hydrogen bonds as connectors, that are also directional and predictable interactions, to sustain the 3D crystal building (Figure 4.1). The underlying strategy that has emerged from this work can be exemplified by the naïf analogy of soft and rigid balls. Soft balls can adjust their shape to provide an efficient packing leaving almost no space in between. However, rigid balls do not have the option of changing their shape and, as a consequence, their packing is less effective giving rise to the presence of voids. In other words, flexible things pack effectively while rigid things do not unless they present very specific and appropriate shape, such as cubes, triangular, rectangular and hexagonal prisms, etc.[180]

Figure 4.1: Comparison between extended architectures based on (a) coordination bonds and (b) hydrogen bonding interactions as structure directing agents.

This simple idea summarizes the synthetic strategy that we have devpoled during the research work to obtain Supramolecular Metal–Organic Frameworks (***SMOFs***) as an alternative to more conventional Metal–Organic Frameworks (***MOFs***). It can be converted to crystal engineering language through the following key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units, and

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[180] Holden, A. *Shapes, Space and Symmetry.* New York: Dover, 1991, p.154.

(iii) the non–coplanarity of functional groups involved in the predictable synthons. The rigidity of the building units (discrete complexes) can be achieved using rigid ligands bonded through multiple positions. It means, in most common cases, a double anchoring of the ligand by means of double coordination bonds or the combination of a coordination bond and an intramolecular hydrogen bond. The predictability and rigidity of the synthons requires the presence of adjacent functional groups, incorporated into the rigid ligands, able to establish complementary hydrogen bonding interactions. Finally, the requisite of non–coplanar arrangement of the synthons comes from our objective of obtaining three–dimensional extended systems that are achieved by the presence of at least three non–coplanar synthons. The use of complexes with non–planar coordination geometries makes this last condition easy to accomplish.

It has become clear that a suitable system that would fulfil all the above described requirements for obtaining ***SMOFs*** are the discrete metal–nucleobase systems, especially those based on purine nucleobases. These ligands provide, at one hand, the advantage of the increased rigidity of the supramolecular building block due to the coordination through multiple positions, and, on the other hand, they present more edges capable of establishing complementary hydrogen bonding interactions.
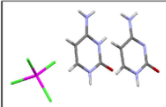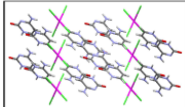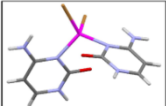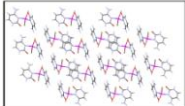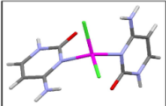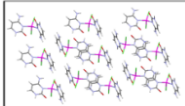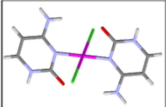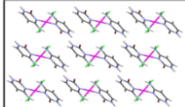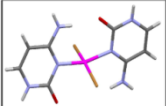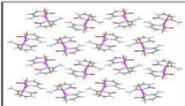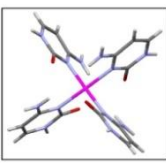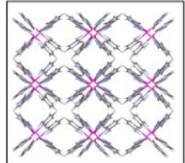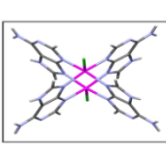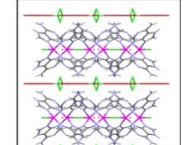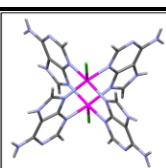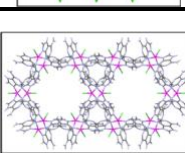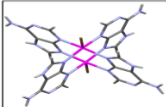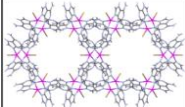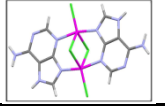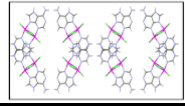
Additionally, the results achieved employing $[Cu_2(\mu–adenine)_4(X)_2]^{2+}$ (X = Cl⁻, Br⁻) as supramolecular building blocks (***CUADECL–B/SMOF–1*** and ***CUADEBR–A/SMOF–2***) show that these compounds present a surface instability because of the ambient humidity that creates a diffusion barrier than can be permeated only by strong interacting adsorbate molecules with high kinetic energy such as CO_2 but not by N_2, H_2, and CH_4, that makes them attractive for selective gas adsorption and separation technologies. More recently, Zaworotko et al. reported an analogous compound, based on the $[Cu_2(\mu–adenine)_4(X)_2]^{2+}$ dinuclear entity, replacing the halides by bulkier TiF_6^{2-} anions improving the chemical stability of the supramolecular network toward humidity, thus avoiding the surface instability, and therefore, being able to adsorb CO_2, CH_4 and N_2.[181] These studies also pointed out the relevance of the solvent selection because strong hydrogen bond donor and acceptor solvents such as water

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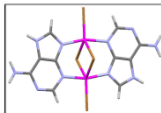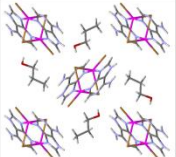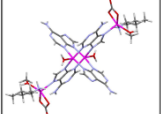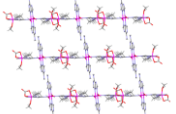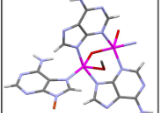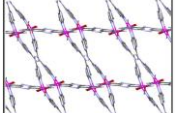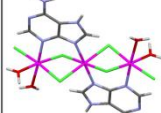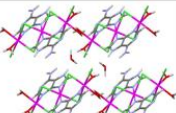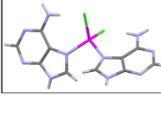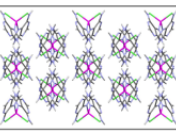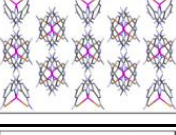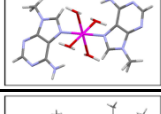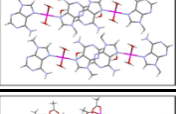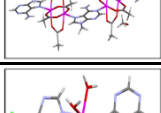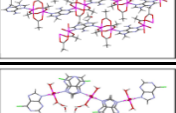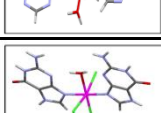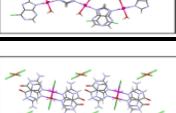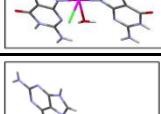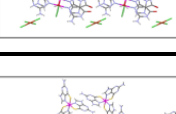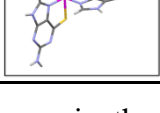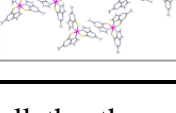
[181] Nugent, P. S. et al. *J. Am. Chem. Soc.* **2013**, *135*, 10950.

could disrupt the direct hydrogen bonding interactions between the nucleobases that are the key factor to achieve these compounds.

In Table 4.2, we make a summary of all the 21 compounds reported in this thesis, accounting for the above mentioned key factors for obtaining supraMOFs. It demonstrates the suitability of this synthetic strategy to afford supramolecular porous materials with eight new *SMOFs* involving different metal centers, nucleobases and complex entities.

Table 4.1: A summary table showing the effect of the key factors determining the formation of porous *SMOFs.*

Compound	Building unit	Rigidity	Rigid synthons	Non–coplanar synthons (≥ 3)	Porosity / structure	
COCYTCL		⊗	⊗	⊗	⊗	
COCYTBR		⊗	✓	✓	⊗	
ZNCYTCL		⊗	✓	✓	⊗	
CUCYTCL		⊗	✓	⊗	⊗	
CUCYTBR		⊗	✓	✓	⊗	
CUCYTSO4		✓	⊗ *counterions*	✓	⊗	
CUADECL–A		✓	⊗ *water*	⊗	⊗	
CUADECL–B SMOF–1		✓	✓	✓	✓	
CUADEBR–A SMOF–2		✓	✓	✓	✓	
CUADECL–C SMOF–3		✓	✓	✓	✓	

CUADEBR–B		✅	❌ *Propanol*	❌	❌	
CUADECO3 SMOF–8		✅	✅	✅	✅	
CUADEOH SMOF–9		✅	✅	✅	✅	
CO3ADECL		✅	❌	❌	❌	
COADECL SMOF–5		✅	✅	✅	✅❌ *Interpenetr–ation*	
COADEBR SMOF–6		✅	✅	✅	✅❌ *Interpenetr–ation*	
CO–9– MEADECL		❌	✅	❌	❌	
CU–9– MEADEACE		❌	❌	❌	❌	
CO–6–CLPUR		❌	✅	❌	❌	
CUGUACL		❌	✅	❌	❌	
CO–6–THIOG SMOF–4		✅	✅	✅	✅	

As shown in the table above, porous **SMOFs** were formed only when all the three criteria were met. In the case of **COCYTBR**, **ZNCYTCL,** and **CUCYTBR** even though they establish direct base pairing interactions and also are non–coplanar, the lack of rigidity of the building unit, because of the monodentate anchoring of the nucleobase, hinders it from developing porosity. In the case of **CUCYTCL**, the synthons are planar. **CUCYTSO4**,

CUADECL–A, ***CUADEBR–B***, ***CUGUACL*** and ***CU–9–MEADEACE*** could have been porous as they provide rigid building units and establish non–coplanar synthons, however in all these cases the direct base pairing interactions were blocked by other competitive groups such as counter ions or solvent molecules. In similar situations, it has been successful to design ***SMOFs*** by selecting solvents with less hydrogen bonding affinity. It demonstrates that the wise selection of solvents is also a key factor for the synthesis of ***SMOFs.***

4.2   FUTURE WORK

Althogh this thesis contains a research work that can be considered as accomplished, there arised many ideas and suggestions during this research activity. These could be developed and implemented as the key points for the future research projects. Some of the future objectives are listed below.

1. Apply the strategies adopted in this work to other metal centres and nucleobase derivatives (hypoxanthine, 6–mercaptopurine) or similar systems with hydrogen bonding ability, to develop more ***SMOFs***.

2. Experiment different synthetic modifications to avoid interpenetration of compounds like ***COADECL*** and ***COADEBR*** and hence to achieve ***SMOFs*** with high pore volume and surface area.

3. Adopt these strategies to design and develop ***SMOFs*** based on other polynuclear building units as a trial to increase the porosity.

4. Apply solvent–free synthesis as a synthetic approach to different metal nucleobase systems to develop ***SMOFs***, since ***COADECL*** was obtained through solvent free synthesis as well.

5. Try to overcome the surface instability of these ***SMOFs*** by growing more stable ***MBioFs*** outside the ***SMOF*** core, protecting it from the atmospheric humidity and related surface thickening and hence increasing the gas uptaking capacity of these ***SMOFs***.

Chapter 5

References

5.1 Introduction

5.2 References

5.1 INTRODUCTION:

In this work, the references are given as footnotes in all the chapters. In this section, the full references are listed in alphabetical order according to the name of the first author and, then, in ascending order of the year of publication. In cases, where the same author has more than one publication in the same year, the names of the rest of the authors are considered for hierarchy. When this criterion is not enough, the publication name and the first page number are taken into account. The reference style followed is that recommended by the American Chemical Society. Additionally, the title of the article is included for better identification.

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ZHANG, T.; LIN, W.: Metal–organic frameworks for artificial photosynthesis and photocatalysis. *Chem. Soc. Rev*. **2014**, *43*, 5982–5993.

ZHANG, X.–H.; HAO; Z.–M.; ZHANG, X.–M.: Spin canting and metamagnetism in the first hybrid cobalt–hypoxanthine open framework with umr topology. *Chem. Eur. J*. **2011**, 17, 5588–5594.

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Chapter 6

Appendices

A.1 Chemicals

A.2 Instrumental techniques

A.3 IR Spectra

A.4 Thermogravimetric analysis

A.5 Experimental and theoretical adsorption measurements

A.6 Articles published from this work

APPENDICES

A.1. CHEMICALS

All chemicals employed for the synthesis of the compounds were of reagent grade and used as commercially obtained. Tables A.1.1 and A.1.2 gather the reactants, formula, commercial supplier (CS), assay (AS), molecular weight (MW), Chemical Abstracts Service number (CAS), and risk (R) and safety (S) statements for their manipulation.

Table A.1.1 Reactants used.

Name	Formula	CS	AS	MW (g/mol)	CAS	R	S
Cobalt(II) bromide	$CoBr_2$	Aldrich	≥99%	218.75	7789–43–7	36–37–38	26–37–39–45–28A
Cobalt(II) chloride hexahydrate	$CoCl_2.6H_2O$	Merck	≥99%	237.93	7791–13–1	49–60–22–42/43–68–50/53	53–45–60–61
Cobalt(II) nitrate hexahydrate	$Co(NO_3)_2. 6H_2O$	Fluka	≥99%	291.03	10026–22–9	8–22–40–43–50/53	17–36/37–60–61
Cobalt(II) sulphate heptahydrate.	$Co(SO4). 7H_2O$	Aldrich	≥99%	281.1	10026–24–1	49–60–22–42/43–68–50/53	–
Copper(II) acetate monohydrate	$Cu(CH_3COO)_2. H_2O$	Scharlau	≥99%	199.65	6046–93–1	22.41–50/53	26–39–46–61
Copper(II) bromide	$CuBr_2$	Fluka	≥99%	223.36	7789–45–9	–	–
Copper(II) chloride dihydrate	$CuCl_2. 2H_2O$	Merck	≥99%	170.48	10125–13–0	24/25	20–37–44
Copper(II) sulphate pentahydrate	$CuSO_4. 5H_2O$	Merck	≥99%	249.68	7758–99–8	22–36/38–50/53	2–22–60–61
Hydrochloric acid	HCl	Fluka	≥37%	36.46	7647–01–0	280–314–339	261–280–305+351+338–310–410+403
n–Pentyl amine	$C_5H_{13}N$	Fluka	≥98%	87.17	110–58–7	11–20/21/22–34	16–26–33–36/37/39–45
Potassium bromide	KBr	Aldrich	≥99%	119.00	7758–02–3	20–21–22–36/37/38	22–36
Zinc(II) chloride	$ZnCl_2$	Merck	≥98%	136.28	7646–85–7	22–34–50/53	1/2–26–36/37/39–45–60–61

Table A.1.2 Ligands used

Name	Formula	CS	AS	MW (g/mol)	CAS	R	S
6–chloropurine	$C_5H_3ClN_4$	Aldrich	≥99%	154.6	87–42–3	22	
6–thioguanine	$C_5H_5N_5S$	Aldrich	≥98%	167.19	154–42–7		
9–methyl adenine	$C_6H_7N_5$	Aldrich	≥97%	149.16	700–00–5	22	
Adenine	$C_5H_5N_5$	Aldrich	≥99%	135.13	73–24–5	22	[26]–36
Cytosine	$C_4H_5N_3O$	Aldrich	≥97%	111.1	71–30–7		24/25

A.2 INSTRUMENTAL TECHNIQUES

A.2.1. Density measurements

Density measurements of the synthesized compounds have been performed on single–crystals by means of the flotation method.[182] The preparation of the mixtures was made employing trichloromethane ($CHCl_3$: ρ = 1.48 g cm^{-3}), carbon tetrachloride (CCl_4: ρ = 1.59 g cm^{-3}), and bromoform ($CHBr_3$: ρ = 2.89 g cm^{-3}).

A.2.2. Quantitative analysis

Elemental analyses (C, H, N) were performed on a Euro EA Elemental Analyzer, whereas the metal content was determined by inductively coupled plasma (ICP–AES) performed on a Horiba Yobin Yvon Activa spectrometer, provided by the SGIker of the University of the Basque Country (UPV/EHU).

A.2.3. Infrared spectroscopy

The IR spectra were recorded on a FTIR 8400S Shimadzu spectrometer of the Inorganic Department of the Science and Technology Faculty of the UPV/EHU in the 4000–400 cm^{-1} spectral region. KBr pellets were prepared, with an approximate concentration of 2–3%. The potassium bromide was of spectroscopic quality and was previously dried at 130 ºC. The pellets were obtained at a pressure of 10 Tm.

Figure A.2.1: FTIR spectrophotometer 8000S Shimadzu.

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[182] Román, P.; Gutiérrez–Zorrilla, J. M. *J. Chem. Educ.* **1985**, *62*, 167.

A.2.4. Thermal analysis

The thermogravimetric studies (TG, DTG, and DTA) were carried out in a TA Instruments SDT 2960 thermobalance of the Inorganic Department of the Science and Technology Faculty of the UPV/EHU. The measures were performed in an atmosphere of synthetic air (79% N_2 / 21% O_2) with a flow rate of 150 cm^3 min^{-1}, between 25 and 800 ºC, with a heating rate of 5 ºC min^{-1}.

Figure A.2.2: Thermobalance TA instrument SDT 2960.

A.2.6. Single–crystal X–ray diffraction

The single crystal X–ray diffraction data collections were done at 293(2) K and at 100(2) K on an Oxford Diffraction Xcalibur (λMo−Kα = 0.71073 Å), STOE IPDS (λMo−Kα = 0.71073 Å), and on an Agilent Technologies Supernova (λMo−Kα = 0.71073 Å and λCu−Kα = 1.5418 Å) diffractometers of the SGIKer of the UPV/EHU.

(a) **(b)**

Figure A.2.3: Single crystal X–ray diffractometer (a) Oxford Diffraction Xcalibur and (b) Stoe IPDS 2T.

The data reduction was done with the CrysAlis PRO[183] and X–RED programs. Mostof the structures were solved by direct methods using the SIR92[184] program and refined by full–matrix least–squares on F^2 including all reflections (SHELXL97),[185] with all calculations performed using the WINGX crystallographic software package.[186] Geometrical calculations were performed with the program PLATON.[187]

A.2.7. X–ray powder diffraction

The X–ray powder diffraction patterns were collected on a Philips X'PERT powder diffractometer of the SGIker of the UPV/EHU with Co–Kα radiation (λ = 1.5418 Å) over the range 5 < 2θ < 50° with a step size of 0.02° and an acquisition time of 2.5 Sper step at 25 ℃. Indexation of the diffraction profiles were made by means of the FULLPROF program (pattern–matching analysis)[188] on the basis of the space group and the cell parameters found for isostructural compounds by single crystal X–ray diffraction. The calculated and observed diffraction patterns are shown in Figures A.3.1–11.

A Bruker D8 Advance Vario powder diffractometer of the SGIKer of the UPV/EHU with Cu–Kα (λ = 1.5406 Å) was used to perform the variable–temperature X–ray powder diffraction measurements, heating the samples from room temperature with a heating rate of 5 ℃·min^{-1} and measuring a complete diffractogram every 20 or 30 ℃ as appropriate.

A.2.8. Adsorption measurements

Micromeritics ASAP 2020 surface area and porosity analyser was used for carbon dioxide at 298 K and 273 K (Grant GR150 thermostatic refrigerated bath) and carbon monoxide (273 K) adsorption experiments. Hiden IGA automatic gravimetric porosimeter was used to collect adsorption isotherms at 196 K (ethanol/dry ice mixture) up to 900 mbar. Adsorption isotherms of N_2 were measured at 77 K using a Micromeritics Tristar II 3020.

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[183] *CrysAlis PRO*, version 1.171.33.55; Oxford Diffraction: Wroclaw, Poland, 2010.

[184] Altomare, A. et al. *J. Appl. Cryst.* **1993**, *26*, 343.

[185] Sheldrick, G. M. *SHELXL–97, Programs for X–ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

[186] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.

[187] Spek, A. L. *Acta Crystallogr.* **2009**, *D65*, 148.

[188] (a) Rodríguez–Carvajal, J. *FULLPROF, a Program for Rietveld Refinement and Pattern Matching Analysis*; Abstacts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the IUCr.: Toulouse, France, 1990, 127. (b) Rodríguez–Carvajal, J. *FULLPROF 2000*, version 2.5d, Laboratoire Léon Brillouin (CEA–CNRS), Centre d'Études de Saclay, Gif sur Yvette Cedex: France, 2003.

Approximately 0.1 g of sample was used for analysis and placed in a glass bulb which is sealed with a rubber seal frit to prevent exposure to the atmosphere. Generally, the material is activated to remove all solvent from the pores by heating and under vacuum for 12 hours prior to adsorption.

A3: IR SPECTRA
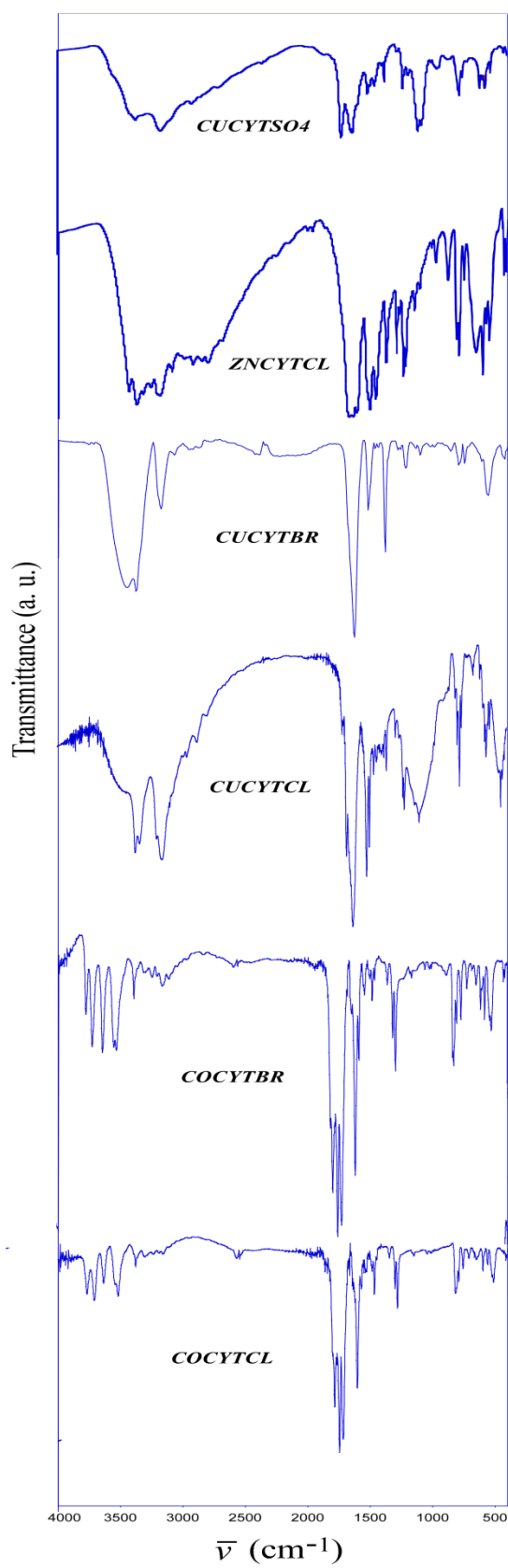
Figure A.3.1: IR spectra of Metal–Cytosine compounds.
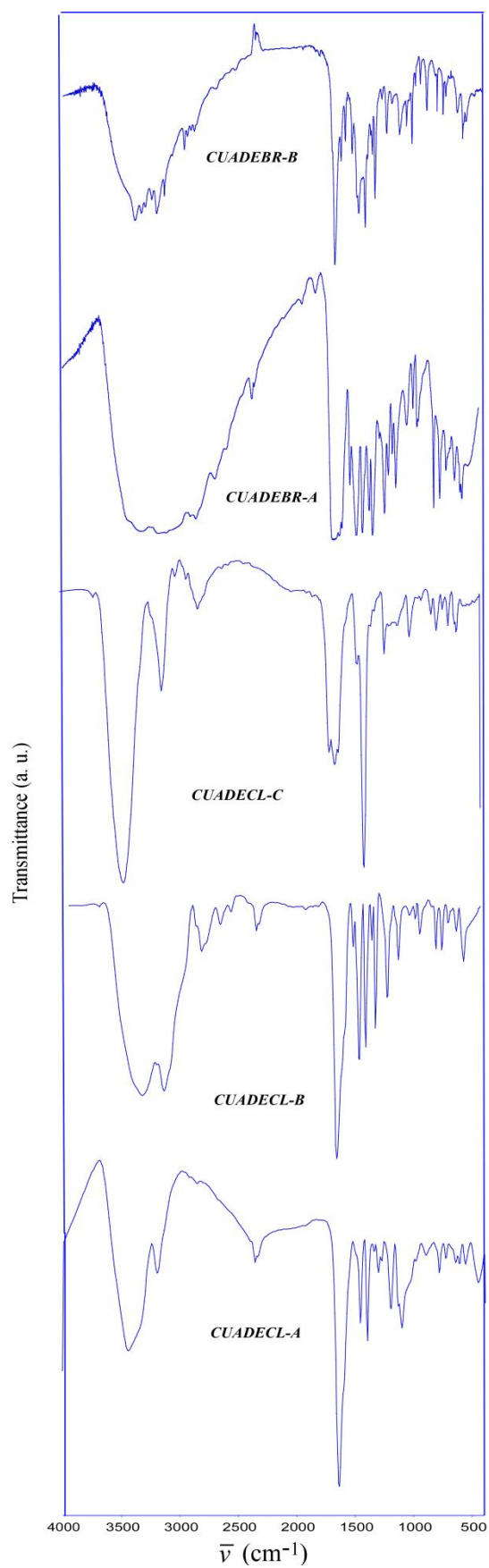
Figure A.3.2: IR spectra of Metal–Adenine compounds.
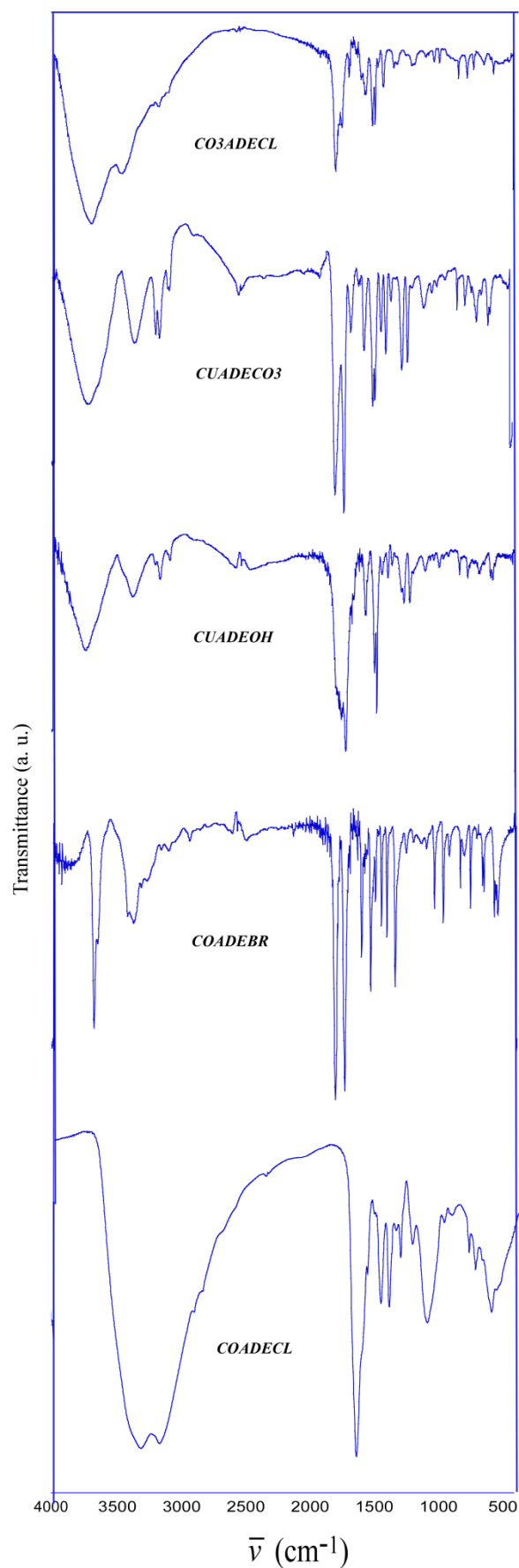
Figure A.3.3: IR spectra of Metal–Adenine compounds.
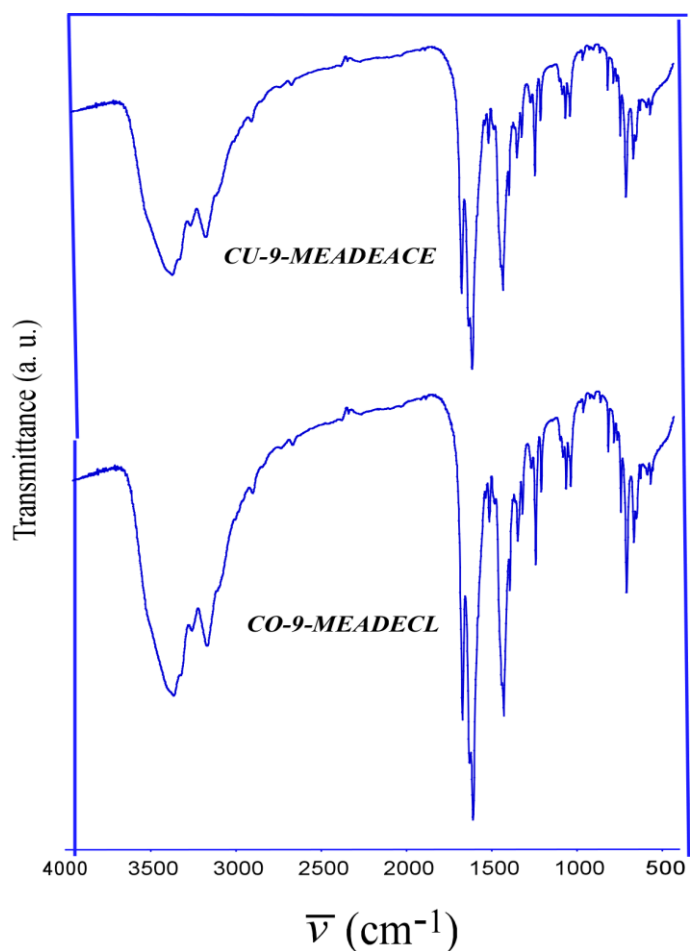
Figure A.3.4: IR spectra of *CU–9–MEADEACE* and *CO–9–MEADECL*.
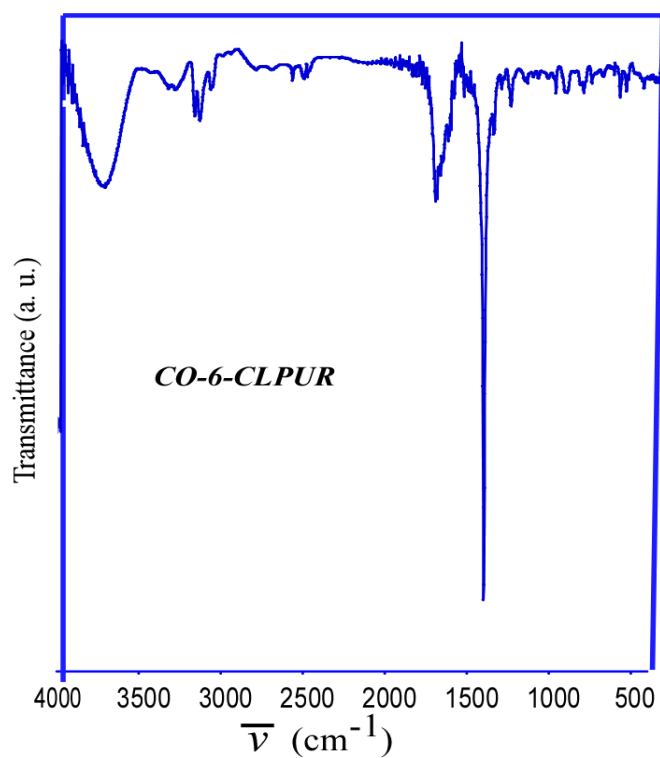
Figure A.3.5: IR spectra of *CO–6–CLPUR.*
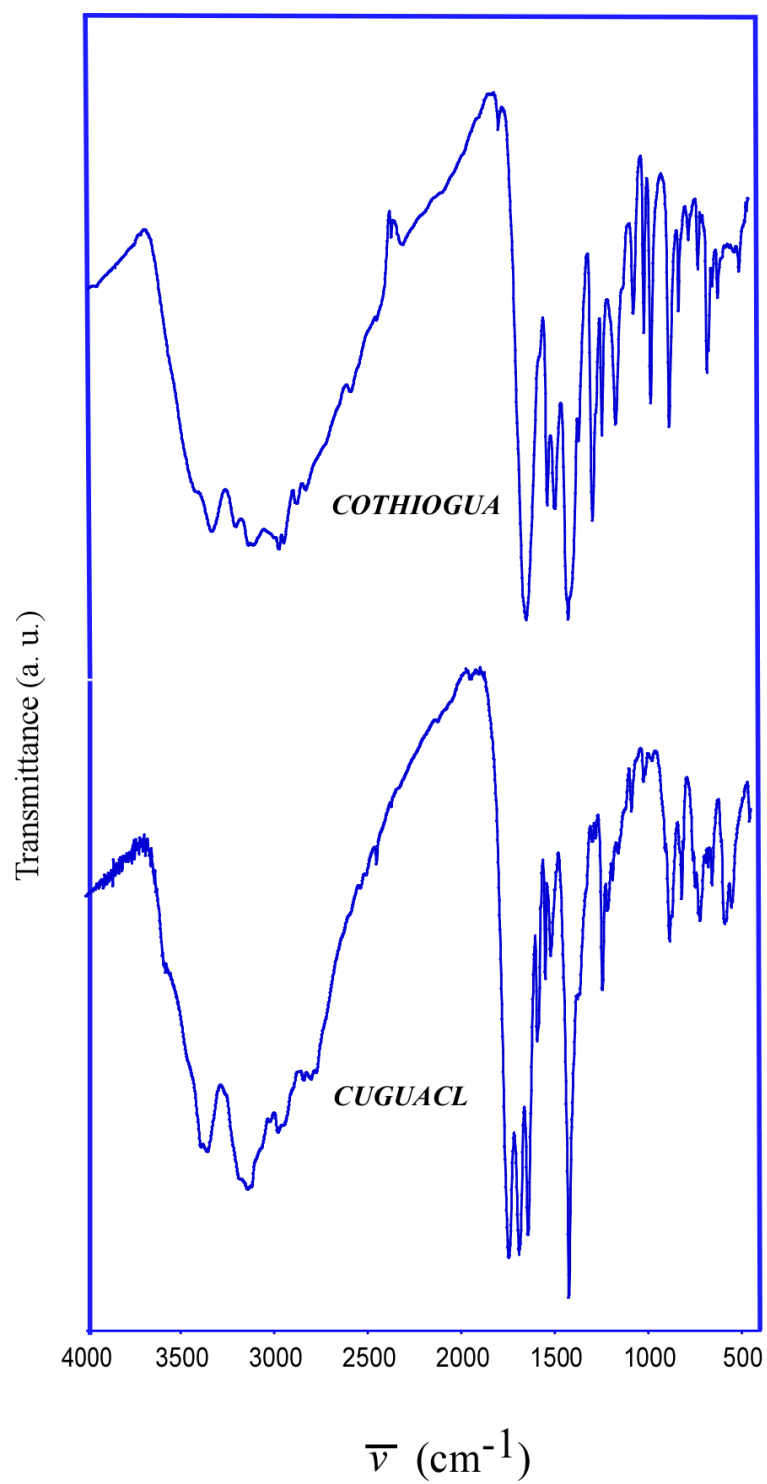
Figure A.3.6: IR spectra of *CUGUACL* and *CO–6–THIOG*.

A4: THERMOGRAVIMETRIC ANALYSIS
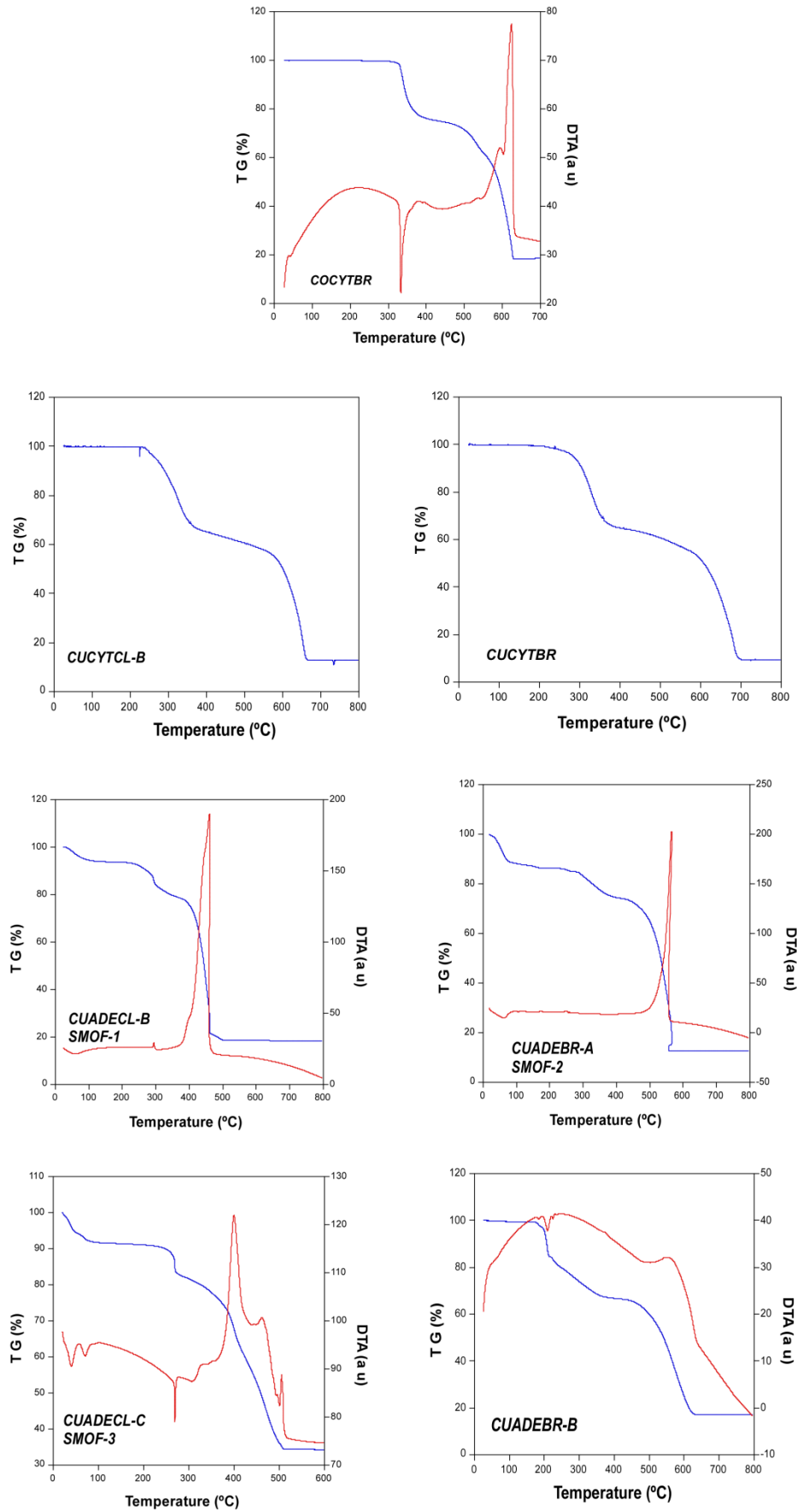
Figure A.4.1: Thermogravimetric analysis.
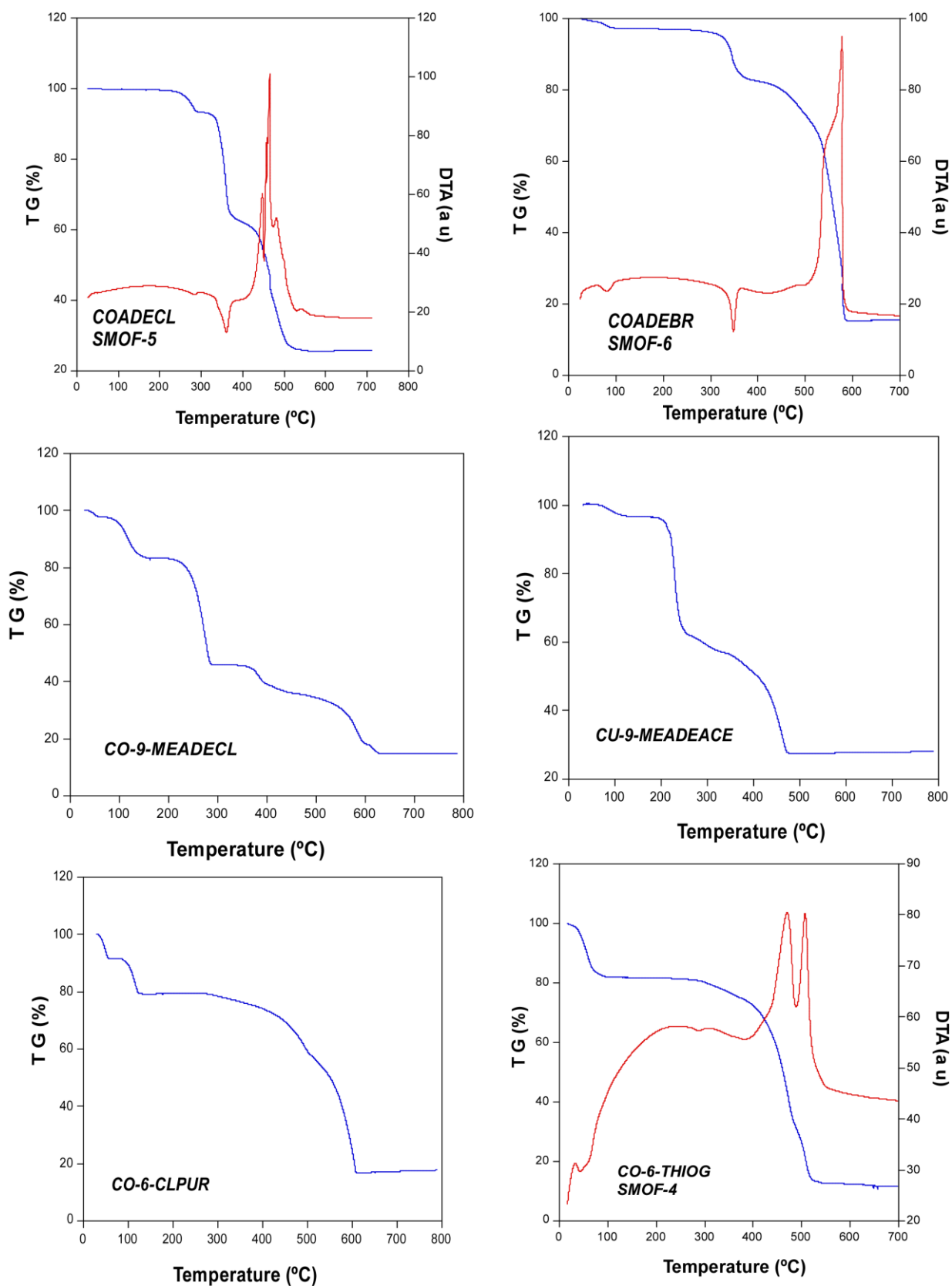
Figure A.4.1 (contd.): Thermogravimetric analysis.

A5: EXPERIMENTAL AND THEORETICAL ADSORPTION MEASUREMENTS

A.5.1. Introduction

The measurement of the adsorption of gases is widely used to determine the surface area, pore volume and pore size distribution of porous solids.[189] The use of selected molecules can also provide information on the pore connectivity and surface chemistry. Adsorption is performed at a constant temperature while the pressure is varied, and it can be measured volumetrically (the amount of adsorption is inferred from pressure measurements made before and after the measurement) or gravimetrically (the sample is weighted as the pressure of the adsorbate is increased, correlating the increase in weight of the sample to the uptake). The uptake of gas can be expressed as an equivalent volume at standard pressure, as a true volume or mass, or as moles per gram. This is plotted against the equilibrium pressure (p/p_0) at a constant temperature, and the plot is an isotherm of the adsorbate uptake. Figure A.5.1 shows the different types of adsorption isotherms which complete the IUPAC classification.[190]
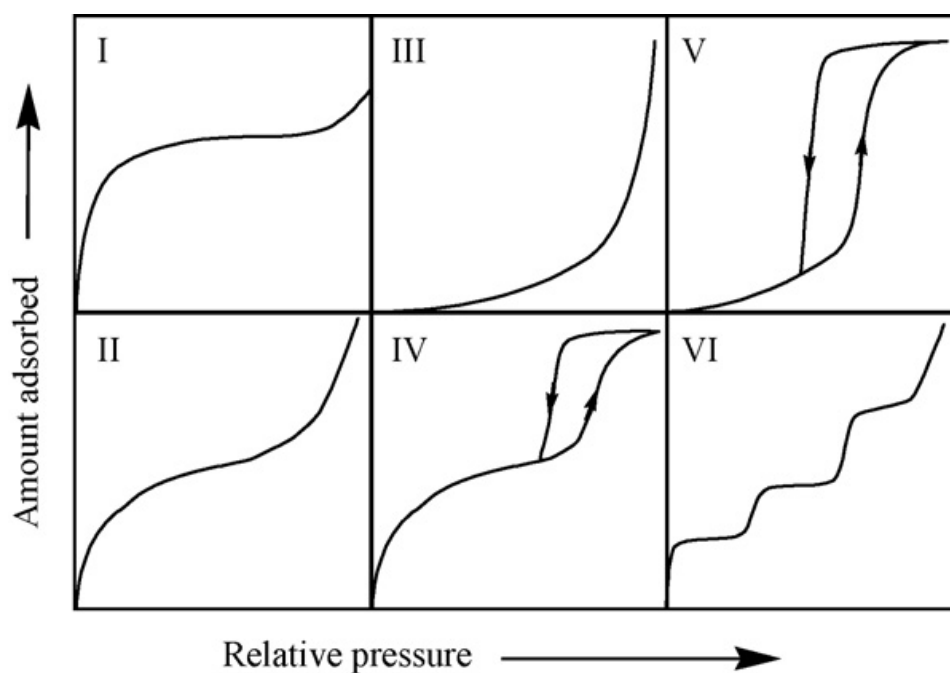
Figure A.5.1: Different types of adsorption isotherms

Type I isotherms are characteristic of microporous materials. The initial step section of the isotherm corresponds to monolayer deposition inside the micropores. Once the pores are

[189] Sing, K. *Colloids and Surfaces A: Physicochem. Eng. Aspects,* **2001**, *187–188*, 3.
[190] (a) Brunauer, S. et al. *J. Am. Chem. Soc.* **1940**, *62*, 1723. (b) Sing, K. S. W. et al. *Pure Appl. Chem.* **1985**, *57*, 603. (c) Rouquerol, J. et al. *Pure Appl. Chem.* **1994**, *66*, 1739.

filled, there is little extra room for adsorption and so the isotherm reaches a saturation value quickly. Condensation of the gas at high partial pressures results in an increase in uptake. Type II and IV isotherms are found from non–porous materials or mesoporous structures. Type II characterises monolayer coverage at low pressures, a plateau when all energetically favourable sites have been covered, and multilayers at higher pressures. The hysteresis effect in type IV isotherms is due to the different energetics of condensation on the surface of the pore and evaporation away from the pore (the curvature of the surfaces is different in the forward and reverse direction). When molecules in a gas have a stronger affinity for each other than for the surface of the adsorbant, type III and V isotherms are found. Type VI isotherms result from distinct monolayers being built up on a surface. For this it requires a material with a very uniform surface and no preferential adsorbant sites.

A.5.2. Langmuir theory

Langmuir theory[191] assumes that all sites on the surface are energetically equivalent and considers only the interactions between gas and surface (assuming that the interaction between gas molecules is negligible). The theory also assumes that during adsorption the collision of the gas with the surface is inelastic. Assuming that the gas forms only a monolayer on the surface gives V_a, volume adsorbed at a certain pressure, P:

$$V_a = \frac{V_m bP}{1 + bP} \qquad (A.5.1)$$

where V_m is the quantity of gas that covers the whole surface in a monolayer and b is an empirical constant. Manipulation of this equation gives:

$$\frac{P}{V_a} = \frac{1}{V_m P} + \frac{P}{V_m} \qquad (A.5.2)$$

A plot of P/V_a vs. P should give a straight line in situations where the Langmuir equation applies, with a gradient equal to $1/V_m$ and a y–intercept of $1/V_m b$. The surface area of the adsorbant can be estimated by using the calculated value of V_m in the equation:

$$s = \frac{V_m \sigma N_A}{mV_0} \qquad (A.5.3)$$

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[191] Langmuir, I. *J. Am.Chem. Soc*. **1916**, *38*, 2221.

where s is the area of the surface covered by a single gas molecule, m is the mass of the adsorbing sample, N_A is the Avogadro constant and and V_0 is the molar volume of the gas. Where nitrogen is used, the surface area covered by a molecule is 16.2 Å^2 so the expression becomes:

$$s\left(\frac{m^2}{g}\right) = \frac{4.35 V_m \left(cm^3 @ STP\right)}{m(g)} \qquad \text{(A.5.4)}$$

A.5.3. BET Theory

BET (Brunauer, Emmett and Teller) theory [192] advances Langmuir theory by incorporating the effect of multilayer gas adsorption. It assumes that the force behind the binding of the gas to a surface is the same as those forces accounting for condensation of gases. The BET method equates the rate of condensation of the gas onto a monolayer with the evaporation of the gas away from the monolayer and then sums this effect over an infinite number of layers to give the BET equation.

$$V_a = \frac{V_m CP}{\left(P_0 - P\right)\left[1 + \left(C - 1\right)\dfrac{P}{P_0}\right]} \qquad \text{(A.5.5)}$$

Where C is a constant and P_0 is the saturation pressure of the gas. C relates to the heat of adsorption of the first layer, q_1, and the heat of liquifaction, q_L, by the relationship:

$$C \infty \exp \frac{q_1 - q_L}{RT} \qquad \text{(A.5.6)}$$

Where R is the gas constant and T is the absolute temperature of the measurement. This equation can be written in the linear form:

$$\frac{P}{V_a\left(P_0 - P\right)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C}\left(\frac{P}{P_0}\right) \qquad \text{(A.5.7)}$$

A plot of $P/[V_a(P_0–P)]$ vs. (P/P_0) can determine V_m and C from the intercept and slope of a regression line . the surface area can be calculated from the volume of the monolayer, by assuming that gas molecules at the surface are close packed and by using the formula:

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[192] Brunauer, S. et. al. *J. Am. Chem. Soc*. **1938**, *60*, 309.

$$\sigma = (4)\,(0.866) \left[\frac{M}{4\left(2N_A\ell\right)^{1/2}} \right]^{2/3} \qquad\qquad (A.5.8)$$

where σ is the mean area per molecule, *M* is the molecular weight, *NA* is Avogadro's number and ρ is the density of the liquid adsorbate. Pore volume per unit mass can be assessed from the maximum uptake by assuming that the nitrogen adsorbed on the surface at 77 K will have the same density as liquid nitrogen.

A.5.4. Atomistic simulations for the determination of the adsorption properties.

A.5.4.1. Computational method details.

Force–field based Grand Canonical Monte Carlo (GCMC) simulations of single component (N_2, CO_2 and H_2) adsorption were carried out using the SORPTION module included in the Accelrys "Materials Studio" package.[193] The theoretical background of GCMC simulations is described in detail elsewhere.[194] For comparison with experimental data, simulations of single–component isotherms were carried out under the same conditions for each adsorbate (P < 1 bar; N_2 at 77 K, CO_2 at 196, 273, and 298 K; H_2 at 77K). The simulations of adsorption isotherms involved 4 million equilibration steps and 6 million production steps.

A.5.4.2. Models of fluid molecules

In all simulations, dispersive and electrostatic interactions were taken into account. Dispersive interactions were modelled using a Lennard–Jones 12–6 potential. Parameters to represent the interaction between different atom types were calculated using Lorentz–Berthelot mixing rules. A cutoff radius of 12.5 Å was employed for dispersive interactions. Electrostatic interactions were modelled by assigning point charges to the atomic sites, and an Ewald summation was used to account for the periodicity of the simulation box. The representation of the models and parameters used for the fluid molecules are gathered in Figure A.5.2 and Table A.5.l, respectively.

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[193] *Materials Studio v. 5.5*; Accelrys Inc. 2011.
[194] (a) Allen, M. P.; Tildesley, D. J. *Computer simulation of liquids*, 1987. (b) Frenkel, D.; Smit, B. *Understanding molecular simulation: from algorithms to applications*, 2002.
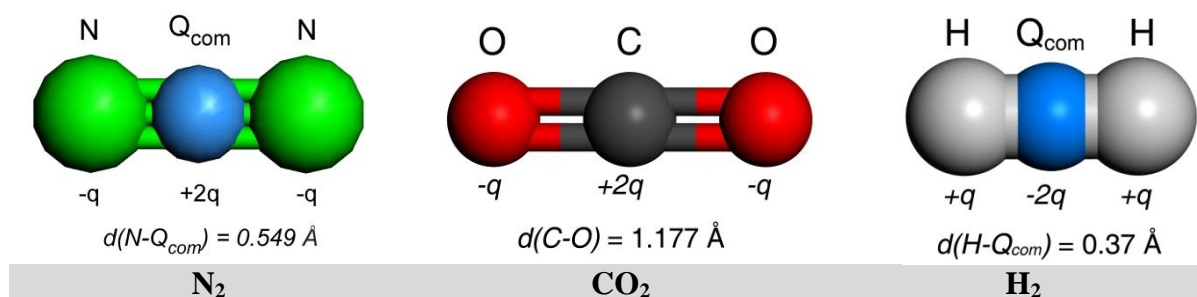
Figure A.5.2. Models for N_2, CO_2 and H_2.

The selection of the models and parameters used to define the fluid molecules have been done based on previous studies. For the N2 molecule, the LJ parameters were taken from the TraPPE model.[195] This model simulates the quadrupolar moment of the N2, placing two negative charges (–0.482) in the positions of the nitrogen atoms and a positive one in the centre of mass (+0.964). The LJ parameters used to represent the CO2 interactions were taken from the work of García–Sánchez and coworkers,[196] and consist of a modified version of the TraPPE potential model. The combination of these parameters with the distribution of the charges calculated in a previous work has proved to be suitably adjusted to experimental data of different MOFs.[197]

Table A.5.1. Lennard–Jones parameters and point charges.

	r_0 / Å	D_0 / kJ mol^{-1}	q / e
N_2			
N	3.7153	0.2993	−0.482
Q_{com}	—	—	+0.964
CO_2			
C	3.0811	0.2444	+0.5810
O	3.3865	0.7121	−0.2905
H_2(77K)			
H	3.4394	2.0503	—
H_2(298K)			
H	—	—	−0.4705
Q_{com}	3.3225	0.2844	−0.9410
CO			
C	—	—	−0.75
Q_{com}	4.2238	0.8330	1.60
O	—	—	−0.85

[195] Potoff, J. J.; Siepmann, J. I. *AlChE J.* **2001**, *47*, 1676.
[196] García–Sánchez, A. et al. *J. Phys. Chem. C,* **2009**, *113*, 8814
[197] Fischer, M. et al. *Chem. Phys. Chem.* **2010**, *11*, 2220.

A.5.4.3. Details on GCMC calculations

Calculation details: Force–field based GCMC simulations of N_2 and CO_2 were carried out using the SORPTION module included in the Accelrys "Materials Studio" package.[198] The theoretical background of GCMC simulations is described in detail many artilces.[199] The selection of the models and parameters used to define the fluid molecules have been done based on previous studies. For the N_2 molecule, the LJ parameters were taken from the TraPPE model.[195] This model simulates the quadrupolar moment of the N_2, placing two negative charges (–0.482) in the positions of the nitrogen atoms and a positive one in the center of mass (+0.964). The LJ parameters used to represent the CO_2 interactions were taken from the work of García–Sánchez and coworkers[200] and consist of a modified version of the TraPPE potential model. The structure of ***CUADECL–B (SMOF–1).***, ***CUADEBR–A (SMOF–2)*** and ***CUADECL–C (SMOF–3)*** was taken from experimental data, for which all solvent molecules were removed. GCMC calculations were performed using 2x2x2–supercells. The LJ parameters for all the atoms of the adsorbents were taken from the Universal Force Field (UFF).[201] The partial charges to represent the electrostatic potential inside the pores were derived from DFT calculations, using the ESP method as described by Singh and Kollman,[202] which is implemented in the DMOL3 code.[203] For this calculation the DNP basis set and the PBE exchange–correlation functional were selected[204] and a dinuclear entity was used the finite cluster model.

Table A.5.2: Lennard–Jones parameters and partial charges

	r_0 / Å	D_0 / kJ mol^{-1}	q / e
N_2			
N	3.7153	0.2993	–0.482
Q_{com}	—	—	+0.964
CO_2			
C	3.0811	0.2444	+0.5810
O	3.3865	0.7121	–0.2905

[198] Materials studio version 5.5, **2011**, Accelrys Inc., San Diego,

[199] (a) Allen, M. P.; Tildesley, D. J. *Computer simulation of liquids*, Clarendon Press, Oxford, UK, 1st edn, 1987. (b) Frenkel, D.; Smit, B. *Understanding molecular simulation: from algorithms to applications*, Academic Press, San Diego, California, USA, 2nd edn. 2002.

[200] García–Sánchez, A. et al. *J. Phys. Chem. C*, **2009**, *113*, 8814.

[201] Rappe, A. K. et al. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

[202] Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129.

[203] (a) Delley, B. J. *Chem. Phys.* **1990**, *92*, 508. (b) Delley, B. J. *Chem. Phys.* **2000**, *113*, 7756.

[204] Perdew, J. P. et al. *Phys. Rev. Lett.* **1996**, *77*, 3865.

Table A.5.3: Resulting ESP charges upon the atoms of the structural models of the *CUADECL–B (SMOF–1)*, *CUADEBR–A (SMOF–2)*, *CUADECL–C (SMOF–3)* adsorbents.

Atom	q / e	Atom	q / e
CUADECL–B (SMOF–1)			
Cu	+0.7570	H61	+0.485
N1	−0.6520	H62	+0.497
C2	+0.5300	N7	−0.105
H2	+0.0620	H7	+0.134
N3	−0.6500	C8	+0.079
C4	+0.719	H8	+0.158
C5	−0.477	N9	−0.442
N6	−0.994	Cl1	−0.536
		Cl2	−1.000
CUADEBR–A (SMOF–2)			
Cu1	+0.451	H61	+0.340
N1	−0.289	H62	+0.336
C2	+0.089	N7	−0.357
H2	+0.265	H7	+0.309
N3	−0.454	C8	+0.142
C4	+0.392	H8	+0.245
C5	+0.140	N9	−0.373
N6	−0.550	Br1	−0.576
		Br2	−1.000
CUADECL–C (SMOF–3)			
Cu1	+0.638	H61	+0.491
N1	−0.730	H62	+0.489
C2	+0.645	N7	−0.018
H2	+0.027	H7	+0.297
N3	−0.813	C8	−0.008
C4	+1.010	H8	+0.182
C5	−0.633	N9	−0.497
N6	−1.093	Cl1	−0.467
		Cl2	−0.436
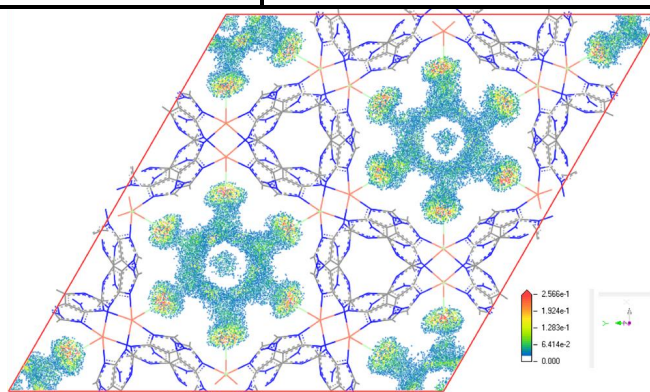
Figure A.5.3: Average occupation profiles for CO_2 at 298 K in *CUADECL–B (SMOF–1)*.

A6: ARTICLES PUBLISHED FROM THIS WORK

This work has led to the publication of several articles in international scientific journals which are listed below:

1. *Porous supramolecular compound based on paddle–wheel shaped copper(II)–adenine dinuclear entities*. Thomas–Gipson, J.; Beobide, G.; Castillo, O.; Cepeda, J.; Luque, A.; Perez–Yañez, S.; Aguayo, A. T.; Roman, P. *CrystEngComm.* **2011**, *13*, 3301–3305.

2. *Metal–carboxylato–nucleobase systems: From supramolecular assemblies to 3D porous materials*. Beobide, G.; Castillo, O.; Cepeda, J.; Luque, A.; Pérez–Yáñez, S.; Román, P.; Thomas–Gipson, J.: *Coord. Chem. Rev.* **2013**, *257*, 2716–273.

3. *Paddle–wheel shaped copper (II) adenine discrete entities as supramolecular building blocks to afford porous supramolecular metal–organic frameworks*. Thomas–Gipson, J.; Beobide, G.; Castillo, O.; Fröba, M.; Hoffmann, F.; Luque, A.; Pérez–Yáñez, S.; Román, P. *Cryst. Growth Des.* **2014**, *14*, 4019–4029.

4. *Unravelling the growth of supramolecular metal–organic frameworks based on metal–nucleobase entities*. Thomas–Gipson, J.; Pérez–Aguirre, R.; Beobide, G.; Castillo, O.; Luque, A.; Perez–Yañez, S.; Roman, P. *Cryst. Growth Des.* **2015**, *15*, 975–983.

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COMMUNICATION

Porous supramolecular compound based on paddle-wheel shaped copper(II)–adenine dinuclear entities†

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The reaction between $CuCl_2$ and adenine in a non-aqueous solvent provides a 3D porous structure based on paddle-wheel [$Cu_2(\mu$-adenine)$_4Cl_2$]$^{2+}$ cations and Cl^- anions that are held together by a robust supramolecular hydrogen bonding network. The desolvated compound is able to host different guest molecules within the ∼6 Å diameter 1D channels.

Crystal engineering comprises an understanding of intermolecular interactions that govern crystal packing.[1] Unfortunately, most of the supramolecular networks based on these non-covalent interactions lack the necessary stability required for many potential applications.[2] The ability to create permanent pores in supramolecular solids is considered as one of the biggest challenges in crystal engineering.[3] Usually, formation of a porous solid requires that the network sustaining interactions are of sufficient strength to pay the energetic penalty for existence of the pores themselves.[4] On the other hand, for these porous supramolecular frameworks to have technological relevance in gas storage, separation, catalysis or for the development of smart materials by combining other functionalities,[5] it is highly desired to be thermally stable and robust enough to retain the porous structure even after the removal of guest molecules.[6] There are few examples of molecular organic compounds that exhibit permanent porosity,[7] but the number of examples of porous molecular crystal structures based on coordination complexes as building units is ever increasing, as the investigations into these molecular based porous materials are an up-and-coming field of research.[8]

At first sight, a reasonable strategy to obtain stable porous crystal structures is to use polynuclear coordination complexes as rigid tectons which can only establish hydrogen bonding interactions along specific directions by means of predictable supramolecular synthons.[9] As a consequence of the rigidity of the tectons, in many cases, the resulting network is unable to occupy the whole space and presents

voids or channels that are usually occupied by solvent molecules. However, there are still many challenges to realize on these tailor-made porous materials because the pursued structural control is often thwarted by the delicate balance of all covalent and noncovalent forces present in the crystal framework, and a slight structural modification may result in the failure to achieve the desired supra-molecular interaction scheme or even the overall three-dimensional (3D) architecture.[10] For example, most of the syntheses methods are performed in aqueous media and the water molecule, a powerful donor and acceptor site of hydrogen bonds,[11] interferes with the desired hydrogen bonding network leading to indirect, water mediated, hydrogen bonds between the tectons affording a non-porous crystal framework. Sometimes the porous 3D structure is achieved but it is thermally unstable because of the well-known flexibility of the hydrogen bond orientation around the water molecules which allows the displacement of the rigid tectons without the rupture of the hydrogen bonds. So that the involvement of water molecules in the supramolecular assembly weakens the stability of the crystal building due to two effects: (a) the water molecules can be easily removed leading to the collapse of the overall crystal structure, as they are involved in the hydrogen bond network and (b) in the case of a hypothetical porous supramolecular network not based on water mediated hydrogen bonds, even the removal of only those solvent molecules placed in the channels may lead to the collapse of the crystal structure due to the flexibility of the remaining hydrogen bonding network.

Taking into account the above-mentioned ideas, we report herein the synthesis‡ and crystal structure§ of a robust supramolecular porous compound of Cu(II) and adenine with the formula [Cu_2-(μ-adenine)$_4Cl_2$]$Cl_2 \cdot \sim 2CH_3OH$ (**1**) which shows a high thermal stability. It has been obtained using methanol as solvent to avoid the instability of the 3D supramolecular architectures due to the presence of crystallization water molecules. Although a handful of covalent 2D and 3D coordination compounds have been reported[12–14] exploiting the ability of the nucleobases to act as polydentated bridging ligands, as far as we are aware, compound **1** represents the first example of a robust porous 3D architecture based on adenine-containing complexes in which the self-assembling of the structural units is only driven by non-covalent interactions.

At room temperature crystals of compound **1** exhibit a blue colour but they undergo a gradual thermochromic transformation to give

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† Electronic supplementary information (ESI) available. CCDC reference numbers 785522 and 785523. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05195d
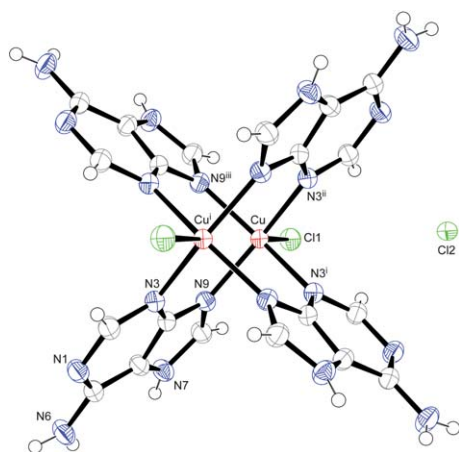
Fig. 1 Structural units of compound **1**.

violet specimens at 100 K. The X-ray analysis at 293 K and 100 K revealed similar crystallographic parameters and the same crystal building so that the thermochromic properties can be probably attributed to subtle changes in the coordination polyhedron around the metallic centre.

The crystal structure is composed of paddle-wheel [Cu₂(μ-adenine)₄Cl₂]²⁺ complexes, chloride counterions, and disordered methanol molecules. Fig. 1 shows a perspective view of the dimeric entity together with the labelling scheme which is conventionally accepted for the adenine nucleobase for chemical and biological purposes. Four bridging adenine molecules are linked to the copper(II) atoms through their N3 and N9 nitrogen atoms to provide the core of the paddle-wheel shaped dinuclear entity[15] and two chloride anions occupy the apical positions of the elongated square pyramidal coordination environment of the metal centers. The complex is sited on a 2/m crystallographic position and shows a UUDD conformation, referring the terms U(up) or D(down) to the coordination of each pyrimidinic N3 atoms to the upper or lower metal centre. The structural parameters listed in Table 1 are similar to those reported for dimeric compounds containing μ-κN3:κN9 bridging purine ligands.[15,16]

The shape and structural features of the dimeric cation resemble those reported for the analogous [Cu₂(μ-adenine)₄Cl₂]Cl₂·6H₂O compound obtained using a similar synthesis method but employing

water as solvent.[17] However, the dissimilar features of the solvation molecules afford drastic changes in the resulting crystal framework. In the hydrated compound the interactions between the complex entities are mediated by water molecules to give a non-porous crystal structure maintained by an intricated network of adenine···water and chloride···water interactions. On the contrary, the weaker ability of methanol to establish hydrogen bonds implies that the crystal packing of **1** is essentially sustained by the assembling of the paddle-wheel dimeric [Cu₂(μ-adenine)₄Cl₂]²⁺ entities through rigid direct intermolecular hydrogen bonds between the adenine molecules, without involving the solvent methanol molecules, together with interactions between the chloride anions and the adenine moieties of the cationic complexes providing extra stability and rigidity to the 3D porous supramolecular network and, as a consequence, increasing the robustness of the crystal framework.

As it can be observed in Fig. 2, the dinuclear entities are cross-linked together by pairs of symmetry-related N6–H···N1 hydrogen bonding interactions between the Watson–Crick faces of two adjacent nucleobases to give a $R_2^2(8)$ ring, a well-known structural synthon involved in the supramolecular recognition processes which determines the self-assembling pattern of the adenine moieties to form supramolecular aggregates in a great diversity of metal-nucleobase systems.[13,18] Furthermore, coordination of the adenine through the N9 atom of the imidazole ring produces the proton transfer to the imidazole N7 site to give the non-canonical 7H-adenine tautomer[19] which favours the formation of a hydrogen-bonded $R_2^1(7)$ ring between the Hoogsteen face [N6H, N7H] of the nucleobase as donor and the chloride anion as acceptor.[20] Structural parameters for the supramolecular interactions are listed in Table 2. Each chloride counterion is joined to two adenine ligands from adjacent dimeric complexes to form a distorted tetrahedral hydrogen bonding environment.

The self-assembling process driven by the above-described rigid interactions results in a supramolecular 3D structure (Fig. 3) containing very large channels along the crystallographic c axis with a diameter of 6.3 Å (distance among van der Waals surfaces of

Table 1 Selected bond lengths and angles (Å, deg) for the coordination polyhedron of compound **1**[a]

	100 K	293 K
Cu–N3ⁱ	2.009(2)	2.002(6)
Cu–N9	2.027(2)	2.031(5)
Cu–Cl1	2.445(1)	2.466(3)
Cu···Cuⁱ	3.0761(9)	3.064(2)
N3ⁱ–Cu–N3ⁱⁱ	87.01(13)	86.9(3)
N3ⁱ–Cu–N9ⁱⁱⁱ	161.49(9)	162.5(3)
N3ⁱⁱ–Cu–N9ⁱⁱⁱ	87.45(9)	87.7(2)
N9–Cu–N9ⁱⁱⁱ	92.27(12)	92.5(3)
N3ⁱ–Cu–Cl1	100.57(7)	99.8(2)
N9–Cu–Cl1	97.80(7)	97.5(2)

[a] Symmetry codes: (i) −x + 2/3, −x + y + 1/3, −z + 1/3; (ii) −x + 2/3, −y + 1/3, −z + 1/3; (iii) x, x − y, z.
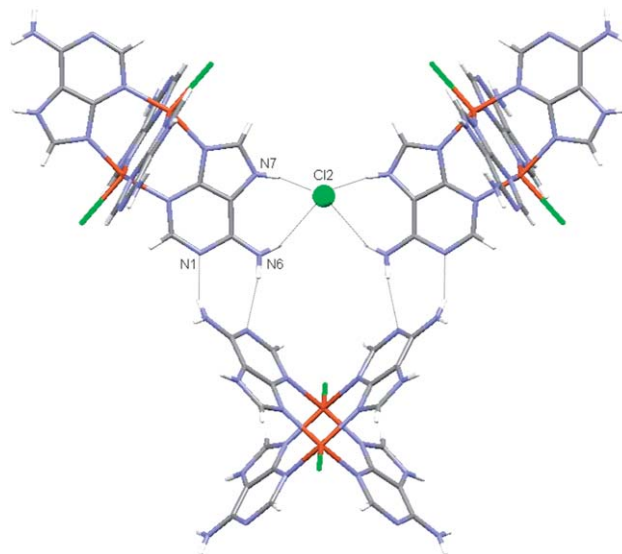
Fig. 2 Details of the adenine···adenine and adenine···chloride interactions in the crystal packing of compound **1**.

Table 2 H-bond parameters (Å, deg) in compound **1**[a]

	H⋯A	D⋯A	D–H⋯A[b]
100 K			
N6–H6A⋯N1[iv]	2.19	3.015(3)	161
N6–H6B⋯Cl2[v]	2.66	3.466(3)	156
N7–H7⋯Cl2[v]	2.24	3.034(2)	154
293 K			
N6–H6A⋯N1[iv]	2.20	3.032(8)	163
N6–H6B⋯Cl2[v]	2.69	3.505(8)	158
N7–H7⋯Cl2[v]	2.23	3.032(7)	156

[a] Symmetry codes: (iv) $x - y$, $-y$, $-z + 1$; (v) y, $-x + y$, $-z$. [b] D: donor and A: acceptor.

opposite chlorine atoms). These channels represent the 36% of the total volume of the unit cell[21] and they are occupied by solvent methanol molecules in a highly disordered manner.

Thermal degradation of compound **1** (see ESI†) starts with an initial well-separated endothermic weight loss of 7.0% from room temperature to 100 °C corresponding to the release of the methanol molecules trapped inside the channels (calcd: 7.3% for two methanol molecules per formula unit). The resulting compound remains stable up to 240 °C and the XRPD patterns at different temperatures (Fig. 4) do not differ substantially from that corresponding to the starting material, suggesting that the 3D open framework is retained after the removal of the methanol molecules. Above this temperature it undergoes successive exothermic processes leading to CuO as final residue above 500 °C.

The thermal stability of the porous 3D crystal structure and the features of its channels, where the coordinated Cl1 chloride atoms are projected inward, suggest that the title compound may provide a suitable opportunity for host–guest interactions in solid-state.[22] In this field, extended metal–organic frameworks containing biological moieties (so-called bio-MOF) are extensively studied to obtain information about a great diversity of molecular recognition processes which play a key role in biological systems,[23] to analyse their efficiency in the selective gas capture,[14] and to advance in the design of artificial systems suitable for the releasing of adsorbed bioactive molecules from the pores at the cellular level.[24]

Fig. 4 Variable-temperature X-ray diffraction powder patterns performed during the thermal degradation of compound **1**.

Preliminary experiments have shown that the desolvated product of compound **1** is able to adsorb in few minutes the humidity of the surrounding atmosphere to fill the empty channels with water molecules undergoing a weight increase of around 8% (*ca.* 4 water molecules per formula unit) and retaining the initial porous crystal structure without substantial changes in the X-ray diffraction powder pattern. Upon heating, the hydrated compound releases again the water molecules which are readsorbed at room temperature. The sample can undergo cycles of sorption and desorption without any loss in capacity or crystallinity. However, a suspension of the compound **1** in water affords an amorphous material after 24 hours. These facts suggest that the title compound is able to accept some amount of water molecules without any remarkable change in its crystal structure, but when the water is used as solvent, it acts as disruptor of the direct hydrogen bonds established between the adenine molecules and, as a consequence, the crystal building collapses.

Compound **1**, following evacuation at 150 °C, was exposed to the vapours of several solvents (methanol, acetone, dichloromethane, tetrachloromethane, and water), as reported for other porous compounds.[25] TGA curves (Fig. 5) show that in all cases the

Fig. 3 Perspective view of the 3D framework along the *c*-axis showing the pores. Solvation methanol molecules are omitted for clarity.
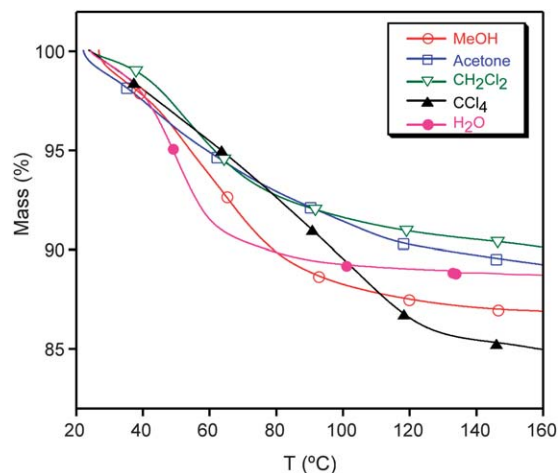
Fig. 5 TGA curves for evacuated compound **1** after exposure to different vapours.

adsorption of the vapour molecules takes place, showing dissimilar mass losses as expected for the different molecular weights and volumes. It is interesting to note that in the case of water and methanol, the amount of guest molecules placed in the channels is greater than that adsorbed in a non-saturated atmosphere of these solvents (for water: 8 and 11%, respectively). For tetrachloromethane and dichloromethane solvents, the TGA data show very different mass loss (15 *vs.* 10%) but the calculated guest molecule amount in the channels is almost the same (~0.5 molecules per dimeric entity), which may suggest a similar anchorage of both guest molecules to the channel surface.

The permanent porosity of the metal–organic framework was also studied by means of N_2 adsorption measurements (see ESI†). Freshly synthesized single crystals of compound **1** were dried under vacuum at 150 °C during 24 h to eliminate solvent guest molecules prior to measurements. The adsorption curve collected at 77 K exhibits features resulting from multilayer adsorption. The fitting of the adsorption area to Langmuir and BET equations leads to surface area values of 30 and 26 m^2 g^{-1}, respectively. These values are substantially smaller than the accessible surface area calculated from the crystal structure (790 m^2 g^{-1}) by a Monte Carlo integration technique where a probe molecule with a diameter equal Lennard-Jones parameter for N_2 (3.681 Å) is "rolled" over the framework.[26] This method has demonstrated to be very appropriate for characterization of microporous metal–organic frameworks fitting rather well the experimental surface areas.[27] Generally, such difference between the experimental surface area and calculated accessible area is attributed to incomplete solvent removal, crystal collapse or a massive presence of impurities. However, the weight loss of the outgassed sample fits the one expected from the compound formula which suggests a quantitative removal of the solvent. Additionally, the XRPD data confirm that the desolvated sample retains its crystal structure and therefore, its bulk porous framework, without any sign of other crystalline phases or amorphous contaminants that may cause the depletion of the surface area. It deserves to note that the minimum pore diameter (6.3 Å) is fairly greater than the molecular and kinetic diameters of N_2 (3.1 and 3.6 Å). This kind of reduced nitrogen adsorption has also been observed in other microporous hydrogen-bonded coordination frameworks (effective pore diameter: 4.0 Å).[28] This behaviour has been attributed to the strong quadrupole interaction between N_2 molecules and the electrostatic-field gradients around the pore window, thus blocking the diffusion of other N_2 molecules into the pores.[29] The relative narrowness of the pore of compound **1** together with the low dimensionality of the pore network (1D channels without connectivity among them) seems to support the latter statement. Another possible explanation is the relative flexibility of the supramolecular structure at the surface that could lead to a temperature induced superficial rearrangement that involves a closure of the pore window.

In conclusion, the adenine molecules in the dimeric units that are rigidly coordinated to the metal centers allow them to establish direct hydrogen bonds only along specific directions, so as to form the rigid supramolecular porous network. In addition to this, the use of methanol instead of water, with very weak hydrogen bonding ability has helped to avoid solvent mediated interactions between the dimeric units. So the robustness of the direct hydrogen bonding interactions between the Watson–Crick edges of the adenine nucleobases in the $[Cu_2(\mu\text{-adenine})_4Cl_2]Cl_2\cdot\sim2CH_3OH$ compound allows crystal framework to maintain its integrity even after the removal of

solvent molecules from the channels. Hence, the use of solvents with weak hydrogen bonding interactions and the resulting absence of solvent mediated interactions can be considered as a good strategy for the synthesis of robust 3D porous metal–organic frameworks sustained only by non-covalent interactions among the building blocks.

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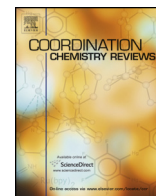
Review

Metal–carboxylato–nucleobase systems: From supramolecular assemblies to 3D porous materials

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ABSTRACT

A complete overview of the preparation of metal–carboxylato–nucleobase architectures that range from supramolecular assemblies to 3D porous materials is reported. The basic building units of these materials consist of metal–nucleobase fragments which link together through coordination bonding or by means of supramolecular assembling among the nucleobases anchored to metal centres. In the case of extended systems based on coordination bonds, the connectivity among the metal centres can be achieved through bridging nucleobases and/or by auxiliary organic linkers such as carboxylate and dicarboxylate anions. The latter bridging mode confers to the nucleobases a greater capacity to involve in molecular recognition processes with other biologically relevant species by means of the establishment of non-covalent inter-actions such as hydrogen bonding and/or π–π stacking among aromatic groups. On the other hand, the geometrical rigidity imposed by several metal–nucleobase fragments and the base pairing interactions through complementary hydrogen bonding, lead to structural restraints that preclude an effective filling of the space, and as a consequence, it favours the growth of tailor-made open-frameworks based either on coordination bonds (MBioFs) or on non-covalent interactions (*supra*MBioFs).

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1. Introduction

Metal-organic frameworks (MOFs) encompass an area of chemistry that has experienced awesome growth during the last decades, as indicated by not only the sheer number of research
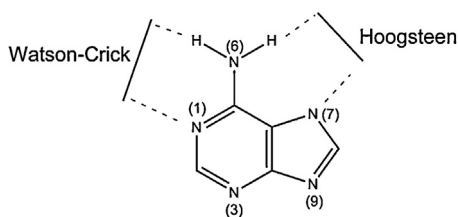
Scheme 1. Adenine nucleobase showing the numbering scheme and the Watson–Crick and Hoogsteen faces.

papers published but also the ever-expanding scope of the research [1]. The combination of the metallic nodes and the linkers provides endless possibilities, so that the judicious selection of the metal atom and the ligands employed, together with the coordination features of both, allows rational design of the resulting compounds and, therefore, their physical and chemical properties can be tuned at will. However, many applications of the MOFs require them to be both biologically and environmentally compatible. In this sense, the biomolecules are suitable to act as building units in the formation of metal-biomolecule frameworks, called MBioFs or BioMOFs. This kind of building block offers several advantages as stated by Maspoch et al.: (i) biomolecules are easily and naturally available, so they can be used to prepare bulk quantities of materials at amenable prices, (ii) biomolecules can lead to biologically compatible MOFs, (iii) biomolecules are structurally diverse, (iv) biomolecules can have many different metal binding sites, (v) many of them have intrinsic self-assembly properties, (vi) some of them are chiral [2].

Among the variety of biomolecules we have focused our research work in the use of nucleobases. Nucleobases are suitable ligands for the construction of MBioFs since they present several heteroatoms allowing them acting as multidentate organic ligands, as well as being able to establish large hydrogen bonding networks. The nucleobase most employed in these kinds of compound is adenine (Scheme 1), which presents five nitrogen atoms that allow a variety of coordination modes, and further, its non coordinated positions remain accessible to interact through hydrogen bonds with other structural units, especially, the Watson–Crick (N1, N6H) and Hoogsteen (N7, N6H) faces. The acid–base balance of the adenine molecule also makes it usable as a cationic, neutral or anionic species [3].

In this review we summarize the preparation of metal–carboxylato–nucleobase architectures that range from supramolecular assemblies to 3D porous materials. In particular, we have focused on the chances that the paddle-wheel shaped SBU (Secondary Building Unit) gives for the construction of porous compounds, based on the synthetic control over the three dicopper paddle-wheel entities built up from the adenine nucleobase and carboxylato ligands. The geometrical rigidity imposed by these fragments and the base pairing interactions through complementary hydrogen bonding, lead to structural restraints that preclude an effective filling of the space, and as a consequence, it favours the growth of tailor-made open-frameworks based either on coordination bonds (MBioFs) or on non-covalent interactions (supraMBioFs).

2. Paddle-wheel shaped secondary building units

The design of coordination frameworks via deliberate selection of metals and multifunctional ligands, including biologically relevant molecules such as nucleobases [3], is one of the most attractive topical areas of chemistry due to the fascinating structural diversity and the development as new materials with tunable properties [4]. An essential part of coordination polymer design, and of the
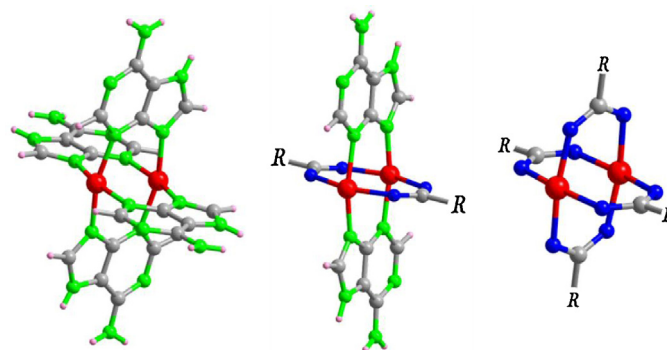
Fig. 1. Paddle-wheel entities for the metal/carboxylato/adenine system. Reproduced from Ref. [37]. Copyright (2012) American Chemical Society.

wider field of crystal engineering, is the use of building blocks that combine the flexibility and the necessary interconnection capability to achieve the required dimensionality, but also enough strength to permit a predictable core which maintains its structural integrity throughout the construction of the solid. In this sense, $[M_2(\mu\text{-}L)_4X_2]$ entities have been known for a long time since the crystal structure of the $[Cu_2(\mu\text{-acetato})_4(H_2O)_2]$ compound was reported [5]. The attractiveness of the paddle-wheel (PW) motif is that structural and functional changes can be achieved, almost at will, by simply varying the metal cores, the bridging moieties, or the apical X-ligands [6]. This functional versatility of the dinuclear PW motifs makes them particularly suitable as secondary building units (SBUs) for the design and synthesis of numerous crystalline materials ranging from zero-dimensional (0D) species to three-dimensional (3D) coordination polymers with interesting properties in areas such as magnetism, medicine, catalysis, and gas storage [4,7,8].

2.1. Composition control

The nitrogen donor atoms disposition of the adenine molecule makes possible to replace carboxylate bridging ligands of the $[Cu_2(\mu\text{-carboxylato})_4]$ dimeric entity retaining the paddle-wheel shaped morphology of the dinuclear unit. Apart from that, it is possible to obtain synthetic control over the three dicopper paddle-wheel entities built up from the adenine nucleobase and carboxylato ligands (Fig. 1).

The first building unit, $[M_2(\mu\text{-adenine})_4]$, in which the metal centres are bridged by the adenine nucleobase acting as N3,N9-bridging ligand, is obtained in the absence of the carboxylic ligand in the reaction media. The second one, $[M_2(\mu\text{-adenine})_2(\mu\text{-carboxylato})_2]$, appears with the simultaneous presence of adenine and carboxylic acid in the reaction media. The last one, $[M_2(\mu\text{-carboxylato})_4]$, where the metal centres are bridged exclusively by carboxylato ligands, is obtained in the absence of adenine or when the nucleobase is functionalized in the N3 or N9 positions.

2.2. Magnetic properties

It is well known that non-linear OCO or NCN bridges cause antiferromagnetic coupling with J values ranging from -210 to $-320\,\text{cm}^{-1}$ [9] and -250 to $-325\,\text{cm}^{-1}$ [9a,10], respectively. However, the coexistence of these two types of bridges requires a more exhaustive analysis than when there is only one type. In fact, when the bridging ligands are different, the two bridges may either add or counterbalance their effects. This problem has been treated by Nishida and Kida [11] and McKee et al. [12], and these phenomena are known as orbital complementarity and countercomplementarity, respectively. In the case of $[M_2(\mu\text{-adenine})_2(\mu\text{-carboxylato})_2]$,
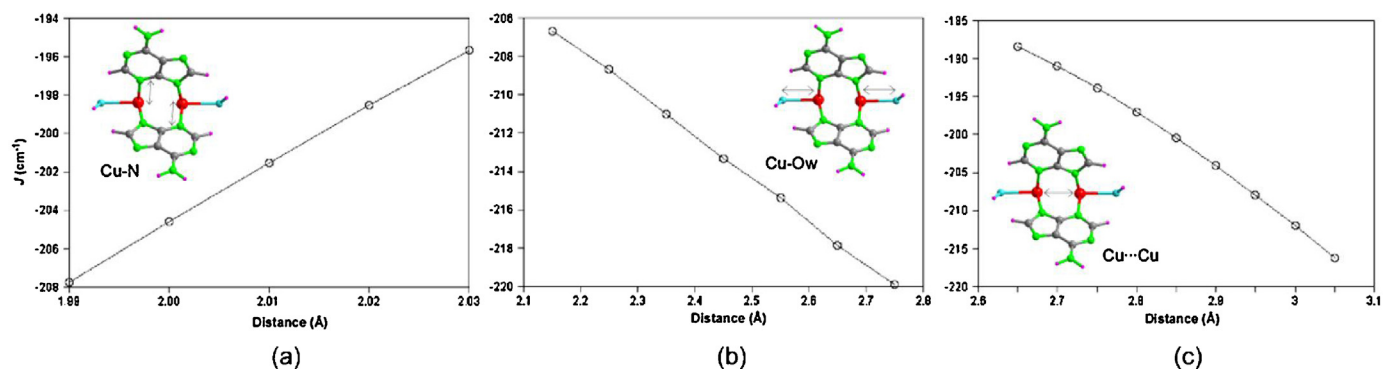
Fig. 2. Variation in the magnetic coupling constant value as a function of (a) the Cu—N bond equatorial distance, (b) the Cu—Ow bond axial distance and (c) the Cu···Cu distance.
Reproduced from Ref. [10b]. Copyright (2009) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the splitting order of the molecular magnetic orbitals is the same for each type of bridging ligand leading as a consequence to J values intermediate between the values found for the nonmixed paddle-wheels (Scheme 2).

Moreover, our research group reported, based on DFT calculations, that for $[Cu_2(\mu\text{-adenine})_4]$ entities the magnitude of the antiferromagnetic coupling is governed by both structural and chemical parameters [10b]. Three main structural parameters were considered: copper–nitrogen, copper–water molecule and copper···copper distances (Fig. 2). The decrease in the Cu–N distances favours the interaction between the magnetic orbitals of the metal and the ligands and reinforces the antiferromagnetism. On the contrary, a shorter Cu–Ow distance brings a decrease in the antiferromagnetism as a result of the increase in the dz^2 character of the magnetic orbitals (decreasing the $dx^2–y^2$ character), as previously reported by Sonnenfroh and Kreilick [10a]. In contrast, longer metal···metal distances cause an increase in the antiferromagnetic interactions. To explain this latter behaviour, it is necessary to pay attention to the orbitals of the bridging ligand, whose lobes positioned on the N3 and N9 atoms further overlap in the vicinity of the central carbon atom as the copper···copper distance increases. Consequently, the energy difference between the resulting magnetic orbitals is enhanced (Scheme 3). As the effect of these structural parameters on the magnetic coupling is of the same order of magnitude, any attempt to obtain experimental magnetostructural correlations on the basis of just one parameter is precluded.
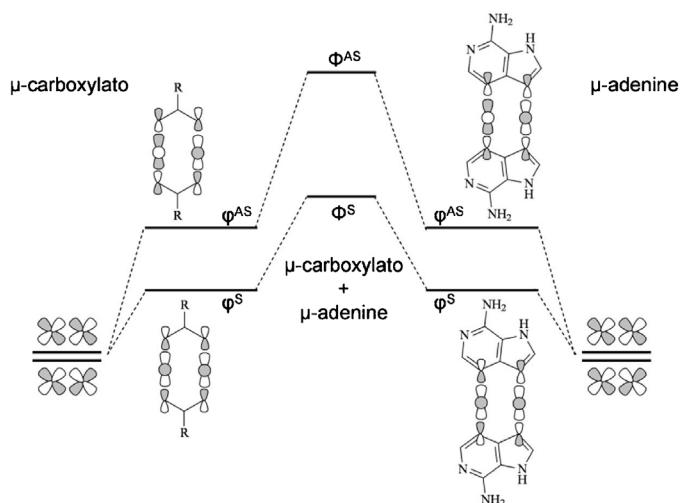
A similar trend is also observed for $[Cu_2(\mu\text{-carboxylato})_4]$ entities [10c].

The charge of the bridging ligand and its substituents also play an important role in the magnitude of the antiferromagnetic interaction. DFT calculations for different models maintaining the same structural parameters but modifying the bridging ligand by adding different substituents in the C6-position left to antiferromagnetic J values with the following relative order: 7H-adenine > 7H-hypoxanthine > 6-chloro-7H-purine > adeninato > hypoxanthinato > 6-chloropurinato (Scheme 4). This order can be related to the increase in the number of electron lone pairs in the bridging ligand (by means of the deprotonation or by substitution of the exocyclic amine group by a chlorine atom). This fact increases the extension of the molecular orbitals of the bridging ligands and the N3 and N9 atoms contribute to a lesser extent, so they overlap less efficiently with the metal-centred magnetic orbitals and a weaker antiferromagnetic interaction is observed.

2.3. Polymerization strategies

Any of the previously stated paddle-wheel shaped dimeric entities can further polymerize to obtain extended systems. There are two main options to achieve this purpose: to make use of polycarboxylato ligands that are able to connect the PW motifs through the equatorial positions and/or to make use of the axial positions of the PW motifs (Fig. 3).

The latter option is not always available because of the steric hindrance exerted by the equatorial ligands over the axial position. Taking into account the van der Waals radii, we have carried out a simple estimation of the closest axial-approach of a pyridine ligand to assess the accessibility of the axial position of each PW motif (Fig. 4). The results indicate that the axial positions are only available for bulky ligands (such as pyridine and other

Scheme 2. Orbital complementarity of the μ-carboxylato-κO:$\kappa O'$ and μ-adenine-$\kappa N3$:$\kappa N9$ bridging ligands.
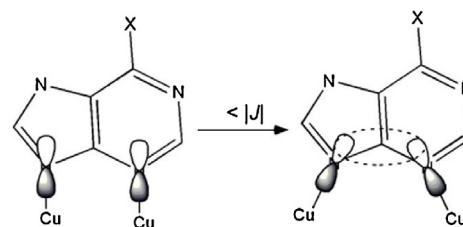
Scheme 3. Increase in the magnetic coupling constant as a result of a greater overlap around the central carbon atom.
Reproduced from Ref. [10b]. Copyright (2009) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
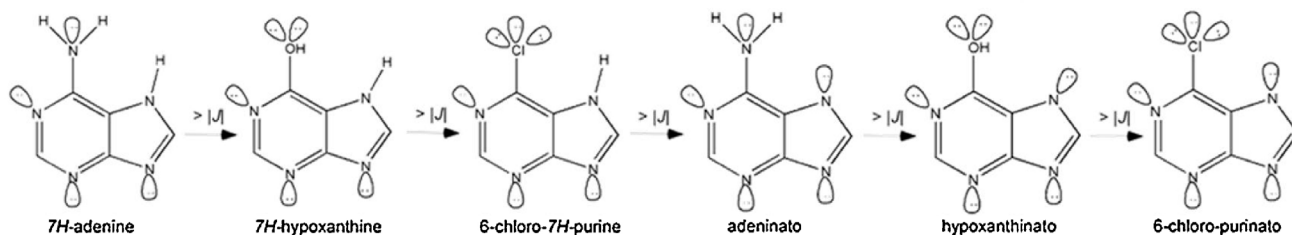
Scheme 4. Calculated order of the bridging ligands according to their ability to transmit magnetic interactions by the superexchange pathway. Reproduced from Ref. [10b]. Copyright (2009) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

aromatic amines) in the case of $[M_2(\mu\text{-adenine})_2(\mu\text{-carboxylato})_2]$ and $[M_2(\mu\text{-carboxylato})_4]$ entities. The $[M_2(\mu\text{-adenine})_4]$ moiety only allows the coordination to the axial positions of small molecules or ions, such as water molecules or halides but not of more sterically hindered molecules.

In this way, the polymerization of the $[M_2(\mu\text{-adenine})_4]$ entity is promoted by means of the deprotonation of the nucleobase, but since the coordination of an adjacent PW entity to the axial position is forbidden, the presence of a second less hindered metal centre becomes requisite for the polymerization.

With the well-known $[M_2(\mu\text{-carboxylato})_4]$ entities, the resulting crystal structure can be directed by means of the correct selection of the polycarboxylato ligand towards a great variety of architectures ranging from polynuclear discrete entities to 3D

Fig. 4. Accessibility of the axial position of each PW motif for aromatic amines. Reproduced from Ref. [37]. Copyright (2012) American Chemical Society.

crystal structures [13]. In these entities, the axial positions, usually occupied by solvent molecules, can be replaced by nucleobase ligands, thus increasing the ability of the systems to establish molecular recognition processes.

In the $[M_2(\mu\text{-adenine})_2(\mu\text{-carboxylato})_2]$ unit, both approaches are possible: (i) polymerization through the deprotonation of the nucleobase and its further coordination, and (ii) polymerization by using polycarboxylato ligands.

3. $[Cu_2(\mu\text{-adenine})_4]$ secondary building unit

The first crystal-structure containing a $[Cu_2(\mu\text{-adenine})_4]$ unit was reported by de Meester and Skapski in 1971: $[Cu_2(\mu\text{-adenine})_4Cl_2]Cl_2\cdot6H_2O$ [14]. A few years later the crystal structure of the analogous perchlorate compound was published: $[Cu_2(\mu\text{-adenine})_4(OH_2)_2](ClO_4)_4\cdot2H_2O$ [15]. In both compounds the adenine molecule remains neutral. However, early studies of Sletten showed the possibility of obtaining the same dimeric unit based on deprotonated adenine: $[Cu_2(\mu\text{-adeninato})_4(OH_2)_2]\cdot5H_2O$, but

Fig. 3. Different polymerization strategies for paddle-wheel shaped entities: (a) through the equatorial positions, (b) through the axial ones and (c) through both of them.
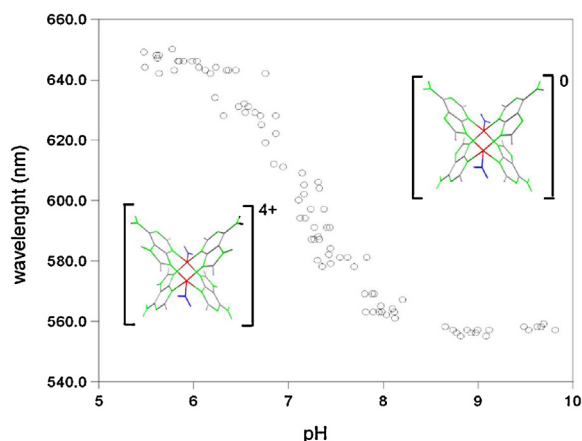
Fig. 5. Position of the absorbance maximum at different pH values for $[Cu_2(\mu\text{-}adenine/adeninate)_4]$.

the author was not aware of its potential to obtain extended frameworks [16]. This work remained more or less forgotten as its coordinate data are not available in the Cambridge Structural Database (CSD) [17] and the assigned structure scheme is also incorrect. Since then, there was no further evidence to decide if the paddle wheel shaped entity would retain its structure upon the deprotonation of the adenine, until the structures of $\{[Cu_2(\mu\text{-}adeninato)_4(H_2O)_2][Cu(ox)(H_2O)]_2\}_n$ and $[Cu_2(\mu\text{-}adeninato)_4(OH_2)_2]\cdot7H_2O$ were reported. These confirmed that the dimeric entity was robust enough to allow the deprotonation of the adenine and offering the opportunities to use it as a secondary building unit (SBU) [18,19].

UV–vis spectroscopy was employed to obtain information on the acid–base behaviour of the $[Cu_2(\mu\text{-}adenine)_4(H_2O)_2]^{4+}$ dimeric entity, because the acid–base balance of the neat adenine molecule ($pK_{a1} = 4.2$ and $pK_{a2} = 9.8$) is affected by its coordination to the metal centres. The dimeric entity in its cationic form (with adenine ligands) shows a characteristic band at 650 nm which is displaced towards shorter wavelengths as the pH increases reaching values close to 555 nm. This fact is indicative of the deprotonation of the adenine ligand. Fig. 5 shows two plateaux, the first one corresponding with the predominance of the cationic $[Cu_2(\mu\text{-}adenine)_4(H_2O)_2]^{4+}$ at pH values below 6 and the second one corresponding with the neutral $[Cu_2(\mu\text{-}adeninato)_4(H_2O)_2]$ at pH values above 9. It can be inferred from the graph that the pK_a value is shifted to a value around 7.2–7.4. There is no evidence of an intermediate species.

Naturally, this information about the pH speciation is crucial in order to fix the synthetic conditions appropriate for the polymerization of the dimeric entities.

3.1. Porous MBioFs based on $[Cu_2(\mu\text{-}adenine)_4]$ units

As previously stated the paddle wheel $[Cu_2(\mu\text{-}adenine)_4]$ units can be polymerized by establishing new coordination bonds to obtain extended systems. For this purpose we need to deprotonate the adenine ligand in order to increase its coordinative capacity. However, the steric hindrance that the four adenine bridging molecules set at the apical positions, requires the presence of a less sterically hindered second node for the polymerization to proceed. The first polymeric compound of this type was reported by us in 2004. It consists of a 3D coordination polymer with formula $\{[Cu_2(\mu\text{-}adeninato)_4(H_2O)_2][Cu(ox)(H_2O)]_2\}_n$ containing the adenine nucleobase as an anionic $N3,N7,N9$-bridging ligand. The deprotonation of the adenine at the reaction media promotes the polymerization of the framework by sequentially bridging $[Cu_2(\mu\text{-}adeninato)_4]$ units through the less sterically hindered $[Cu(ox)(H_2O)]$ units (Fig. 6). The resulting structure contains one-dimensional (1D) tubular channels with a diameter of about 13 Å and that represent around a 40% of the total volume [18].

The same strategy was employed later on by Niclós-Gutiérrez et al. to obtain a discrete hexanuclear complex of formula $\{[(H_2O)_2Cu_2(\mu\text{-}adeninato)_4][Cu(oda)(H_2O)_4]_2\}\cdot6H_2O$ (oda: oxydiacetato(2-)ligand) [19]. In these two examples the adenine adopts a $\mu_3\text{-}N3,N7,N9$ bridging tridentate mode that it is reinforced by a simultaneous hydrogen bonding interaction of the exocyclic amino group. There are many examples of this kind of reinforcement in the coordination chemistry of the nucleobases [20]. The magnetic behaviour of this compound is dominated by the intradimer exchange pathway that provides strong antiferromagnetic coupling as previously mentioned. The references show that the interdimeric exchange pathway through the imidazolic ring provides very weak antiferromagnetic coupling between the Cu(II) ions [20b,21].

3.2. Porous supraMBioFs based on $[Cu_2(\mu\text{-}adenine)_4]$ units

The neutral adenine presents a well-known capacity to establish strong complementary hydrogen bonding interactions that can lead to generation of robust supramolecular porous materials. In fact, the Watson–Crick and Hoogsteen faces of the adenine ligands are accessible in the $[Cu_2(\mu\text{-}adenine)_4]$ units opening a new way to polymerize the dimeric entities just by means of non-covalent interactions. At first sight, a reasonable strategy to obtain stable porous crystal structures is to use discrete mononuclear or polynuclear coordination complexes as rigid tectons which can only establish hydrogen bonding interactions along specific directions by means of predictable supramolecular synthons [22]. As a consequence of the rigidity of the tectons, in many cases, the resulting network is unable to occupy the whole space and presents
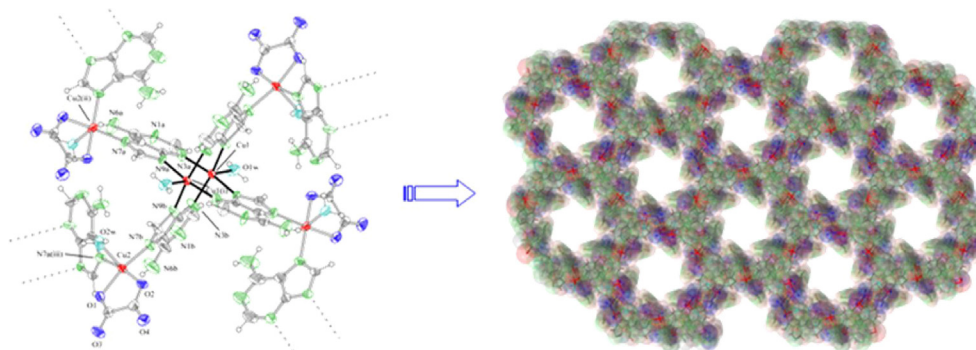
Fig. 6. Crystal structure of compound $\{[Cu_2(\mu\text{-}adeninato)_4(H_2O)_2][Cu(ox)(H_2O)]_2\}_n$ [18].
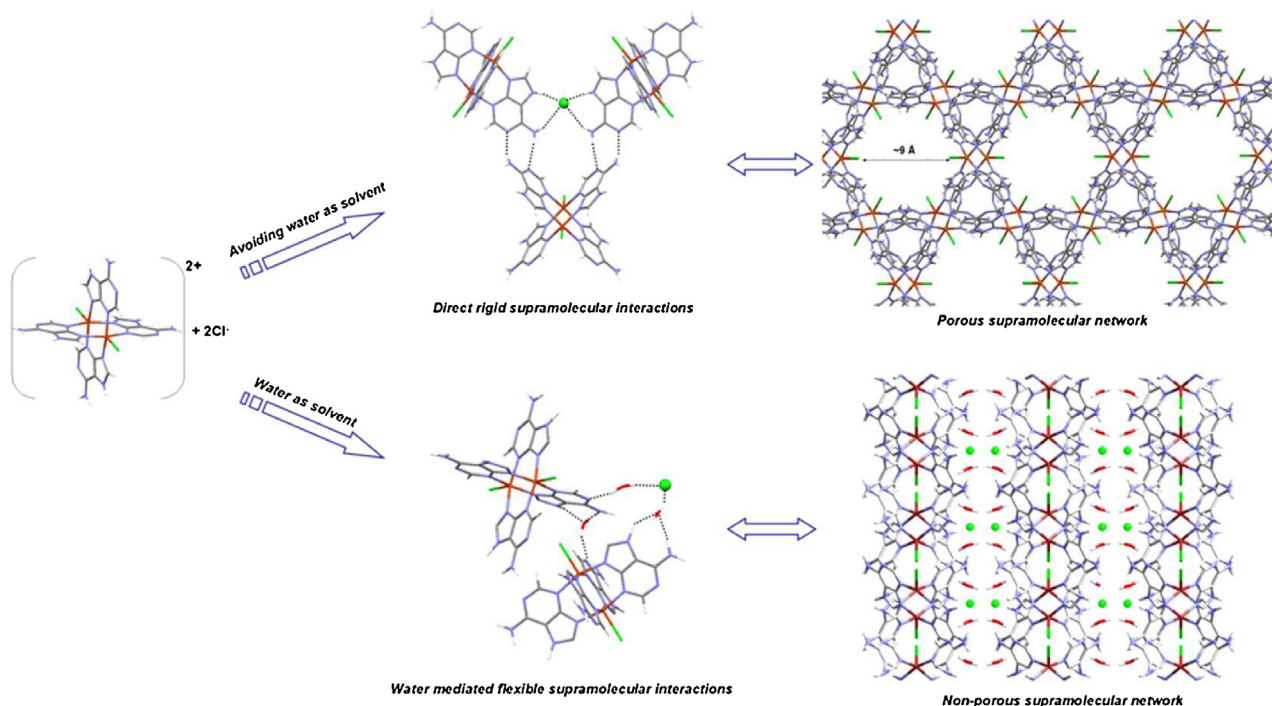
Fig. 7. Solvent influence on the crystal packing of [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$ [14,24].

voids or channels that are usually occupied by solvent molecules. However, there are still many challenges to realize on these tailor-made porous materials because the pursued structural control is often thwarted by the delicate balance of all covalent and nonco-valent forces present in the crystal building, and a slight change in the synthetic approach may result in the failure to achieve the desired supramolecular interaction scheme and thus, in the overall three-dimensional architecture [23].

Proceeding in this way, we obtained a robust supramolecular porous compound of Cu(II) and adenine with the formula [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·∼2CH$_3$OH which shows a high thermal stability (stable up to 220 °C) [24]. De Meester and Skapski reported many years ago, a similar but non-porous compound crystallized in water: [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·6H$_2$O [14]. The apparently striking difference is due to hydrogen bonding characteristics of the water molecule, a powerful donor and acceptor site of hydrogen bonds [25]. It therefore can interfere, as is the case, with the predicted hydrogen bonding network leading to indirect, water mediated, hydrogen bonds between the tectons that produces the crystal structure collapse upon their removal (Fig. 7).

The weaker ability of methanol to establish hydrogen bonds implies that the crystal packing of the supramolecular porous compound [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·∼2CH$_3$OH, is essentially com-manded by the assembling of the windmill dimeric [Cu$_2$(μ-adenine)$_4$Cl$_2$]$^{2+}$ entities through rigid direct hydrogen bonding pairing interactions between the adenine molecules. Moreover, interactions between the chloride anions and the adenine moieties of the cationic complexes provide extra stability and rigidity to the 3D porous supramolecular network and, as a consequence, increase the robustness of the crystal building. The dinuclear entities are cross-linked together by pairs of symmetry-related N6—H···N1 hydrogen bonding interactions between the Watson–Crick faces of two adjacent nucleobases to give a R$_2^2$(8) ring, a well-known structural synthon involved in the supramolecular recognition pro-cesses which determines the self-assembling pattern of the adenine moieties in a great diversity of metal–nucleobase systems [26]. Fur-thermore, coordination of the adenine through the N9 atom of the

pyridine ring produces the proton transfer to the imidazole N7 site to give the non-canonical *7H*-adenine tautomer which favours the formation of a hydrogen-bonded R$_2^1$(7) ring between the Hoog-steen face [N6H, N7H] of the nucleobase as donor and the chloride counterion as acceptor in such a way that each counterion is joined to two adenine ligands from adjacent dimeric complexes.

The self-assembling process driven by the rigid interactions described above, results in a supramolecular 3D structure contain-ing 1D cylindrical channels along the crystallographic c axis with a diameter of ∼9 Å, that are occupied by the solvent molecules and that represent 36% of the total volume. This supramolecular net-work remains stable after the release of the methanol molecules and only collapses at temperatures above 240 °C. The compound is also stable against the surrounding humidity and only when immersed in water for several hours, does the crystal structure collapse leading to an amorphous material. This fact is also fur-ther evidence of the direct adenine–adenine hydrogen bonding disruptor effect of the water molecules. The permanent porosity of this material was ensured by the adsorption of several vapour molecules, finding that almost 0.5 molecules of dichloromethane and tetrachloromethane were adsorbed per dimeric entity. How-ever, the N$_2$ adsorption isotherm measurements at 77 K showed very low adsorption capability and accessible surface area, just 3% of what would be expected (790 m^2 g^{-1}). This kind of reduced nitrogen adsorption has also been observed in other microporous hydrogen-bonded coordination frameworks [27]. This behaviour has been attributed to the strong quadrupole interaction between N$_2$ molecules and the electrostatic-field gradients around the pore window, thus blocking the diffusion of other N$_2$ molecules into the pores [28]. However, another possible explanation is the rel-ative flexibility of the supramolecular structure at the surface that could lead to a temperature or humidity induced superficial rearrangement that involves a closure of the pore window. In fact, a recent paper of Matzger et al. proves, by means of positron anni-hilation lifetime spectroscopy (PALS), that the surface instability of several MOFs after solvent removal can render an impermeable barrier that hinders the adsorption of gas molecules [29].
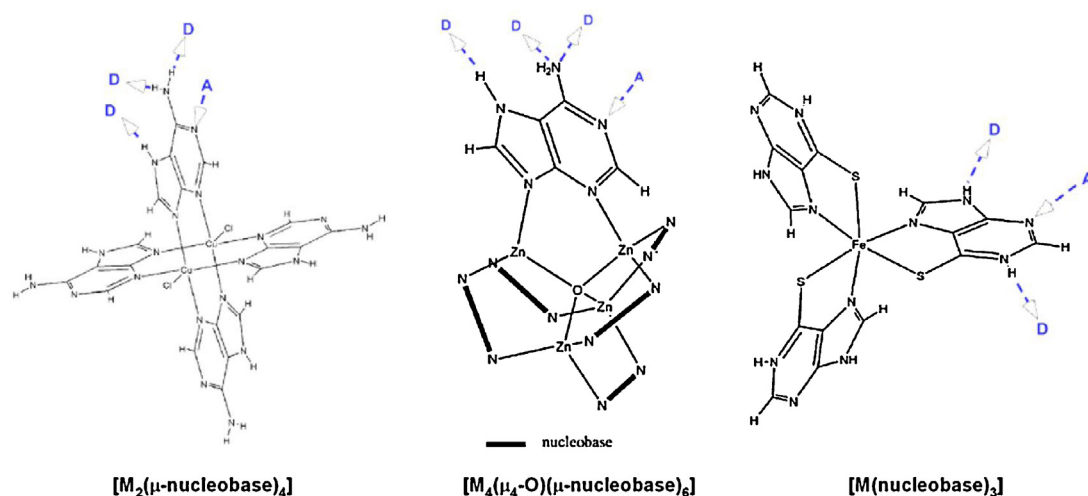
Fig. 8. Metal–nucleobase discrete entities suitable for the synthesis of *supra*MOFs.

This compound represents one of the first members of a new family of porous materials based on supramolecular interactions that differ from the extended supramolecular materials based on organic molecules because in this case the building units are coordination complexes or clusters that are connected through non-covalent interactions. Focusing on the synthons that imply the metal–nucleobase systems (Fig. 8), the opportunities to grow novel supramolecular metal-organic frameworks (*supra*MOFs), as named by Reger et al., are many [30]. A special feature of these systems is the geometrical angles set between the synthons, which are otherwise difficult to achieve in organic molecules.

4. [Cu$_2$(μ-adenine)$_2$(μ-carboxylato)$_2$] secondary building unit

There are few examples of the simultaneous presence and cooperation of μ-carboxylato and μ-adenine bridges (Fig. 9). The first example of this type corresponds with a 2D compound {[Cd$_3$(μ$_3$-adeninato-κN3:κN7:κN9)$_2$(μ$_3$-adipate-κ^{2}O,O′:κ^{2}O′,O″:κ^{2}O″,O‴)$_2$(H$_2$O)$_2$]·1.5H$_2$O}$_n$ composed of trimeric entities in which both the adenine ligand and the adipate ligand cooperatively bridge the same metal centres [31]. More recently Rosi et al. provided new examples of this successful strategy. The first one corresponds with a porous network of formula (Me$_2$NH$_2$)$_2$[Zn$_8$(μ$_4$-adeninato-κN1:κN3:κN7:κN9)$_4$(μ-BPDC-κO:κO′)$_4$(μ-BPDC-κ^{2}O,O′:κ^{2}O″,O‴)$_2$(μ$_4$-O)]·8DMF·11H$_2$O (BPDC: biphenyldicarboxylate) and commonly named bio-MOF-1 [32]. It consists of an anionic network that allows the exchange of the cationic counterions to provide a way to storage and release cationic drug molecules. The second one, (Me$_2$NH$_2$)$_4$[Zn$_8$(μ$_4$-adeninato-κN1:κN3:κN7:κN9)$_4$(μ-BPDC-κO:κO′)$_6$(μ-O)]·49DMF·31H$_2$O, corresponds with a novel topology using the same components that are arranged in such a way that they build up a mesoporous material with a high surface area (4300 m^2 g^{-1}) and one of the largest metal-organic framework pore volume reported to date (4.3 cm^3 g^{-1}) [33]. Almost at the same time, additional examples of this strategy appeared but using 2,6-diaminopurine instead of adenine [34]. These pioneer compounds envisaged the possibility to develop porous metal-organic frameworks based on the combined action of deprotonated adenine and carboxylate ligands.

There has been some other different approaches to synthesize these kinds of adeninate and carboxylate mixed compounds as it is the case for a series of compounds based on carboxylate functionalized adenines [9-(carboxypropyl)adenine] reported by Kumar and

Verma [35]. This strategy increases the coordination capacity of the adenine molecule, which is able to coordinate five different silver ions providing a polymeric crystal structure composed of hexameric silver-adenine rings.

In all the examples described above, the adenine and carboxylato ligands although they cooperate in the polymerization process, do not present the expected coordination mode similarity (Scheme 5). This fact is mainly due to the use of SBUs in which both ligands play different roles. In our case, due to the similarities between the μ-carboxylato-κO:κO′ and μ-adenine-κN3:κN9 coordination modes it was possible to foresee the formation of mixed rigid paddle-wheel shaped [Cu$_2$(μ-adenine)$_x$(μ-carboxylato)$_y$] entities (where x + y = 4) that can be later used as SBUs, to provide extended porous systems as will be described below.

4.1. Porous MBioFs based on [Cu$_2$(μ-adenine)$_2$(μ-carboxylato)$_2$] units

Using the strategy described above we obtained a family of 3D metal-organic compounds, {[Cu$_2$(μ$_3$-adeninato-κN3:κN7:κN9)$_2$(μ$_2$-OOC(CH$_2$)$_x$CH$_3$-κO:κO′)$_2$]·yH$_2$O}$_n$ [x from 0 (acetate) to 5 (heptanoate)], whose adsorption measurements have demonstrated that the length of the aliphatic chain of the caboxylate ligands modifies the porosity of the open-framework structures [36]. The synthesis of this family of compounds is relatively simple as they can be obtained as green polycrystalline powder just by the addition of carboxylic acid to an aqueous solution containing the nucleobase and a copper(II) salt at room or near room temperature. The crystal structure, as predicted, consists of paddle-wheel shaped centrosymmetric dimeric units in which two copper(II) atoms are bridged by two adenine ligands coordinated by their N3 and N9 nitrogen atoms and two carboxylic ligands with a μ-O,O′ coordination mode. These units are cross-linked (Fig. 10) through the apical coordination of the imidazole N7 atom of the adeninato ligands in such a way that each PW is linked to four adjacent entities with a Cu···Cu separation across the imidazole N9/N7 bridge of ca. 6.0 Å. This self-assembling process directed by the metal-adeninate linkages generates a 4-connected uninodal net with a *lvt* topology and a (4^2.8^4) point symbol, using as a node the dinuclear building unit. The net exhibits a three-dimensional system of intersecting cavities (Fig. 10) whose effective volume comprises 37% and 25% of the unit cell volume for the acetate and butanoate compounds, respectively. The free volume is directly related to the length of the aliphatic chain, which is pointing

(a)

(b)

(c)
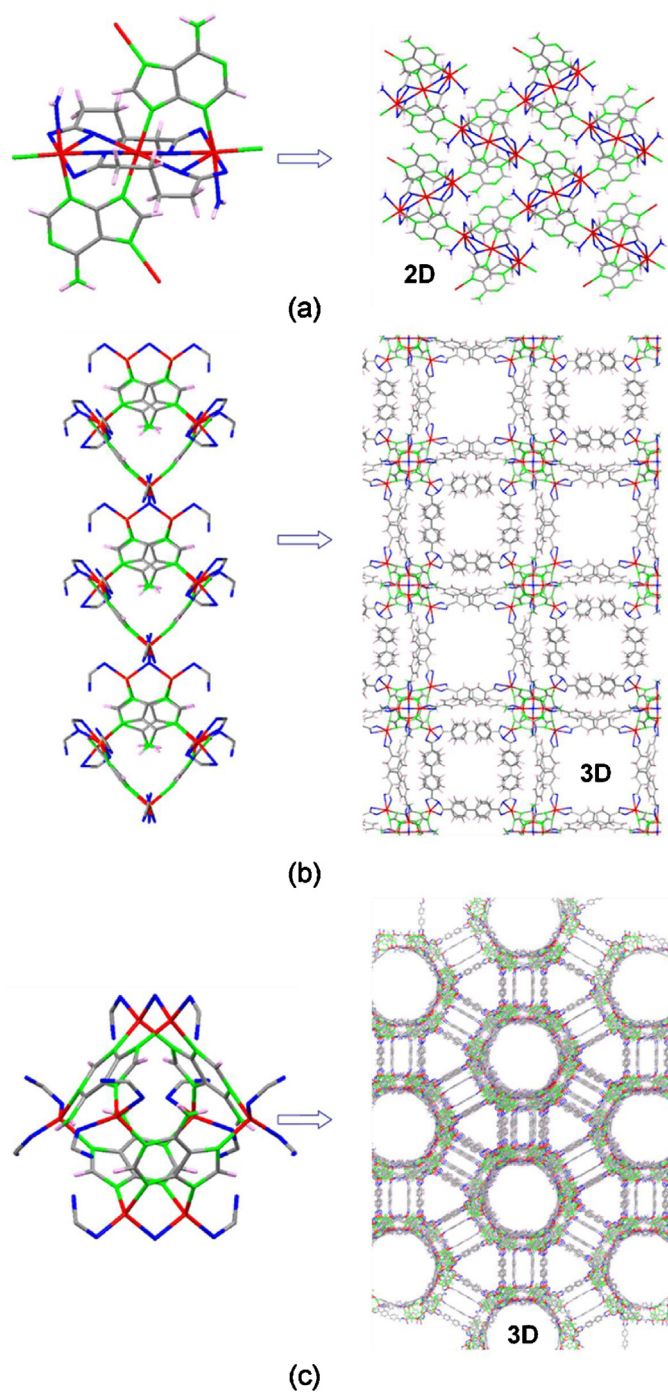
Fig. 9. SBUs and the resulting crystal structures of compounds (a) $\{[Cd_3(\mu_3\text{-}adeninato)_2(\mu_3\text{-}adipate)_2(H_2O)_2]\cdot1.5H_2O\}_n$ [31], (b) $(Me_2NH_2)_2[Zn_8(\mu_4\text{-}adeninato)_4(\mu\text{-}BPDC)_6(\mu_4\text{-}O)]\cdot8DMF\cdot11H_2O$ [32], and (c) $(Me_2NH_2)_4[Zn_8(\mu_4\text{-}adeninato)_4(\mu\text{-}BPDC)_6(\mu\text{-}O)]\cdot49DMF\cdot31H_2O$ [33].
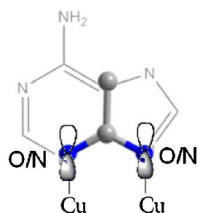
Scheme 5. Coordination similarities between the μ-carboxylato-κO:$\kappa O'$ and μ-adenine-$\kappa N3$:$\kappa N9$ coordination modes.
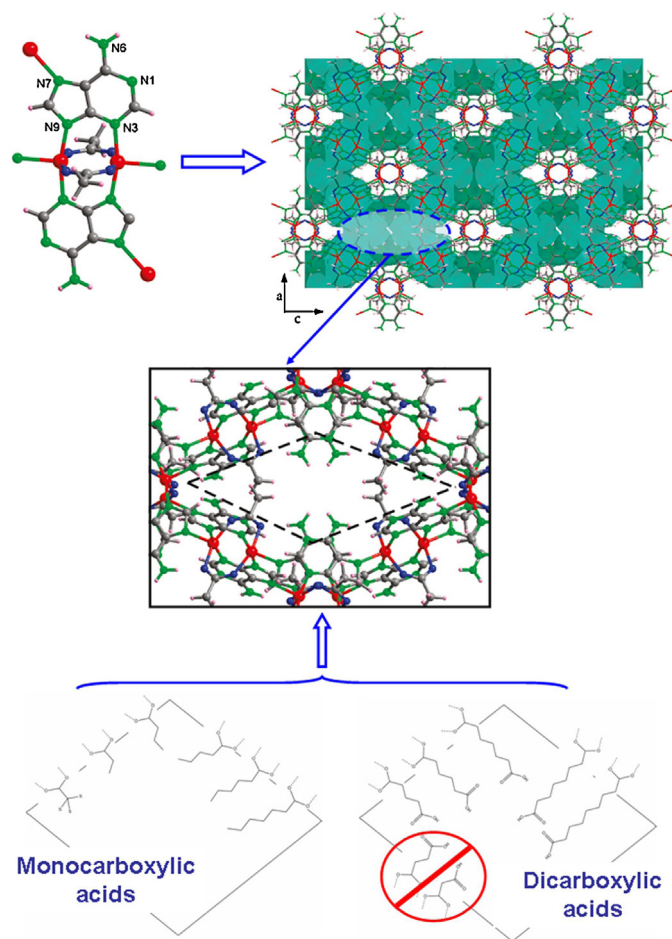
Fig. 10. Top: $[Cu_2(\mu_3\text{-}adeninato)_2(\mu_2\text{-}OOCCH_3)_2]_n$ compound, showing the paddle-wheel core, the crystal packing and the cavity with the Watson–Crick face and the aliphatic chains pointing towards it. Bottom: monocarboxylic and dicarboxylic acids of different length employed in the preparation of the compounds [36,37].

towards the inner portion of the channels, so that a longer chain implies less free volume.

Moreover, the 3D crystal structure seems to be so robust that it is obtained even when using long chain aliphatic dicarboxylic acids: $HOOC(CH_2)_nCOOH$ [n from 3 to 5] [37]. Surprisingly, only one of the two carboxylic groups is deprotonated and coordinated to the metal centres, μ-$\kappa O1$:$\kappa O2$, while the other remains protonated inside the channels of the crystal structure in such a way that the dicarboxylic ligands do not join the dimeric fragments as could in principle be expected. Only when short chain dicarboxylic acids are employed a different crystal structure is obtained. In this last case the great tendency of these acids to chelate metal ions disturbs the paddle-wheel shaped SBUs providing crystal structures based on discrete complex entities that will be further discussed in Section 6. Almost at the same time that we reported this new family, Rosi et al. reported the synthesis of the analogous $[Co_2(\mu_3\text{-}adeninato\text{-}\kappa N3$:$\kappa N7$:$\kappa N9)_2(\mu_2\text{-}OOCCH_3\text{-}\kappa O$:$\kappa O')_2]\cdot2DMF\cdot0.5H_2O$ (Bio-MOF-11) [3d]. The synthesis of this last compound is more exigent than that of copper(II) based ones, as it requires a prior lyophilization of the reagent mixture, the use of solvothermal conditions and DMF solvent. All attempts to obtain this analogous compound and others (using Zn^{2+}, Ni^{2+} and Mn^{2+} as metal centres) by means of simple aqueous solvent synthesis were unsuccessful. The reason for this failure seems to be a subtle balance of the acid constants when coordinated to the metal centres that allows the deprotonation of the adenine when coordinated to copper(II) ions but not for the other metal centres. In the case of

the cobalt(II) analogous it becomes clear that the presence of the alkylamines generated during the partial decomposition of the DMF solvent at the solvothermal condition is necessary to deprotonate the adenine.

4.2. Fine tuning of the adsorptive properties

All the compounds of this family of porous MBioFs are relatively highly thermally stable. They are able to release the solvent molecules without the collapse of the crystal structure, after which they remain stable up to around 250 °C. This behaviour offered the opportunity to use them as adsorptive materials.

The permanent porosity of the MBioFs with formula $[Cu_2(\mu_3$-adeninato-$\kappa N3{:}\kappa N7{:}\kappa N9)_2(\mu_2$-OOC$(CH_2)_xCH_3$-$\kappa O{:}\kappa O')_2]_n$ was studied by means of measuring N_2 (77 K), CO_2 (273 K) and H_2 (77 K) isotherms (Fig. 11) [38]. Compounds containing acetate, propionate and butanoate showed a type I isotherm with a sharp knee at low relative pressures ($p/p_0 \sim 0.01$), followed by a plateau, which is characteristic of a crystalline microporous solid with uniform pore-size distribution. On the other hand, the pentanoate compound exhibited an isotherm corresponding with an essentially non-adsorbing solid. The results also showed that the permanent porosity of guest-free compounds is easily tunable by means of the length of the aliphatic chains. Longer tails reduce the accessible space decreasing accordingly the amount of adsorbed gas molecules. It must be emphasized that the amount of CO_2 adsorbed in the acetate compound exceeds the values reported for many other well-known MOFs.

Their microporous nature, the presence of the Watson–Crick face in the pore walls and the tunability of the channels by means of the length of the aliphatic chain makes them good candidates for studying their behaviour in gas capture and separation technologies [39] where a high adsorptive selectivity towards a specific species is fundamental. In relation to the latter, the suitability of the MOFs in CO_2 capture and sequestration (CCS, Carbon Capture and Sequestration) technologies is remarkable, where compared with the existing methods thus far the CO_2 capture by means of adsorption in porous materials presents a higher energetic efficiency [40]. Nowadays, CO_2 capture is of special interest in combined cycle power plants with integrated gasification [41] or in the H_2 production by means of fuel or biomass gasification processes [42], where the syngas (mixture mainly composed by CO and H_2) is converted by the water gas shift reaction to a mixture composed of H_2 and CO_2. Furthermore, the purification of H_2 destined for catalytic hydrogenation reactions or to fuel cells, where impurities such as CO can be harmful, is also relevant.

Considering all the aspects mentioned above the presence of MBioFs is vital as they decorate the pore walls with the Watson–Crick faces of the adenine, which facilitates these coordination polymers to selectively capture CO/CO_2 based on the basicity of this site and also the H-bonding interactions with polar CO and quadrupolar CO_2 [3c,43]. Therefore, we have carried out the study of the adsorption selectivity of binary mixtures of CO_2/H_2 and CO/H_2 [38]. Owing to the experimental complexity of this kind of analysis and the good fits that Grand Canonical Monte Carlo (GCMC) calculations have shown in previous works, the estimation of the selectivity values was performed by computing the values of the Henry constants and the adsorption isotherms of the binary gas mixtures (Fig. 12).

In general, the selectivity towards CO_2 and CO increases as the pore gets smaller and as the temperature is lowered. In fact, at the lower temperature boundary noticeably greater values are estimated for compound containing butanoate. In all cases, with increasing temperature the selectivity falls exponentially and the selectivity values of each compound tend to be comparable. This fall is more pronounced for butanoate, which at 373 K reaches
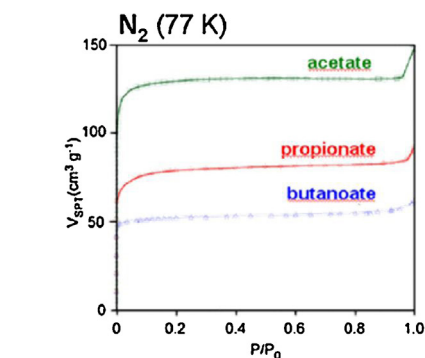
Compound	Area$_{BET}$ (m²/g)	N_2 (mmol/g)	$V_{t\text{-plot}}$ (cm³/g)
acetate	505	5.8	0.173
propionate	301	3.4	0.107
butanoate	202	2.4	0.073
pentanoate	8.9	--	--
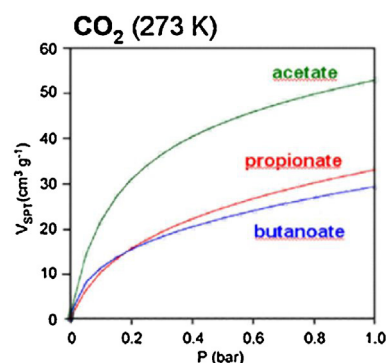
Compound	CO_2 (mmol/g)	$V_{t\text{-plot}}$ (cm³/g)
acetate	2.3	52.90
propionate	1.5	33.04
butanoate	1.3	29.41
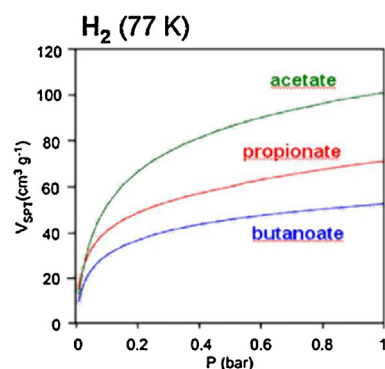
Compound	H_2 (mmol/g)	H_2 (wt.-%)	$V_{t\text{-plot}}$ (cm³/g)
acetate	4.51	0.9	98
propionate	3.17	0.6	67
butanoate	2.33	0.5	46

Fig. 11. N_2 (77 K), CO_2 (273 K) and H_2 (77 K) experimental adsorption isotherms. Reproduced from Ref. [38]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

selectivity values only slightly above that of acetate and propionate containing compounds. The adsorption selectivity values match the Henry's selectivity at low pressure values.

In acetate and propionate compounds, the CO_2 vs. H_2 adsorption selectivity shows a comparable evolution as a function of pressure.
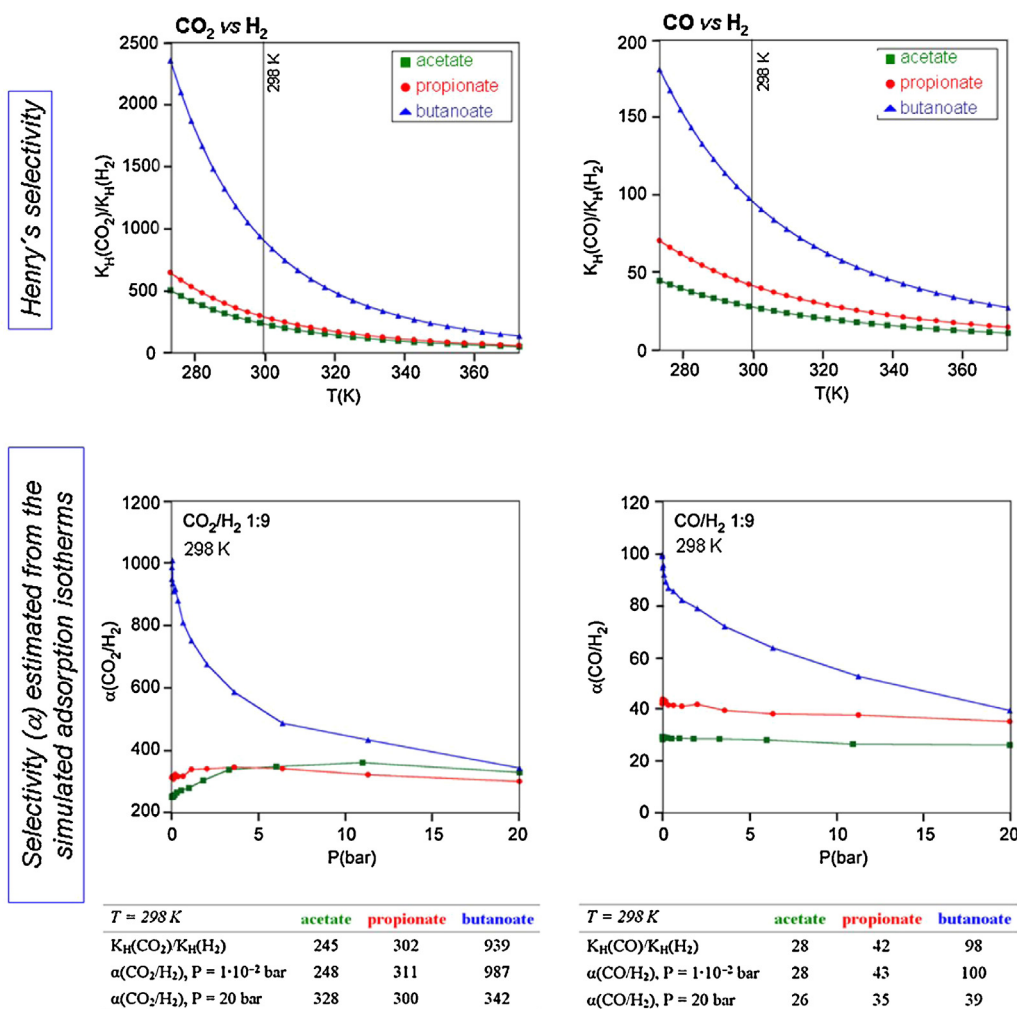
Fig. 12. Adsorption selectivities for binary CO_2/H_2 and CO/H_2 mixtures: Henry's selectivity, $K_H(A)/K_H(B)$, and selectivity (α) estimated from the simulated adsorption isotherms at 298 K.

Reproduced from Ref. [38]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As the pressure increases these values undergo a slight rise, which after reaching a maximum remain stable or decrease slightly. The selectivity of these compounds is intermediate with respect to other microporous materials [44]. On the contrary, the butanoate analogue shows comparatively high selectivity values (ca. 1000) over the low-pressure range. The pressure increment produces an exponential fall reaching the selectivity values described for the acetate and propionate compounds at high pressure. On the other hand, in the case of the CO/H_2 binary mixture, the initial selectivity values for acetate and propionate (α: 28 and 43 at $P = 1 \times 10^{-2}$ bar) show a slight fall with increasing pressure, stabilizing at somewhat lower values (26 and 35) at ca. 5 bar. These values can be considered as intermediate and comparable to those described for other microporous materials [45]. In the butanoate compound, the CO/H_2 selectivity shows uncommonly high values at low pressure (ca. 100, one of the highest reported to date for CO/H_2 mixtures), which falls again exponentially to reach the selectivity values similar to the acetate and propionate ones at high pressures.

In order to have deeper insight into the unusual behaviour of the butanoate analogue, we analyzed the preferential adsorptive sites from the interpretation of the potential energy maps obtained by GCMC simulations. The potential energy maps for N_2 reveal two types of adsorption cavities in the acetate compound (Fig. 13). The first one consists of two minima whose centroids are in two symmetrically equivalent positions sandwiched by the pyrimidine rings of two adeninato ligands (site 1). The second cavity is somewhat wider and it presents four symmetrically equivalent energy minima oriented towards the Watson–Crick faces of four adenine molecules in a pseudo-tetrahedral disposition (site 2). Considering the crystallographic multiplicity of the positions of the centroids there are 32 preferential adsorption sites within the unit cell (site-1: 16 and site-2: 16). Site-2, due to its very polar nature is specially well-suited for the adsorption of CO_2 (having a relatively high quadrupolar moment) and CO (having a weak dipolar moment and relatively high quadrupolar moment). In the acetate and propionate derivatives both sites are accessible for any of the three adsorbates (CO_2, CO and H_2) according to the potential energy maps. However for the butanoate analogue, the occupancy of site 1 is hindered by the aliphatic tail of the carboxylato ligand which is oriented towards this cavity. Thus, at low pressures the guest molecules go into site 2 whose high affinity towards CO_2 and CO leads to a negligible coadsorption of H_2 and explains the high selectivity values achieved at low pressures. On the contrary, the abrupt drop in the selectivity values at high pressures is explained because although at low pressures the adsorption on site 1 is negligible for the three adsorbates (CO_2, CO and H_2), at high pressures only H_2 is able to populate site 1. Therefore, as the pressure increases, CO_2 and CO molecules saturate site 2, while H_2 molecules easily occupy site 1, leading to a more significant coadsorption of H_2 that promotes
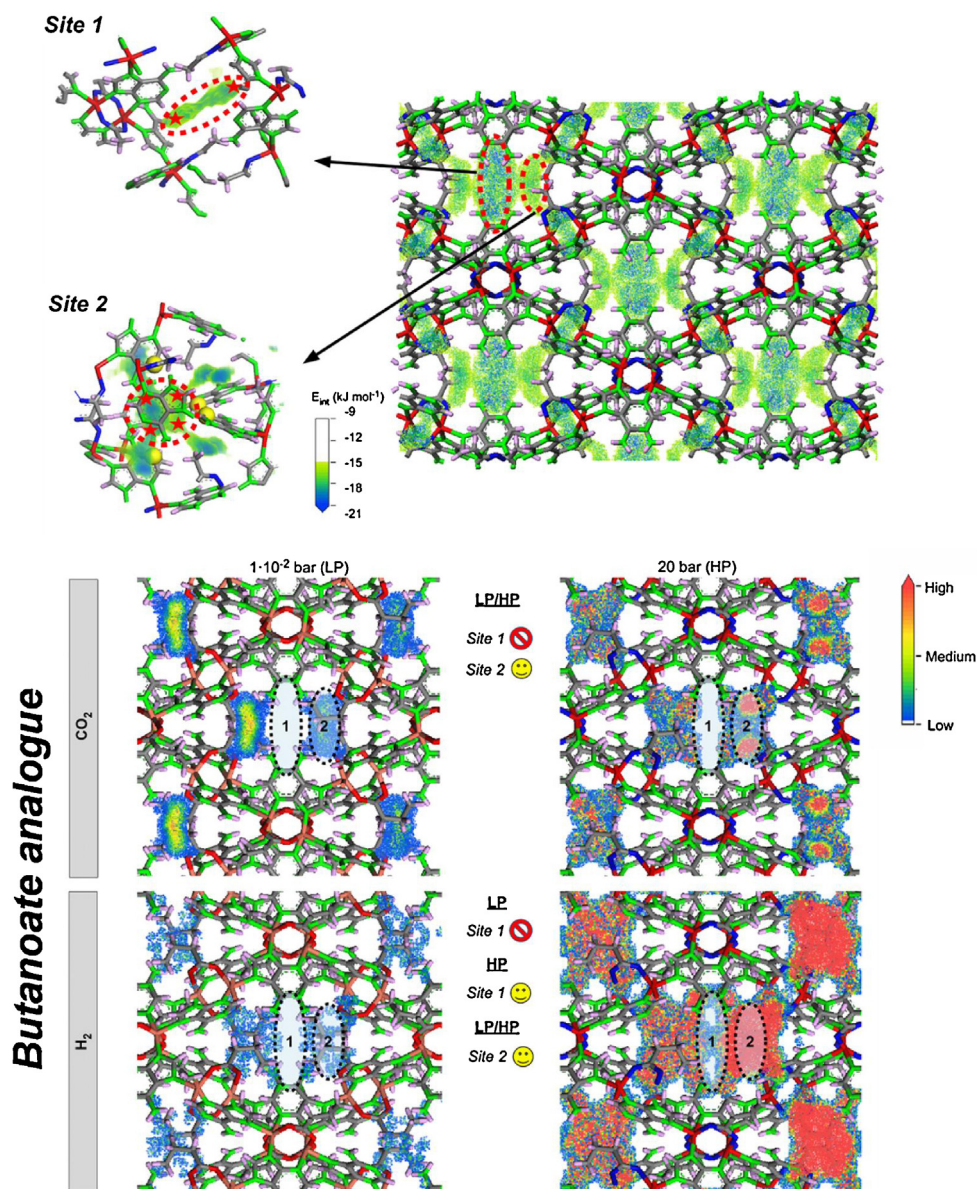
Fig. 13. Preferred adsorption sites and accessibility at low pressure (LP: 1×10^{-2} bar) and high pressure (HP: 20 bar). Reproduced from Ref. [38]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the marked exponential decrease in the selectivity observed for the butanoate compound.

4.3. Overtaking gas uptake capacity limited by the crystal structure

During our work with this family of porous MBioFs we noticed that to ensure the complete miscibility of monocarboxylic acids longer than propionate it is mandatory to use a mixture of water and methanol as solvent. This fact is something not surprising as far as we all know that short chain carboxylic acid such as acetic and propionic acids are completely miscible in water but long chain ones are immiscible. However at intermediate situations there is an opportunity to obtain stable microemulsions and the micelles present in it can be used as templating agents. Therefore we take some time to search for information about the miscibility of these acids in different solvents and we found an old paper, published in 1929, that clearly indicates the formation of a stable microemulsion in mixtures of butyric acid and water [46]. After that, there was

some research based on this paper in subsequent years but after 1952 the interest for this system apparently ceased and references to butanoic acid as surfactant almost disappeared [47].

We reproduced this work to ensure the presence of the micelles and to determine, by means of conductivity measurements, the critical micelle concentration (CMC) above which a stable microemulsion is obtained. The value obtained at 4 °C is around 1 M for a butyric acid/water mixture in agreement with the data previously published. However, in the presence of copper(II) ions the CMC drops to a 0.05 M value, that ensures the presence of micelles under the common reagent concentrations used for the synthesis of the butanoate MBioF.

As previously mentioned the micelles are usually employed as templating agents to incorporate pores within a material by means of the removal of the surfactant molecules from the embedded micelles. Obviously, depending on the size of the template the resulting pore will fall into the micropore (<2 nm), mesopore (2–50 nm) or macropore (>50 nm) regime. It becomes clear that due to the length of the commonly employed surfactants (SDS,
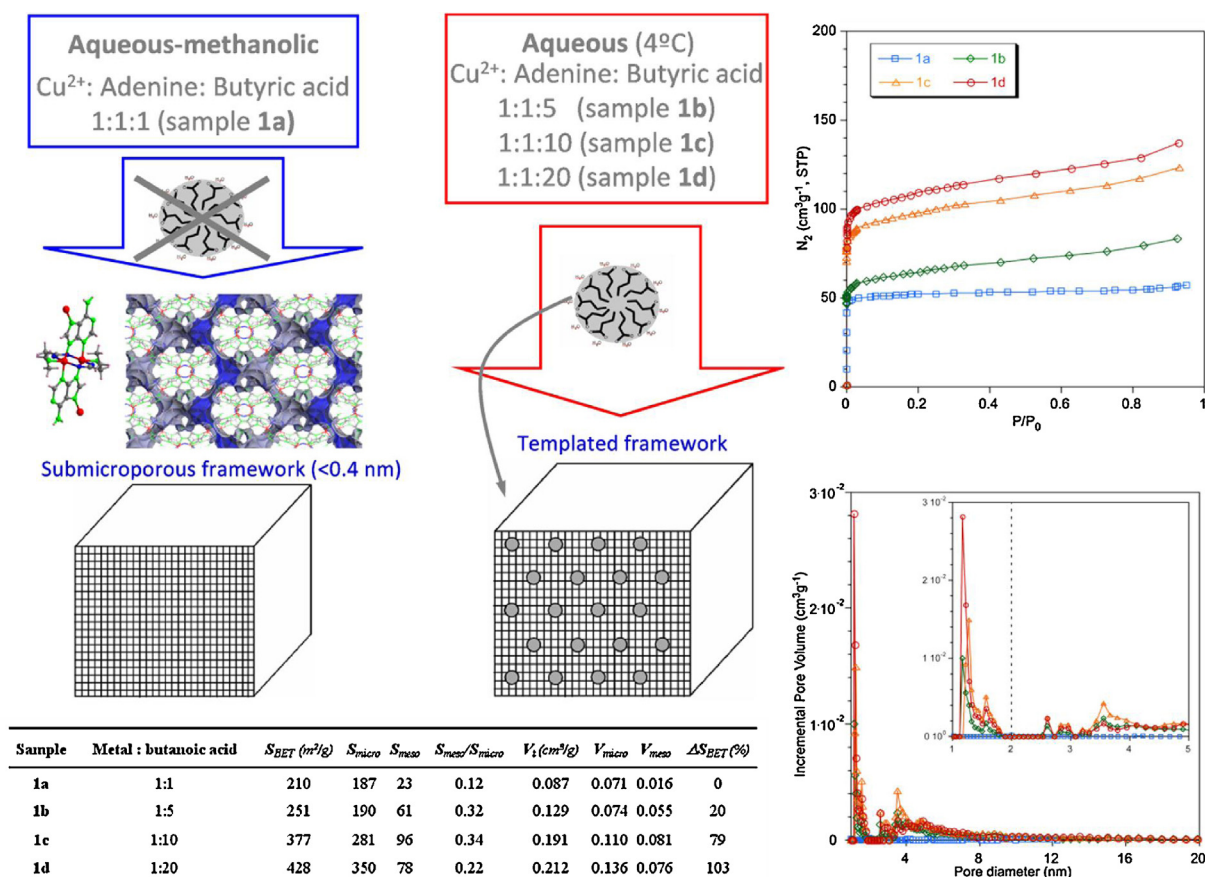
Fig. 14. Schematic representation of the butanoic acid templating effect, N$_2$ adsorption isotherms at 77 K and pore size analysis [48].

Sample	Metal : butanoic acid	S_{BET} (m²/g)	S_{micro}	S_{meso}	S_{meso}/S_{micro}	V_t (cm³/g)	V_{micro}	V_{meso}	ΔS_{BET} (%)
1a	1:1	210	187	23	0.12	0.087	0.071	0.016	0
1b	1:5	251	190	61	0.32	0.129	0.074	0.055	20
1c	1:10	377	281	96	0.34	0.191	0.110	0.081	79
1d	1:20	428	350	78	0.22	0.212	0.136	0.076	103

AOT, Tween, etc.), the generated pores fall well into the mesopore regime. Before the publication of the work described below there was no reported method able to incorporate extra microporosity to a material. This work took advantage of the relatively short tail of the butyric acid, around 6.4 Å, to generate small micelles that will fall into the micropore regime [48].

The use of micelles to incorporate porosity is a well-known strategy in many areas such as the synthesis of mesoporous silicates, carbons and other ceramics [49]. More recently, it has been applied to the synthesis of hierarchically ordered micro- and mesoporous MOFs in which the microporosity is limited by the crystal structure and the mesoporosity arises from the inclusion of long chain micelles [50,51]. Unfortunately, the methods developed that provide the mesoporous characteristics to the starting material usually also affect the material by lowering the contribution of the microporosity to the total porosity and by decreasing the available total surface area [50,52]. In many cases, the addition of mesoporous features is a desired objective for example to provide technologically relevant ordered mesoporous materials with high specific surface areas. However, in other cases, for instance to improve the performance in gas separation and purification processes [53], it is a superior option to increase the porosity just in the micropore range.

In order to ensure the viability of this route to enhance the microporosity (Fig. 14), we prepared several samples of [Cu$_2$(μ_3-adeninato)$_2$(μ-butanoato)$_2$]$_n$ with the following metal:butanoic acid ratios: **1a** (1:1), **1b** (1:5), **1c** (1:10) and **1d** (1:20). The first sample **1a**, to be used as reference material, was synthesized in a water: methanol mixture to avoid strictly any micelle formation. In contrast, samples **1b**–**1c** were prepared at 4 °C using solely water as solvent to favour the micellar aggregation. The crystallinity of the

material was retained after the inclusion of the micelles and even after the release of the butyric acid molecules from the incorporated micelles. The N$_2$ adsorption isotherms at 77 K for the four samples shows that a significant increase in the total gas uptake takes place as the amount of butanoic acid is raised. The sample prepared with the highest butanoic acid concentration (**1d**) doubles the surface area of the reference material (**1a**), reaching a maximum value of 428 m^2 g^{-1}.

The pore size distribution, modelled by density functional theory (DFT), shows the appearance of a maximum around 1.3 nm, followed by some contribution of pores between 2.6 and 4 nm. The maximum, located in the microporous range, shows a continuous raise as the micelle concentration increases and its diameter agrees fairly well with the expected one. No clear trend was observed for the less contributing pores of greater size, which source is probably related to the presence of some bigger aggregates of butanoic acid coming from the coalescence of some original micelles during the crystallization process. None of these maxima were observed in the untemplated sample (**1a**).

5. [Cu$_2$(μ-carboxylato)$_4$] secondary building unit

The correct selection of the polycarboxylato ligand can direct the resulting crystal structure from the assembly of the well-known [Cu$_2$(μ-carboxylato)$_4$] entities towards a great variety of architectures ranging from polynuclear discrete entities to 3D crystal structures. As example: flexible dicarboxylic connectors provide 1D infinite chains, rigid linear dicarboxylates generate 2D infinite sheets, rigid angular carboxylates afford octahedral clusters, and linear but not coplanar carboxylates give rise to 3D porous nets (Fig. 15) [13a,54]. There are many other combinations using
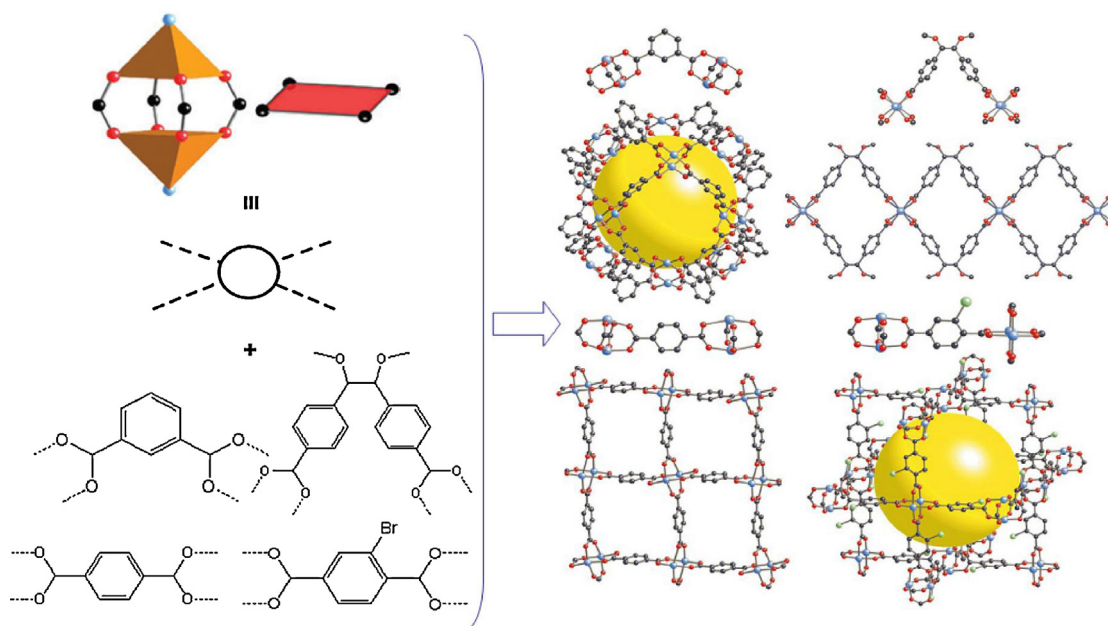
Fig. 15. Dimmensionality control of the [Cu$_2$(μ-carboxylato)$_4$] paddle-wheel units assembly by means of precise dicarboxylate linker geometry [13a,54].

connectors containing additional carboxylate groups that provided different topologies [55]. The axial positions of these entities, usually occupied by solvent molecules, can be replaced by nucleobase ligands increasing the ability of the systems to establish molecular recognition processes [4].

Adenine molecules methylated at N3/N9 positions were employed to preclude the adenine μ-$\kappa N3$:$\kappa N9$ bridging mode that is the key factor to obtain the mixed dimeric [Cu$_2$(μ-adenine)$_2$(μ-carboxylato)$_2$] entities that were used as building blocks in Section 4. In this way, we promoted the formation of the [Cu$_2$(μ-carboxylato)$_4$] entities and their polymerization through the careful selection of the dicarboxylato bridge. In the first stage of this research line we prepared a series of infinite 1D metal-organic structures using long chain dicarboxylato ligands: $^-$OOC(CH$_2$)$_n$COO$^-$ [n being 3 (glutarate) and 5 (pimelate)] altogether with 3-methyl- and 9-methyladenine. The obtained compounds {[Cu$_2$(μ_4-glutarato)$_2$(3-methyladenine-$\kappa N7$)$_2$]·4H$_2$O}$_n$, {[Cu$_2$(μ_4-glutarato)$_2$(9-methyladenine-$\kappa N7$)$_2$]}$_n$, and {[Cu$_2$(μ_4-pimelato)$_2$(9-methyladenine-$\kappa N7$)$_2$]·2(pimelic acid)}$_n$ contain chains of interconnected paddle-wheel entities in which the dicarboxylato ligands show the expected μ_4-$\kappa O1$:$\kappa O2$:$\kappa O3$:$\kappa O4$ binding mode. The methylated nucleobases exhibit their usual monodentate N7-coordination pattern to anchorage to the apical positions of the dimeric entity [37]. This assembling strategy provides neutral chains where the paddle-wheel motifs are doubly bridged by the tetratopic dicarboxylate anions (Fig. 16). The supramolecular architecture of glutarato based ones is essentially knitted by pairing interactions between the Watson–Crick faces of adjacent adenines, whereas that of pimelato shows the inclusion of guest pimelic molecules which are anchored to the polymeric chains through fork-like hydrogen bonding interactions between one of the carboxylic groups and the peripheral adenine moieties, affording a supramolecular layered structure.

6. Other metal–carboxylato–adenine systems

As previously mentioned short chain dicarboxylate ligands have a great tendency to coordinate metal centres establishing five or six member chelating rings. This precludes the presence of the paddle-wheel shaped dimeric entities that we were using

to generate the previously described systems. In any case they provide many interesting systems ranging from discrete monomers and dimers to infinite polymeric chains that can, in some cases, be rationalized on the basis of their coordination properties.

6.1. Metal-malonato-adenine discrete systems. Magnetic properties

Malonato ligand exhibits a remarkable versatility in adopting different modes of bonding, including monodentate, chelating and bridging, with more than one of these modes sometimes occurring in the same compound. Fig. 17 shows the most usual coordination modes of this short chain dicarboxylato ligand [56]. There is
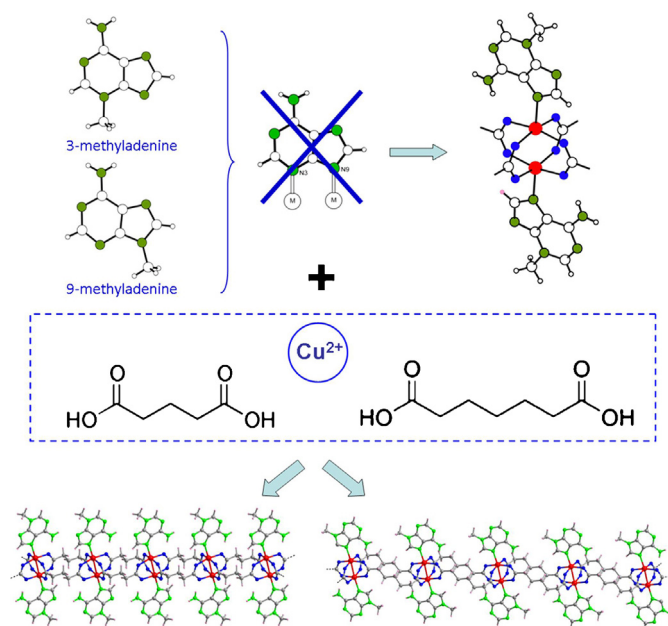
Fig. 16. Schematic representation of the design of infinite 1D chains based on [Cu$_2$(μ-carboxylato)$_4$] with long chain dicarboxylato ligands and decorated with methylated adenine moieties [37].
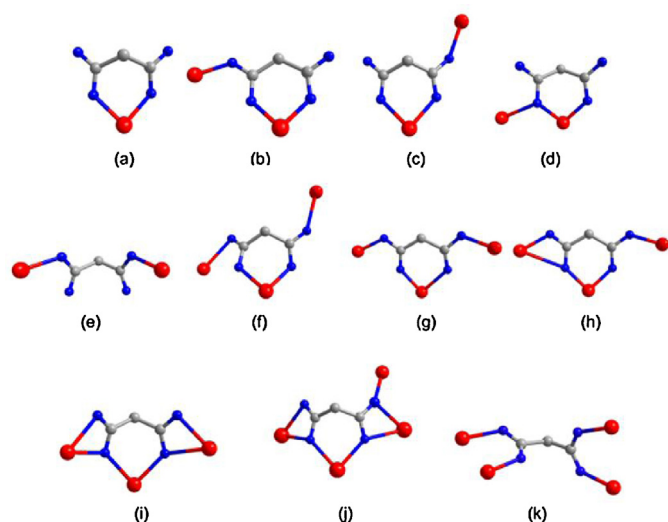
Fig. 17. Most common coordination modes of malonato ligand.

Scheme 6. Orbital countercomplementarity of the μ-malonato-$\kappa^2O1,O2$:$\kappa O1$ and μ-adenine-$\kappa N3$:$\kappa N9$ bridging ligands.
Reproduced from Ref. [57]. Copyright (2009) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

only one crystal structure registered in the CSD with the malonate ligand coordinated to a first row transition metal centre showing the μ_4-$\kappa O1$:$\kappa O1'$:$\kappa O2$:$\kappa O2'$ bridging mode, which is the key factor to obtain the extended systems described in Section 5. The trend of malonato ligand to establish five membered chelate rings hinders the individual carboxylate groups to afford the μ-κO:$\kappa O'$ bridging mode which is necessary to obtain the [M$_2$(μ-carboxylato-κO:$\kappa O'$)$_4$] or [M$_2$(μ-adenine-$\kappa N3$:$\kappa N9$)$_2$(μ-carboxylato-κO:$\kappa O'$)$_2$] secondary building units. In spite of all the above drawbacks, we obtained pseudo "paddlewheel" dinuclear [M$_2$(μ-adenine-$\kappa N3$:$\kappa N9$)$_2$(μ-malonato-$\kappa^2O1,O2$:$\kappa O1$)$_2$(H$_2$O)$_2$] (M^{II} = Ni, Co) units (Fig. 18) [57]. Each metal is coordinated to three oxygen atoms from the malonato ligands and two nitrogen atoms of adenine nucleobases. The octahedral distorted polyhedron is completed with a water molecule to give a N$_2$O$_3$Ow donor set. The malonate anion shows an unusual tridentate μ-$\kappa^2O1,O2$:$\kappa O1$ coordination mode where O1 links both metal atoms and O2 is only bonded to one

of these metal centres, thus forming a six-membered chelate ring (coordination mode d in Fig. 17).

The hexacoordination of the metal centres in these pseudo paddle-wheel units contrast with the pentacoordination found in normal paddle-wheel units. Additionally the coordinated water molecules and the angles between the M–Ow bond and the metal⋯metal axis are around 34–45°. This differs significantly with the collinear disposition between the M—X axial bonds (X = Cl, H$_2$O) and the M⋯M axis in common carboxylate/adenine PW motifs. This structural feature precludes the controlled polymerization through the malonato ligand but it leaves open the opportunity to achieve it by means of the deprotonation and further coordination of the adenine ligands to the apical position of adjacent dimeric entities.

The study of the magnetic properties of these compounds provided a striking difference with respect to the behaviour of the common paddle-wheel dimeric entities. At low temperatures the ferromagnetic nature of the interaction mediated simultaneously by the bridging adenine and malonato becomes evident. This behaviour is in great contrast with the strong antiferromagnetic interaction observed for the [Cu$_2$(μ-adenine-$\kappa N3$:$\kappa N9$)$_2$(μ-carboxylato-κO:$\kappa O'$)$_2$] units. The differences come from the coordination mode of the malonate which resembles a μ-oxo bridge. As a consequence, the splitting of the molecular magnetic orbitals is reversed for each type of bridging ligand (adenine and malonato), thus leading to an almost negligible energy difference between them (Scheme 6). This phenomenon, called orbital countercomplementary, favours a parallel alignment of the unpaired electron spins and it is responsible for the observed ferromagnetic behaviour.

6.2. Metal-oxalato-adenine extended systems

The oxalato ligand (dianion of oxalic acid; ox) has appeared as a fruitful tecton for the design of a great diversity of homonuclear and heteronuclear transition metal compounds, which have played a key role in areas such as inorganic crystal engineering and molecule-based magnetism [58]. The main reasons for the extensive use of this old but evergreen ligand are (a) its remarkable ability to mediate electronic effects between metal centres, affording compounds with a wide range of magnetic properties; and (b) the prevalence of its rigid bischelating bridging mode, that provides

Fig. 18. Pseudo paddle-wheel shaped entities in compounds [M$_2$(μ-adenine)$_2$(μ-malonato)$_2$(H$_2$O)$_2$] (M^{II} = Ni, Co).
Reproduced from Ref. [57]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
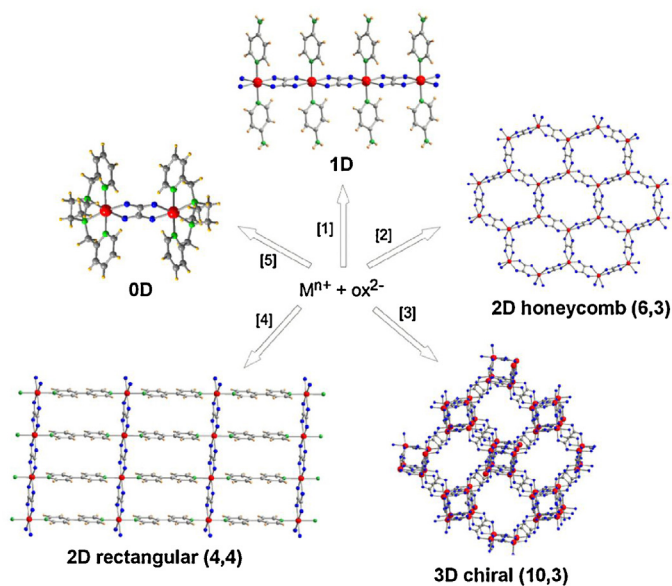
Fig. 19. Tailoring of metal-oxalato frameworks by using different organic ligands and/or templating counterions: [1] monodentate N-containing rings; [2] achiral cations; [3] chiral tris-chelated diimine cationic complexes; [4] bidentate ligands such as 4,4-bipy, piperidine, bpe, and bpa; and [5] multidentate blocking N- or O-donor ligands.

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some degree of predictability with regard to the structural characteristics of the resulting metal-oxalato networks. The topology and dimensionality of polymeric networks based on the oxalate bridging ligand essentially depend on the shape of the templating counterions, on the features of the auxiliary organic ligands used to complete the metal coordination sphere, or on both (Fig. 19) [59].

In the framework of our previous research on the chemistry of polymeric complexes based on the oxalato-bridging ligand, a strategy for the design of one-dimensional complexes with general formula $[M(\mu\text{-ox})(L)_2]_n$ containing substituted pyridine derivatives as terminal ligands has been derived [60]. By using similar synthetic routes, a family of one-dimensional (1D) complexes has been prepared, in which the pyridine bases are replaced by nucleobases, such as purine (pur) and/or adenine (Hade), whose structural characterization allows one to perform a fruitful data harvesting on the effects of the supramolecular interactions on the adenine preferred coordination mode and tautomeric form [61,62].

The main structural feature common to all compounds is the presence of 1D *zigzag* chains (Fig. 20) in which *cis*-$[M(H_2O)(\text{adenine/purine})]^{2+}$ (M^{2+} = Cu, Co, Mn, Zn and Cd) units are sequentially bridged by bis-bidentate centrosymmetric oxalato ligands. The metal atoms exhibit a distorted octahedral MO_4OwN chromophore formed by four oxygen atoms from two bridging oxalato ligands, one water molecule and one endocyclic nitrogen atom of the nucleobase in the *cis* position. The main differences comprise the coordination mode of the nucleobase and the tautomeric form it exhibits.

With regard to the coordination mode of purine, in all cases, it binds to the metal centres through N9 whereas adenine molecule always uses N3 position. If we consider the basicity of the adenine donor positions (basicity order: N9 > N1 > N7 > N3 > N6-exocyclic) an N9-binding mode would be expected, like in purine. As it is not the case, it becomes clear that this behaviour cannot be attributed to inherent electronic effects of the adenine molecule [63]. Therefore the source must be found somewhere else. Several authors have explained the modifications observed in the coordination sites by the presence of additional intramolecular hydrogen
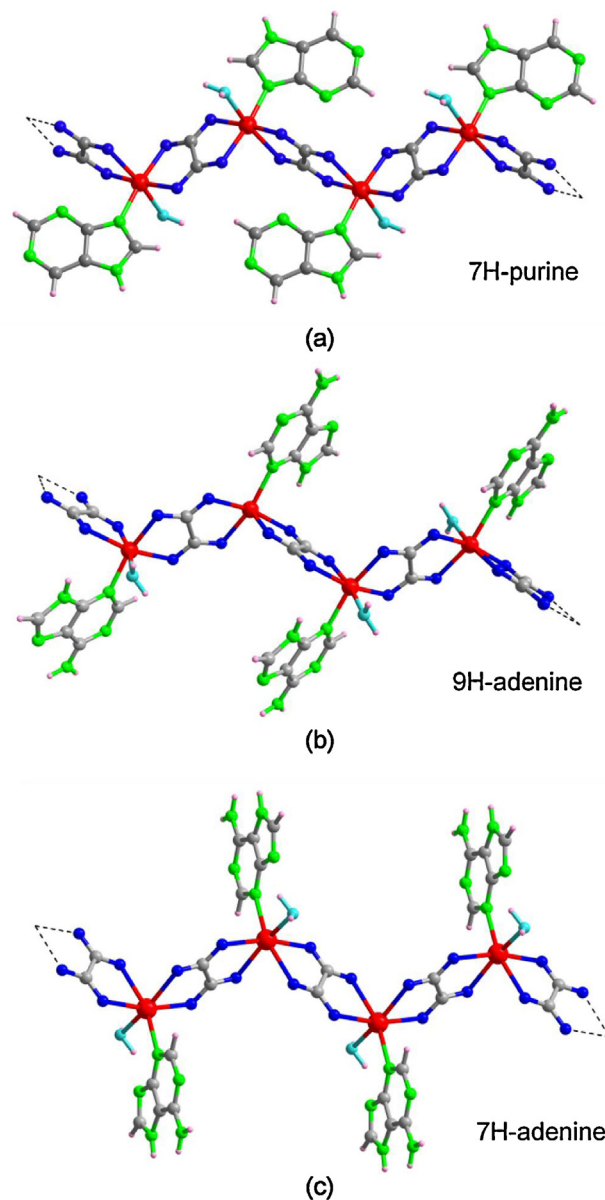
Fig. 20. Polymeric chains of compounds (a) $[M(\mu\text{-ox})(H_2O)(7H\text{-purine-}\kappa N9)]_n$ (M^{II} = Cu, Co, Mn, Zn) [61], (b) $\{[M(\mu\text{-ox})(H_2O)(9H\text{-adenine-}\kappa N3)]\cdot 2(9H\text{-adenine})\cdot(H_2O)\}_n$ (M^{II} = Co, Zn) [61] and (c) $\{[Cd(\mu\text{-ox})(H_2O)(7H\text{-adenine-}\kappa N3)]\cdot H_2O\}_n$ [62].

bonding interactions that deviate the coordination site from the most basic and usually preferred N9 nitrogen atom [64,65]. However in our case, less basic N3-binding mode is not responsible for the intramolecular interactions, as usually pointed, because both purine and adenine ligands are pointing the same hydrogen bonding donor/acceptor groups towards the metal-oxalato backbone. Therefore the reasons must be found in the different intermolecular interactions that they present. As evidence of this fact, it is possible to perform a random partial substitution of purine ligands in compound $[Co(\mu\text{-ox})(H_2O)(7H\text{-purine-}\kappa N9)]_n$ by adenine molecules rendering compound $[Co(\mu\text{-ox})(H_2O)(7H\text{-purine-}\kappa N9)_{0.76}(7H\text{-adenine-}\kappa N9)_{0.24}]_n$ in which the adenine binds metal centre by N9 site [61].

The second difference that must be mentioned is the presence of two tautomeric forms of the adenine molecule although retaining the same N3-coordination mode: *9H* tautomer for the adenine bonded to Co(II) and Zn(II) and *7H*-adenine when coordinated to
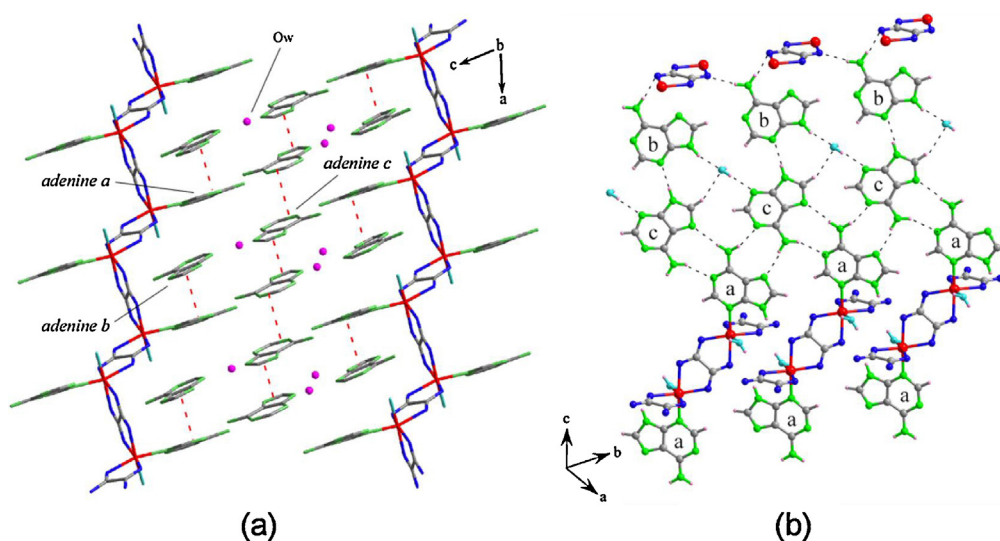
Fig. 21. Supramolecular interactions among the *9H*-adenine molecules in compounds {[M(μ-ox)(H$_2$O)(*9H*-adenine-κ*N3*)]·2(*9H*-adenine)·(H$_2$O)}$_n$ (M^{II}: Co, Zn): (a) π–π contacts and (b) hydrogen bonds [61].

Cd(II). This apparently insignificant hydrogen dissimilar placement and the absence/presence of the exocyclic amino group lead to a very difference supramolecular arrangement.

In the case of purine containing compounds, the parallel orientation of the nucleobase with respect to the metal-oxalato framework locates the nonprotonated minor groove N3 atom over the carbon–carbon bond of one oxalate ligand with a mean intra-chain N3···C distance of 3.0 Å and a dihedral angle between the pyrimidinic ring and the oxalato plane of ∼90°. This fact precludes the involvement of the potential hydrogen-bonding N3 atom in any other interaction. In fact, the supramolecular cohesion among the chains is ensured by means of π–π aromatic stacking and hydrogen bonding interactions between the coordinated water molecules, the oxalate and the purine ligand that do not imply this position.

On the other hand, the adenine molecules in compound {[M(μ-ox)(H$_2$O)(*9H*-adenine-κ*N3*)]·2(*9H*-adenine)·(H$_2$O)}$_n$ (M^{II}: Co, Zn) are arranged perpendicularly to the chain propagation direction providing bulkier chains, which pack less effectively allowing the inclusion of crystallization water molecules and noncoordinated adenine molecules. All these coordinated and noncoordinated adenines establish an intricate network of π–π aromatic stacking interactions and of hydrogen bonding interactions involving both the Watson–Crick and Hoogsteen sides of the adenines (Fig. 21). In compound {[Cd(μ-ox)(H$_2$O)(*7H*-adenine-κ*N3*)]·H$_2$O}$_n$, the proton placement at N7 permits the formation of an intramolecular hydrogen bond involving the coordinated water molecule (donor) and the N9 atom (acceptor) which reinforces the observed metal-binding pattern of the nucleobase. Moreover, the intermolecular interactions do not require the presence of additional adenine molecules and it is sustained by hydrogen bonding pairing inter-actions between the Watson–Crick faces of adenines belonging to adjacent faces and with those established with the crystallization water molecules (Fig. 22).

On the other hand, there are reported examples of Mn(II) binding to N donor sites of nucleobases in biopolymeric systems, but coordinative Mn–N linkages involving non-substituted nucleobases, as seen in [Mn(μ-ox)(H$_2$O)(purine-κ*N9*)]$_n$, are extremely rare in structurally characterized coordination compounds [66]. Probably because of this, all attempts to obtain 1D chains with the adenine nucleobase being anchored to a manganese(II)-oxalate framework were unsuccessful, obtaining compound {[Mn(μ-ox)(H$_2$O)$_2$]·(*7H*-adenine)·(H$_2$O)}$_n$ [67]. Its crystal structure is made

up of *zigzag* chains with the Mn(II) centres bridged by bisbidentate oxalato ligands, but the adenine nucleobase remains free within the crystal and the metal coordination polyhedron is filled by two water molecules.

Interestingly, the adenine nucleobase exists in the lattice in its *7H*-amino form due to the efficient stabilization of this non-canonical tautomer by means of a molecular recognition process among the nucleobase, the water molecules, and the manganese-oxalato framework (Fig. 23). In 2006, this compound represented the first X-ray crystallography characterization of the *7H*-amino tautomer of the adenine nucleobase as free molecule (without metal coordination). Thereafter, Mastropietro et al. isolated the *7H*-adenine tautomeric form in compounds [Mg(H$_2$O)$_6$]X$_2$·2(*7H*-adenine) (X = Cl$^-$ and Br$^-$) [66a]. It is well known that DNA bases can undergo proton shifts while keeping their neutrality and form different tautomers. Each tautomer has a specific H-bonding donor and acceptor pattern, which increases the possibility of mispairing of purine and pyrimidine bases in DNA, leading to spontaneous point mutations in the genome [68]. Due to its biological impact, the tautomerism of nucleobases has been largely studied using a variety of experimental and theoretical methods which support the relevance of the isolation of unusual tautomeric forms in the solid state [69].

A similar synthetic procedure to that employed for the family of metal/oxalate/nucleobase compounds described above but using K$_2$[Cu(ox)$_2$]·2H$_2$O as metal source gives a different compound {[Cu(μ-ox)(H$_2$O)(*7H*-adenine-κ*N9*)][Cu(μ-ox)(μ-OH$_2$)(*7H*-adenine-κ*N9*)]·∼10/3H$_2$O}$_n$ [67]. Its structure consists of crystallization water molecules and two crystallographically independent and roughly planar [Cu(ox)(H$_2$O)(*7H*-adenine-κ*N9*)] units, molecule A and molecule B, as shown in Fig. 24. In both complex fragments, the Cu(II) atoms are coordinated to two oxygen atoms from a bidentate oxalato ligand, one water molecule, and the imidazole N9 atom from the adenine ligand. The planar complex units are connected through weaker axial Cu–O interactions to create neutral ribbons. The adenine ligands are located in the same side of the polymeric framework and they are ring-to-ring stacked, suggesting that π–π stacking interactions contribute to the formation of the one-dimensional chains. Polymeric one-dimensional chains are further interlinked through an intricate hydrogen bonding network that implies again the Watson–Crick and Hoogsteen edges, but in this case there is not direct interaction between the adenines.
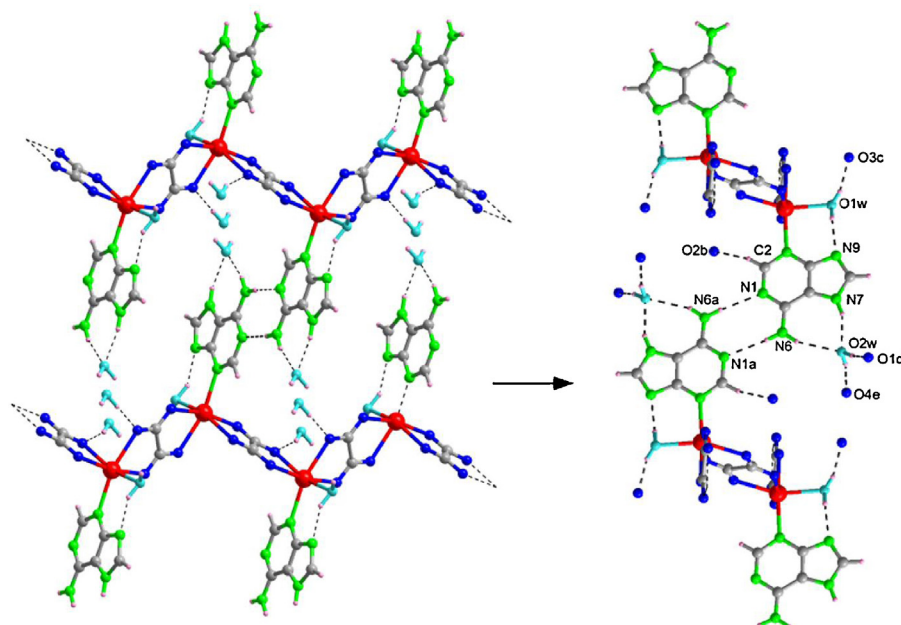
Fig. 22. Supramolecular interactions in compound $\{[Cd(\mu\text{-}ox)(H_2O)(7H\text{-adenine-}\kappa N3)]\cdot H_2O\}_n$. Reproduced from Ref. [62]. Copyright (2011) Elsevier B.V.

After the success in the coordinative anchorage of non-substituted nucleobases to metal-oxalato frameworks, the next step was to explore new coordination modes apart from N3 and N9, which was achieved by methylating the adenine at N3 and guanine at N9. The alkylation by itself and otherwise the steric hindrance exerted by the methyl group will force the coordination of the nucleobase through any of the remaining positions except N3 and N9. For that purpose copper-oxalato skeletons were employed obtaining compounds $\{[Cu(ox)(H_2O)(3\text{-methyladenine-}\kappa N7)]\cdot H_2O\}_n$ and $[Cu(ox)(H_2O)_2(9\text{-methylguanine-}\kappa N7)]\cdot 2.5H_2O$ in which both nucleobases act as monodentate ligands through N7 that is the most frequent coordination metal binding pattern for both 3-methyladenine and 9-methylguanine ligands (Fig. 25) [62,70,71].

Compound $\{[Cu(ox)(H_2O)(3\text{-methyladenine-}\kappa N7)]\cdot H_2O\}_n$ shows again the presence of *zigzag* chains comprised of

Fig. 23. Hydrogen-bonded network (dashed lines) around the *7H*-adenine tautomer in compound $\{[Mn(\mu\text{-}ox)(H_2O)_2]\cdot(7H\text{-adenine})\cdot(H_2O)\}_n$ [67].

cis-$[Cu(H_2O)(3\text{-methyladenine-}\kappa N7)]^{2+}$ fragments joined by bisbidentate oxalato ligands (Fig. 23). In contrast, compound $[Cu(ox)(H_2O)_2(9\text{-methylguanine-}\kappa N7)]\cdot 2.5H_2O$ is comprised of discrete distorted square pyramidal complexes (A and B) in which the basal plane is occupied by a bidentate oxalato ligand, one water molecule, and the N7 site of the nucleobase. The apical position is occupied by the remaining water molecule. These monomeric complexes are held together establishing a complicated recognition process that involves, among others, the formation of a triple hydrogen bonding interaction between the adenine Watson–Crick face and the oxygen atoms of an adjacent unit that resembles the complementary guanine–cytosine molecular recognition pattern. This interaction is extended by additional hydrogen bonds to give rise to centrosymmetric metal-organic quartets which resembles the homonucleobase tetrameric aggregates (G4) presented in the guanine-rich zones of the multistranded nucleic acid structures. These tetrameric aggregates are further interconnected to give rise to infinite tapes.

Apart from the relevance of this work in a merely crystal design sense, 3-methyladenine is highly cytotoxic and mutagenic as a result of its ability to block DNA replication since the N3-methyl group protrudes into the minor groove of the DNA double helix and thereby stops replication [72]. So that, the design and structural analyses of coordination compounds containing this methylated adenine can supply useful information to understand the conformational damages induced by the N-alkylation of nucleobases in biological systems and the molecular recognition processes to repair them.

6.3. Hybrid systems based on metal-oxalato entities and protonated nuclebases

The metal-oxalato matrix has demonstrated a high efficiency not only to permit the covalent anchoring of nucleobases but also to embed supramolecular nucleobase architectures by means of molecular recognition processes involving non-covalent interactions such as those in the organic–inorganic hybrid compounds $(1H,9H\text{-adeninium})_2[Cu(ox)_2(H_2O)]$, $(3H,7H\text{-adeninium})_2[M(ox)_2(H_2O)_2]\cdot 2H_2O$ (M^{II} = Co, Zn) and
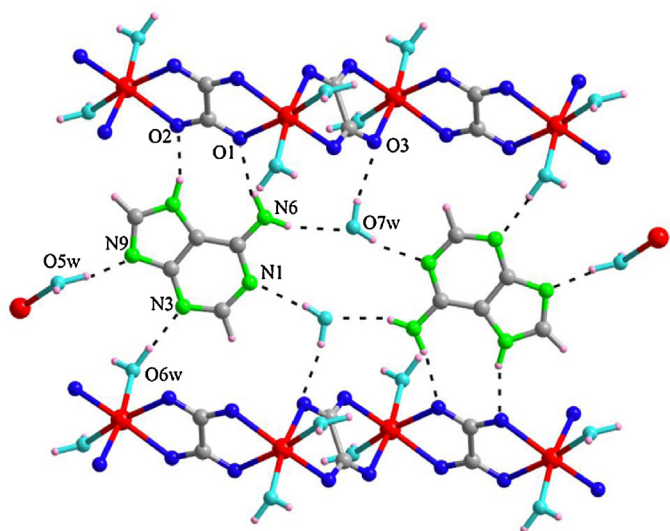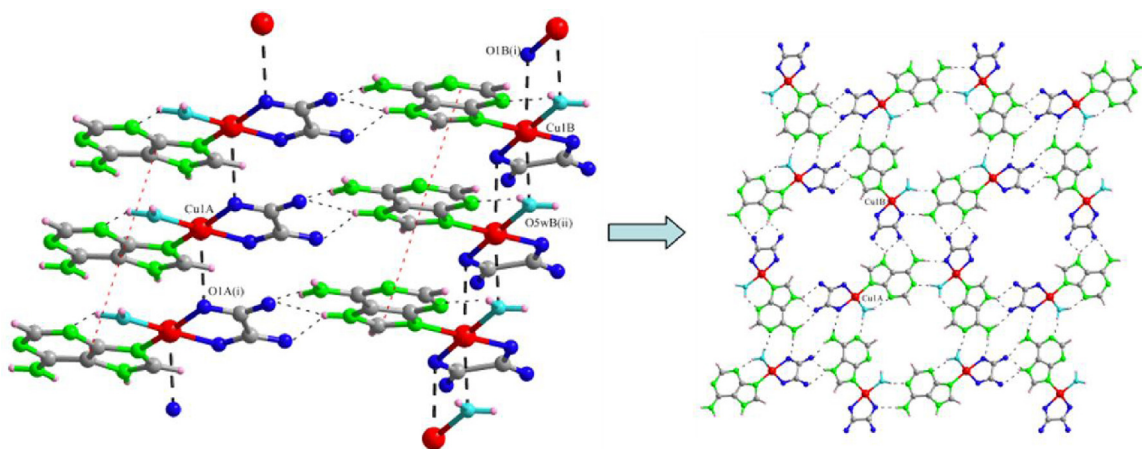
Fig. 24. One-dimensional chains and hydrogen bonding scheme in compound {[Cu(μ-ox)(H$_2$O)(7H-adenine-κN9)][Cu(μ-ox)(μ-OH$_2$)(7H-adenine-κN9)] ∼10/3H$_2$O}$_n$ [67].

(a)

(b)

Fig. 25. (a) Polymeric chain of compound {[Cu(ox)(H$_2$O)(3-methyladenine-κN7)]·H$_2$O}$_n$ and (b) infinite tapes of metal-organic quartets in compound [Cu(ox)(H$_2$O)$_2$(9-methylguanine-κN7)]·2.5H$_2$O.
Reproduced from Ref. [62]. Copyright (2011) Elsevier B.V.

(1H,3H-cytosinium)$_2$[M(ox)$_2$(H$_2$O)$_2$] (M^{II} = Mn, Co, Cu, Zn) [73,74]. In all the cases, the supramolecular architecture is quite similar and its overall crystal packing can be regarded as a lamellar network built up of anionic sheets of metal-oxalato-water complexes and cationic nucleobase layers sandwiched among them. Each wide organic layer serves as "double-sided adhesive tape" to tightly join adjacent inorganic layers by means of electrostatic forces and a strong hydrogen bonding network.
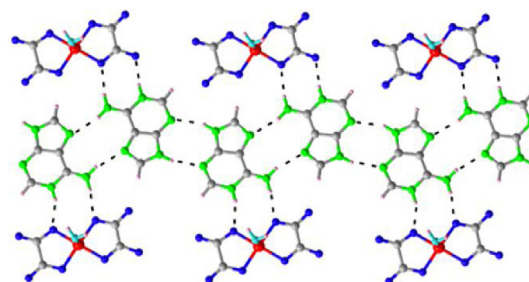
(a)
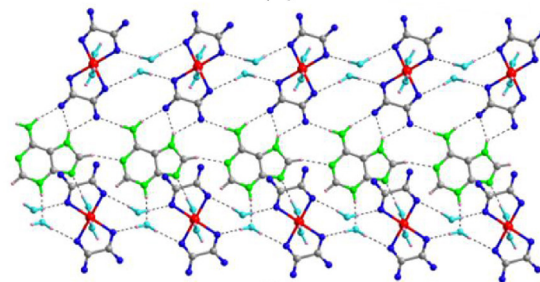
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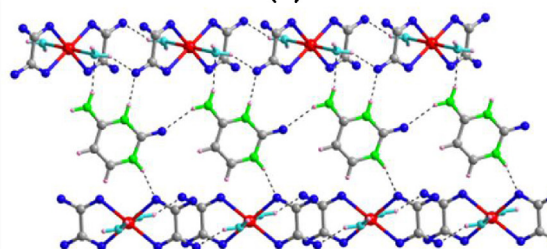
(c)

Fig. 26. Supramolecular surrounding of the protonated nucleabases in compounds (a) (1H,9H-adeninium)$_2$[Cu(ox)$_2$(H$_2$O)] [73], (b) (3H,7H-adeninium)$_2$[M(ox)$_2$(H$_2$O)$_2$]·2H$_2$O (M^{II} = Co, Zn) [73] and (c) (1H,3H-cytosinium)$_2$[M(ox)$_2$(H$_2$O)$_2$] (M^{II} = Mn, Co, Cu, Zn) [74].
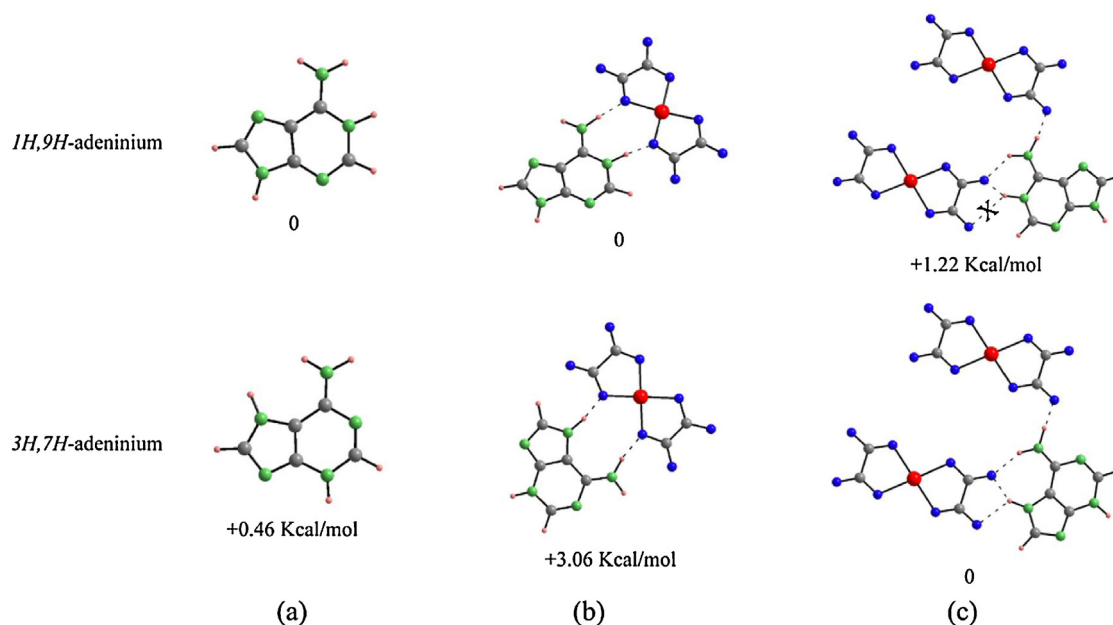
Fig. 27. Relative energies between the *1H,9H*- and *3H,7H*-adeninium forms for different environments: (a) gas phase, (b) interacting with a $[M(ox)_2]^{2-}$ fragment and (c) interacting simultaneously with two $[M(ox)_2]^{2-}$ fragments [73].

The supramolecular structure of these inorganic–organic hybrids is created by three types of molecular recognition: between complex anions, between cationic nucleobases, and between ribbons of nucleobases and layers consisting of oxalato-complexes (Fig. 26). Molecules of complexes located within the anionic layers are joined among them by hydrogen bonds. The interaction between the organic base molecules results in the hydrogen bonding recognition unit and leads to ribbon formation. Finally, the third group of hydrogen bonds completes the closely packed structure. The most interesting aspect of this family of compounds is that the metal-oxalato matrix exerts a decisive effect on the tautomerism of the nucleobase cations. In fact, compounds (*3H,7H*-adeninium)$_2$[M(ox)$_2$(H$_2$O)$_2$]·2H$_2$O (M^{II} = Co, Zn) represent the first solid-state characterized *3H,7H*-adeninium tautomer (CSD mining statistics and gas phase calculations indicate that the canonical form is *1H,9H*-adeninium).

DFT calculations for this compound including the presence of one $[M(ox)_2]^{2-}$ fragment in all of its possible dispositions around the adeninium cation show that the energy order of *1H,9H*- and *3H,7H*-tautomers is not altered. However, when two $[M(ox)_2]^{2-}$ fragments with the experimental disposition of compounds are included, the *3H,7H*-adeninium cation becomes the most stable (Fig. 27). This fact is due to the demanding conditions for an efficient hydrogen bonding interaction that are better fulfilled by the *3H,7H*-adeninium cation than by the *1H,9H*-form. The optimized *1H,9H*-adeninium entity establishes only three hydrogen bonds with the $[Cu(ox)_2]^{2-}$ fragments, indicating a less efficient hydrogen bonding stabilization.

7. Summary and perspective

Herein we have presented a complete overview of the preparation and properties of a series of metal–carboxylato–nucleobase architectures that range from supramolecular assemblies to 3D porous materials. In particular, we have taken advantage of the synthetic control over the three dicopper paddle-wheel entities built up from the adenine nucleobase and carboxylato ligands. These entities can further polymerize to obtain extended systems, connecting the dimeric entities either through the equatorial positions or/and by means of the axial positions.

The polymerization of the [Cu$_2$(μ-adenine)$_4$] entity was first achieved in the {[Cu$_2$(μ-adeninato)$_4$(H$_2$O)$_2$][Cu(ox)(H$_2$O)]$_2$}$_n$ compound, by means of the deprotonation of the adenine and its coordination to less sterically hindered [Cu(ox)(H$_2$O)] units. This building unit also allowed us to obtain a porous material, [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·∼2CH$_3$OH, based only on supramolecular interactions, with a high thermal stability and a computed accessible surface area of 790 m^2 g^{-1}.

The replacement of two adenine molecules by two dicarboxylato ligands led to a family of 3D metal-organic compounds based on [Cu$_2$(μ-adenine)$_2$(μ-dicarboxylato)$_2$] entities. This fact suggested us to use monocarboxylic acids, with which we obtained the corresponding isostructural series of compounds but with an accessible free volume. The adsorption measurements of these porous compounds demonstrated that the length of the aliphatic chain of the carboxylato ligands modifies the porosity of the open-framework structures. Additionally, the study of the adsorption selectivity of binary mixtures of CO$_2$/H$_2$ and CO/H$_2$ at 298 K carried out for these compounds shows that the selectivity towards CO$_2$ and CO can be tuned by changing the carboxylato ligand, increasing its value with increasing the length of the aliphatic chain.

In the light of these results, the next step of this research consists on preparing core–shell particles employing this family of MBioFs, starting from a core of a porous MBioF which will be covered with a thin layer of a compatible metal-organic compound. Moreover, there is work in progress to extrapolate the systems described in this work to other metal centres (Ni^{II}, Co^{II}, Zn^{II}, etc.), which may have higher thermal stability for a subsequent use in adsorption applications, as well as, expand this study to other purine bases (guanine, purine, hypoxanthine, xanthine, etc.) with ability to form analogous SBUs capable to generate novel MBioFs.

Another remarkable fact is the pronounced increase of microporosity achieved through the template effect of butanoic acid micelles in the reaction media of compound [Cu$_2$(μ_3-ade)$_2$(μ_2-OOC(CH$_2$)$_2$(CH$_3$)$_2$]$_n$, doubling the intrinsic adsorption capacity of the pristine crystal network. Thus, one of our research areas attempts to extrapolate this methodology to other systems.

In case of using [Cu$_2$(μ-carboxylate)$_4$] entity, long chain flexible dicarboxylate connectors promote the formation of one-dimensional metal-organic architectures, where methylated

adenine nucleobases decorate the axial positions of the paddle-wheel units. When these flexible linear ligands are replaced by rigid dicarboxylate connectors the structural variability can be directed towards extended systems of higher dimensionality.

On the other hand, the chelating nature of short chain dicarboxylic ligands, such as the oxalate and malonate anions, leads to substantially different structures. When the malonic acid is used, the pseudo paddle-wheel entities are obtained with Ni(II) and Co(II) salts. In the case of the oxalate ligand, two different families of compounds are achieved. When the adenine is in its neutral form, polymeric chains are obtained, whereas lamellar inorganic–organic compounds are achieved by using it as a cation.

Magnetic properties have also been analyzed for all the compounds reported. The magnitude of the antiferromagnetic coupling in the $[Cu_2(\mu\text{-adenine})_4]$ entities has been evaluated on the basis of different structural parameters. In the case of $[M_2(\mu\text{-adenine})_2(\mu\text{-carboxylato})_2]$ entities, the splitting order of the molecular magnetic orbitals is the same for each type of bridging ligand leading as a consequence to J values intermediate between the ones found for the non-mixed paddle-wheels. Surprisingly, in the case of $[M_2(\mu\text{-adenine})_2(\mu\text{-malonato})_2]$, (where M = Ni(II), Co(II)), the orbital countercomplementarity leads to ferromagnetic interactions.

Acknowledgements

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Paddle-Wheel Shaped Copper(II)-Adenine Discrete Entities As Supramolecular Building Blocks To Afford Porous Supramolecular Metal−Organic Frameworks (SMOFs)

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S *Supporting Information*

ABSTRACT: The present work assesses the ability of $[Cu_2(\mu\text{-adenine})_4(X)_2]^{2+}$ and $[Cu_2(\mu\text{-adenine})_2(\mu\text{-}X)_2(X)_2]$ (X: Cl^- or Br^-) metal-nucleobase dinuclear entities to build up supramolecular metal−organic frameworks (SupraMOFs) based on the complementary hydrogen bonding interactions established by the Watson−Crick and Hoogsteen faces of adjacent adenine moieties. The noncoplanar disposition of these synthons in the $[Cu_2(\mu\text{-adenine})_4(X)_2]^{2+}$ building unit leads to an open framework with one-dimensional (1D) channels of ca. 6 Å in compounds $[Cu_2(\mu\text{-adenine})_4(Cl)_2]\cdot Cl2\cdot\sim2MeOH$ (**1, SMOF-1**) and $[Cu_2(\mu\text{-adenine})_4(Br)_2]\cdot Br_2\cdot\sim2\ MeOH$ (**2, SMOF-2**) sustained through the hydrogen bonding base pairing interactions among the Watson−Crick faces. In the case of the second building unit, $[Cu_2(\mu\text{-adenine})_2(\mu\text{-}X)_2(X)_2]$, the coplanar arrangement of the two adenines in the dimeric unit does not allow a three-dimensional (3D) supramolecular architecture based only on the complementary hydrogen bonding interactions between the nucleobases. Therefore, other supramolecular interactions involving the halide ions and solvent molecules are crucial for determining the features of the crystal packing. In compound $[Cu_2(\mu\text{-adenine})_2(\mu\text{-Cl})_2(Cl)_2]\cdot2MeOH$ (**3, SMOF-3**), base pairing interactions between adjacent adenines produce 1D supramolecular ribbons of dinuclear entities. These ribbons establish additional hydrogen bonds between the Hoogsteen face and the chloride anions of adjacent ribbons that are also reinforced by the presence of $\pi−\pi$ stacking interactions among the adenines leading to a rigid synthon that gives rise to a robust 3D skeleton with the presence of micropores occupied by solvent molecules. In the case of the bromide analogue, the weaker hydrogen acceptor capacity of the bromide allows the solvent molecules to disrupt the self-assembly process of the dinuclear entities and prevents the formation of an open-framework supramolecular structure leading to the nonporous $[Cu_2(\mu\text{-adenine})_2(\mu\text{-Br})_2(Br)_2]\cdot2PrOH$ (**4**) compound. According to gas adsorption studies, **SMOF-1**, **SMOF-2**, and **SMOF-3** present a surface instability that creates a diffusion barrier that can be permeated only by strong interacting adsorbate molecules with high kinetic energy such as CO_2 but not N_2, H_2, and CH_4. This feature makes them attractive for selective gas adsorption and separation technologies.
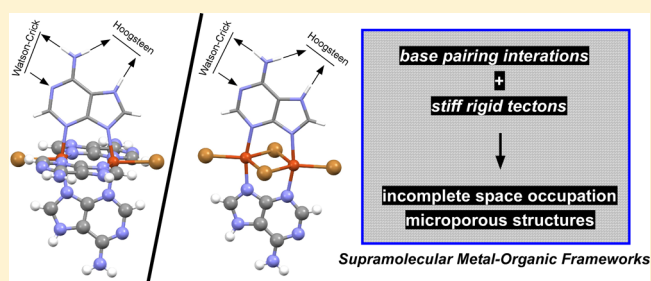
INTRODUCTION

The coordination chemistry of metal ion interactions with purine nucleobases has attracted enormous attention because of its biological relevance, structural diversity, molecular recognition behaviors, and potential applications as advanced functional materials.[1] Adenine (6-aminopurine) has a wide range of binding possibilities through the endocyclic N9, N7, N3, N1, and exocyclic N6 nitrogen atoms as donor sites[2] resulting in a vast number of products. Moreover, when a metal−adenine complex is formed, the noncoordinated nitrogen donor sites confer the ability to establish a wide variety of hydrogen bonding based supramolecular interactions.[3] On the other hand, the purine ligands are well-known for their ability

to build dinuclear complexes by means of the N3 and N9 bridging mode,[4] and previous works have demonstrated that either adenine or adeninate ligands tend to form paddle-wheel shaped dinuclear complexes, such as $[Cu_2(\mu\text{-adenine})_4]^{4+}$, $[Cu_2(\mu\text{-adeninato})_4]$, or $[Cu_2(\mu\text{-adeninato})_2(X)_2]$ (where X: $RCOO^-$, halide···).[5] These entities can self-assemble by means of the well-known base pairing of the Watson−Crick (N6−H, N1) and Hoogsteen faces (N6−H, N7) and by $\pi−\pi$ stacking interactions. Nonetheless, additional factors present in the

Scheme 1

$[Cu_2(\mu\text{-ade})_4(Cl)_2]Cl_2 \cdot \sim 2MeOH$ ← (1:2, MeOH) — (1:0.25, MeOH) → $[Cu_2(\mu\text{-ade})_2(\mu\text{-Cl})_2(Cl)_2] \cdot 2MeOH$

(1, SMOF-1) · · · **(3, SMOF-3)**

$\boxed{CuCl_2/CuBr_2 : \text{adenine}}$

$[Cu_2(\mu\text{-ade})_4(Br)_2]Br_2 \cdot \sim 2MeOH$ ← (1:4, MeOH) — (1:0.25, PrOH) → $[Cu_2(\mu\text{-ade})_2(\mu\text{-Br})_2(Br)_2] \cdot 2PrOH$

(2, SMOF-2) · · · **(4)**
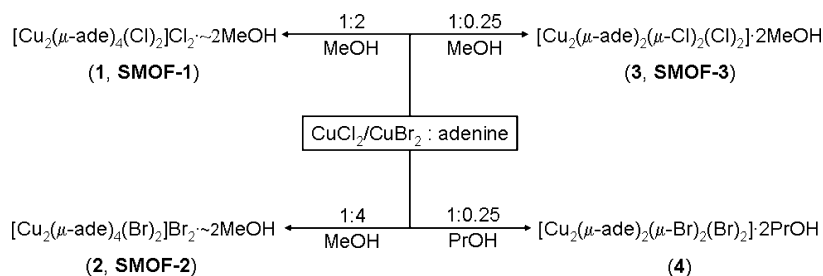
reaction media, such as interactions with solvent molecules or counterions, can disrupt the direct hydrogen bonding interactions between the nucleobases.[6]

On the basis of these facts, we have designed a synthetic strategy to develop rigid supramolecular open-networks showing permanent microporosity as an alternative to more conventional metal−organic frameworks (MOFs).[7] It deserves mentioning that examples of microporous compounds whose crystal structure is sustained by noncovalent interactions are scarce, mainly due to the difficulties inherent to the design of such systems and the usually assumed weakeness of the supramolecular connectivity.[8] Our approach is based on employing as supramolecular building blocks discrete metal−adenine complexes in which two or more nucleobases are tightly anchored to the metal centers by at least two donor positions (N3, N9 sites of the adenine in the present case). This coordination motif imposes a rigid structure to the building unit that is a key factor of our crystal design. In addition, the geometrical arrangement of the nucleobases around the metal centers is otherwise difficult to achieve for other systems such as organic molecules functionalized with adenine residues. In these discrete complexes, as many hydrogen donor/acceptor positions of the nucleobase remain free, the entities are able to self-assemble among them by means of rigid double or triple complementary hydrogen bonds. Due to the geometric restraints of the H-bonding synthons and of the metal-nucleobase complex itself, an efficient packing of the supramolecular building units is hindered allowing the presence of a large empty volume: an open-framework supramolecular crystal building. The voids will be usually occupied by solvent molecules, and as consequence, in order to achieve a compound with permanent porosity, the scheme of supramolecular interactions established among the metal-nucleobase entities must be strong enough to avoid the collapse of the crystal structure when the solvent is evacuated. This fact is the reason to select metal-nucleobase systems. The nucleobases self-recognize by double or triple hydrogen bonding ensuring a superior strength of the resulting supramolecular crystal building. The pioneering example that makes use of this strategy to provide a molecular porous material with formula $[Cu_2(\mu\text{-adenine})_4Cl_2]Cl_2$ was published by us in 2011.[9] Later, Zaworotko et al. reported an analogous compound replacing the chlorides by bulkier TiF_6^{2-} anions improving the chemical stability of the supramolecular network toward humidity.[10]

In this work we assess the ability of two types of metal-nucleobase dinuclear entities $[Cu_2(\mu\text{-adenine})_4(X)_2]^{2+}$ and $[Cu_2(\mu\text{-adenine})_2(\mu\text{-X})_2(X)_2]$ (where X: Cl^- or Br^-) to build up supramolecular metal−organic frameworks (SMOFs) based on base pairing interactions between either Watson−Crick faces or Hoogsteen faces. The control over the molecular structure of the dinuclear entities is easily achieved by means of the copper(II) halide/adenine ratio. As a result of the non-coplanarity of the adenines in $[Cu_2(\mu\text{-adenine})_4(X)_2]^{2+}$ entities, the base pairing sustained self-assembling process yields an open framework with one-dimensional (1D) channels occupied by methanol solvent molecules: $[Cu_2(\mu\text{-adenine})_4(Cl)_2]$-$Cl_2 \cdot \sim 2MeOH$ (1, SMOF-1) and $[Cu_2(\mu\text{-adenine})_4(Br)_2]Br_2$-$\cdot \sim 2MeOH$ (2, SMOF-2). Regarding $[Cu_2(\mu\text{-adenine})_2(\mu\text{-}X)_2(X)_2]$ dinuclear entity, compounds $[Cu_2(\mu\text{-adenine})_2(\mu\text{-}Cl)_2(Cl)_2] \cdot 2MeOH$ (3, SMOF-3) and $[Cu_2(\mu\text{-adenine})_2(\mu\text{-}Br)_2(Br)_2] \cdot 2PrOH$ (4) were yielded. In the latter cases, the coplanar arrangement of the adenines reduces the dimensionality of the supramolecular polymer obtained from the base pairing interactions. As a consequence, the coordinated halides and solvent molecules play a crucial role stabilizing the overall three-dimensional (3D) crystal structure. In the case of the chloride-based compound 3 (SMOF-3), the combination of base pairing, $\pi-\pi$ stacking, and additional hydrogen bonding interactions involving the chloride anions provides a rigid scheme of supramolecular interactions that precludes an efficient occupation of the space leading to a robust open-framework supramolecular structure. The weaker nature of the hydrogen bonds involving bromide anions allows the solvent molecules to disrupt the previously described supramolecular interaction scheme leading to nonporous compound 4. Even though previously reported N_2 adsorption experiments performed on samples of $[Cu_2(\mu\text{-adenine})_4(Cl)_2]Cl_2$ (SMOF-1)[11] did not show significant adsorption, the present work will prove the permanent porosity of SMOF-1, SMOF-2, and SMOF-3 compounds by means of CO_2 adsorption isotherms at 273 K. The different adsorption behavior is attributed to a surface instability, because of the air humidity, that creates a diffusion barrier that only can be permeated by well-suited adsorbates under specific adsorption conditions. Therefore, these compounds can be envisaged as potential materials for selective gas adsorption or separation purposes.

■ EXPERIMENTAL SECTION

Synthesis. All the chemicals were of reagent grade and were used as commercially obtained. The purity of the synthesized samples was checked by means of powder X-ray diffraction, along with the elemental and thermogravimetric analyses. Scheme 1 describes the most notorious synthesis conditions to afford compounds **1**−**4**.

$[Cu_2(\mu\text{-adenine})_4Br_2]Br_2 \sim 2MeOH$ (2, SMOF-2). A total of 0.0112 g of cupric bromide (0.05 mmol) dissolved in 5 mL of methanol was added dropwise to the hot stirring solution of 0.0273 g of adenine (0.2 mmol) dissolved in 30 mL of methanol at 50 °C. Immediately after the reagents were mixed, compound **2** precipitated as a blue polycrystalline product. Yield: 90%. Anal. Calcd (found) for $C_{22}H_{28}Br_4Cu_2N_{20}O_2$: C, 25.13 (25.24); H, 2.68 (2.81); N, 26.65 (26.53); Cu, 12.09 (11.97). IR (KBr, cm^{-1}): 3330s, 3170s, 1650vs, 1515w, 1460m, 1348w, 1320m, 1260w, 1215m, 1182w, 1148w,

Table 1. Single-Crystal Data and Structural Refinement Details of Compounds 2, 3, and 4

compound	2	3	4
formula	$C_{22}H_{28}Br_4Cu_2N_{20}O_2$	$C_{12}H_{18}Cl_4Cu_2N_{10}O_2$	$C_{16}H_{26}Br_4Cu_2N_{10}O_2$
MW [g mol^{-1}]	1051.36	603.24	837.19
crystal system	trigonal	monoclinic	monoclinic
space group	$R\bar{3}m$	$C2/c$	$P2_1/c$
a [Å]	27.1979(9)	22.2245(18)	9.1344(7)
b [Å]	27.1979(9)	13.8069(10)	11.0778(10)
c [Å]	15.4999(4)	7.0204(6)	13.0778(11)
α [°]	90	90	90
β [°]	90	108.280(6)	103.873(7)
γ [°]	120	90	90
V [Å^3]	9929.6(5)	2045.5(3)	1284.7(2)
Z	9	4	2
ρ_{calcd} (g·cm^{-3})	1.582	1.959	2.164
μ (mm^{-1})	4.630	2.636	7.912
reflections collected	31767	9439	18741
unique data/parameters	2837/109	9439/127	3059/161
R_{int}	0.0465	0.0695	0.0942
goodness of fit $(S)^a$	1.234	1.089	1.119
$R_1{}^b/wR_2{}^c$ $[I > 2\sigma(I)]$	0.0927/0.2997	0.0778/0.2048	0.0504/0.0927
$R_1{}^b/wR_2{}^c$ [all data]	0.1112/0.3107	0.1119/0.2342	0.0688/0.1005

$^a S = [\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}.$ $^b R_1 = \sum ||F_o| - |F_c||/\sum|F_o|.$ $^c wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2, 0) + 2Fc^2)/3$ with $a = 0.2000$ (**2**), 0.1437 (**3**), 0.0235 (**4**), and $b = 9.0683$ (**4**).

1117m, 1022w, 970w, 934w(sh), 922w(sh), 790m, 738m, 683w, 610w, 563w, 545m. Crystals suitable for single crystal X-ray diffraction studies were grown by using the slow diffusion of a methanolic solution (12 mL) of adenine (0.0111 g, 0.08 mmol) into a propanolic solution (12 mL) of cupric bromide (0.0088 g, 0.04 mmol). After 1 week, compound **2** crystallized as deep blue colored single crystals along with some poor quality red crystals of compound **4**.

[Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·~2MeOH (1, SMOF-1). Compound **1** was prepared following the synthetic method mentioned in one of our previous works.[11] A total of 0.0171 g of cupric chloride dihydrate (0.1 mmol) dissolved in 5 mL of methanol were added dropwise to a hot stirring solution (50 °C) of 0.0273 g of adenine (0.2 mmol) dissolved in 30 mL of methanol. A blue precipitate corresponding to compound **1** was formed immediately on the addition of the cupric chloride solution. Yield: 90%. Anal. Calcd (found) for C$_{22}$H$_{28}$Cl$_4$Cu$_2$N$_{20}$O$_2$: C, 30.25 (30.19); H, 3.23 (3.19); N, 32.07 (32.26); Cu, 14.55 (14.62). IR (KBr, cm^{-1}): 3360s; 3170s; 1650vs; 1515w; 1460m; 1400m; 1350w; 1320m; 1210m; 1110w; 785w; 740w; 550m.

[Cu$_2$(μ-adenine)$_2$(μ-Cl)$_2$(Cl)$_2$]·2MeOH (3, SMOF-3). A total of 0.0682 g of cupric chloride dihydrate (0.4 mmol) dissolved in 10 mL of methanol were added dropwise to a hot stirring solution (50 °C) of 0.0136 g of adenine (0.1 mmol) dissolved in 20 mL of methanol and stirred for half an hour. After the reagents were mixed, compound **3** appeared as a green precipitate. Yield: 95%. Anal. Calcd (found) for C$_{12}$H$_{18}$Cl$_4$Cu$_2$N$_{10}$O$_2$: C, 23.89 (23.92); H, 3.01 (3.14); N, 23.22 (23.18); Cu, 21.07 (21.03). IR (KBr, cm^{-1}): 3387s, 3142s(sh), 3103s(sh), 1666vs, 1611m, 1580m, 1520m, 1478m, 1450s, 1404vs, 1383w, 1356w(sh), 1347w(sh), 1318vs, 1262w, 1244w, 1215m, 1291w, 1170m, 1111vs, 1016w, 976w(sh), 970w(sh), 931m, 788m, 737m(sh), 722m(sh), 680m, 633w, 597m, 573w, 548s. Single crystals were obtained by slow diffusion of a methanolic solution (10 mL) 0.0171 g of cupric chloride (0.1 mmol) into another methanolic solution (30 mL) containing 0.0277 g of adenine (0.2 mmol) and 16.9 μL of concentrated hydrochloric acid (37%). Green-colored single crystals of compound **3** were formed along with blue colored crystals of compound **1**.

[Cu$_2$(μ-adenine)$_2$(μ-Br)$_2$(Br)$_2$]·2PrOH (4). A hot propanolic solution (40 mL, 50 °C) of 0.0136 g of adenine (0.1 mmol) was added dropwise to a second propanolic solution (10 mL) of 0.0893 g of cupric bromide (0.4 mmol). Immediately, an unidentified brown precipitate appears. The reaction mixture was left stirring for half an

hour. Afterward the precipitate is collected by filtration, and the mother-liquid solution is left evaporating at room conditions. One month later, red crystals of compound **4** are obtained. Yield: 20%. Anal. Calcd (found) for C$_{16}$H$_{26}$Br$_4$Cu$_2$N$_{10}$O$_2$: C, 22.96 (22.91); H, 3.13 (3.09); N, 16.73 (16.78); Cu, 15.18 (15.15). IR (KBr, cm^{-1}): 3380s, 3226s,3293s, 3240s, 3193s, 3130s, 2953s, 1666vs, 1612m, 1476w, 1460w, 1405m, 1384w, 1357w, 1344w, 1320s, 1262w, 1220m, 1175w, 1112m, 1050w, 1002s, 972w, 930w, 875m, 802w, 876m, 736m, 711w, 677w, 663w, 613m, 569m, 538w, 472w, 463w.

Physical Measurements. Elemental analyses (C, H, N) were performed on an Euro EA elemental analyzer, whereas the metal content was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) from Horiba Yobin Yvon Activa. The IR spectra (KBr pellets) were recorded on a FTIR 8400S Shimadzu spectrometer in the 4000−400 cm^{-1} spectral region. Thermal analyses (TG/DTA) were performed on a TA Instruments SDT 2960 thermal analyzer in a synthetic air atmosphere (79% N$_2$/ 21% O$_2$) with a heating rate of 5 °C·min^{-1}. Prior to gas adsorption measurements all samples were activated in vacuum at 100−180 °C for 6−24 h. Lower and greater activation temperatures did not result in samples with higher gas uptake capacity. The powder X-ray diffraction patterns on the outgassed samples showed that the structure remains stable without loss of crystallinity. Nitrogen physisorption data were recorded with a Quantachrome QUADRASORB-SI-MP at 77 K. The specific surface area was calculated from the adsorption branch in the relative pressure interval from 0.01 to 0.10 using the Brunauer−Emmett−Teller (BET) method. Volumetric carbon dioxide and hydrogen physisorption data were recorded at 273 K on a Quantachrome Autosorb-iQ-MP and at 77 K on a Quantachrome Autosorb-1C (purity of hydrogen: 99.999%).

X-ray Diffraction Data Collection and Structure Determination. The single crystal X-ray diffraction data collections were done at 293(2) K for compound **2** and at 100(2) K for compounds **3** and **4** on an Oxford Diffraction Xcalibur diffractometer with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). The data reduction was done with the CrysAlisPro program.[12] All the structures were solved by direct methods using the SIR92 program[13] and refined by full-matrix least-squares on F^2 including all reflections (SHELXL97).[14] All calculations for these structures were performed using the WINGX crystallographic software package.[15] After the initial structure solution was completed, the difference Fourier map for
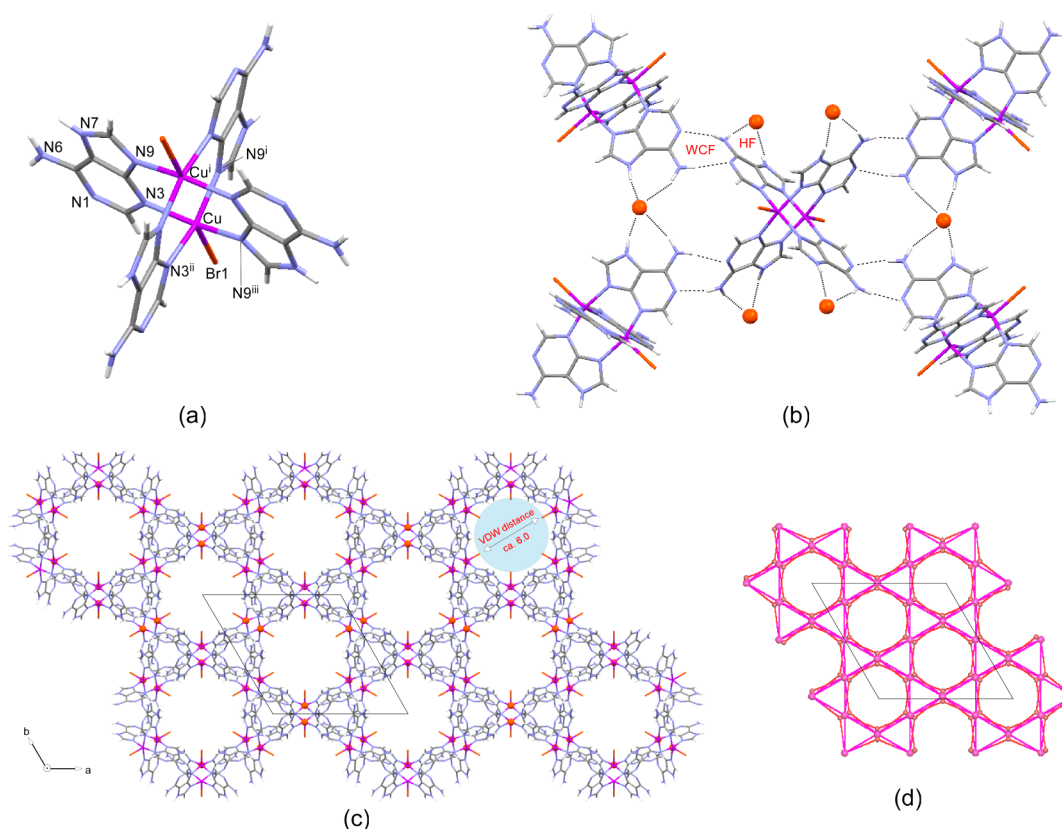
Figure 1. Crystal structure features of **SMOF-2**: (a) Structural units with the atomic numbering scheme. (b) Details of the adenine base pairing interaction through the Watson−Crick face (WCF) and of the Hoogsteen Face (HF) mediated adenine···bromide interaction (free bromide anions are represented as orange spheres). (c) Perspective view of the 3D framework along the c-axis showing the pores. Solvated methanol molecules are omitted for clarity. (d) Network topology.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Compounds 2, 3, and 4[a]

compound **2**			compound **3** (X = Cl)	compound **4** (X = Br)
Cu−N3	1.994(5)	Cu−N3[i]	2.006(4)	1.963(5)
Cu−N9[i]	2.016(6)	Cu−N9	1.983(4)	1.962(5)
Cu−Br1	3.080(2)	Cu−X1	2.241(1)	2.378(1)
		Cu−X2	2.342(1)	2.540(1)
		Cu−X2[i]	2.757(1)	2.656(1)
Cu···Cu[i]	3.082(1)	Cu···Cu[i]	2.942(1)	2.902(1)
N3−Cu−N3[ii]	88.1(3)	N3[i]−Cu−N9	164.83(17)	165.8(2)
N3−Cu−N9[i]	86.5(2)	N3[i]−Cu−X1	96.71(13)	98.02(14)
N3−Cu−N9[iii]	161.6(3)	N3[i]−Cu−X2	87.19(14)	87.23(14)
N3−Cu−Br1	100.2(2)	N3[i]−Cu−X2[i]	83.77(13)	86.58(13)
N9[i]−Cu−N9[iii]	93.1(3)	N9−Cu−X1	94.32(13)	95.56(14)
N9[i]−Cu−Br1	98.0(2)	N9−Cu−X2	87.19(14)	86.78(14)
		N9−Cu−X2[i]	83.21(13)	83.73(14)
		X1-Cu−X2	144.00(6)	132.35(3)
		X1−Cu−X2[i]	105.81(6)	115.45(3)
		X2−Cu−X2[i]	110.07(4)	112.12(3)

[a]Symmetry codes. Compound **2**: (i) $x−y$, $−y$, $−z+2$; (ii) $−x+y+1$, y, z; (iii) $−x+1$, $−y$, $−z+2$. Compound **3**: (i) $−x+1/2$, $−y+1/2$, $−z+1$. Compound **4**: (i) $−x+1$, $−y$, $−z+2$.

compound **SMOF-2** showed the presence of substantial electron density at the voids of the crystal structure that was impossible to model. Therefore, its contribution was subtracted from the reflection data by the SQUEEZE method[16] as implemented in PLATON.[17] Crystal parameters and details of the final refinements of compounds **2**, **3**, and **4** are summarized in Table 1. The X-ray powder diffraction (PXRD) patterns for polycrystalline samples were collected on a Phillips X'PERT powder diffractometer with Cu−Kα radiation (λ =

1.54060 Å) over the range $5 < 2\theta < 70°$ with a step size of 0.02° and an acquisition time of 2 s per step at 20 °C.

■ **RESULTS AND DISCUSSION**

Structural Description of [Cu$_2$(μ-adenine)$_4$Br$_2$]Br$_2$·∼2MeOH (2, SMOF-2). This compound is isostructural to compound **1** (**SMOF-1**) whose crystal structure has been previously reported by us.[11] The crystal structure consists of

(a)

(b)

(c)

(d)

(e)
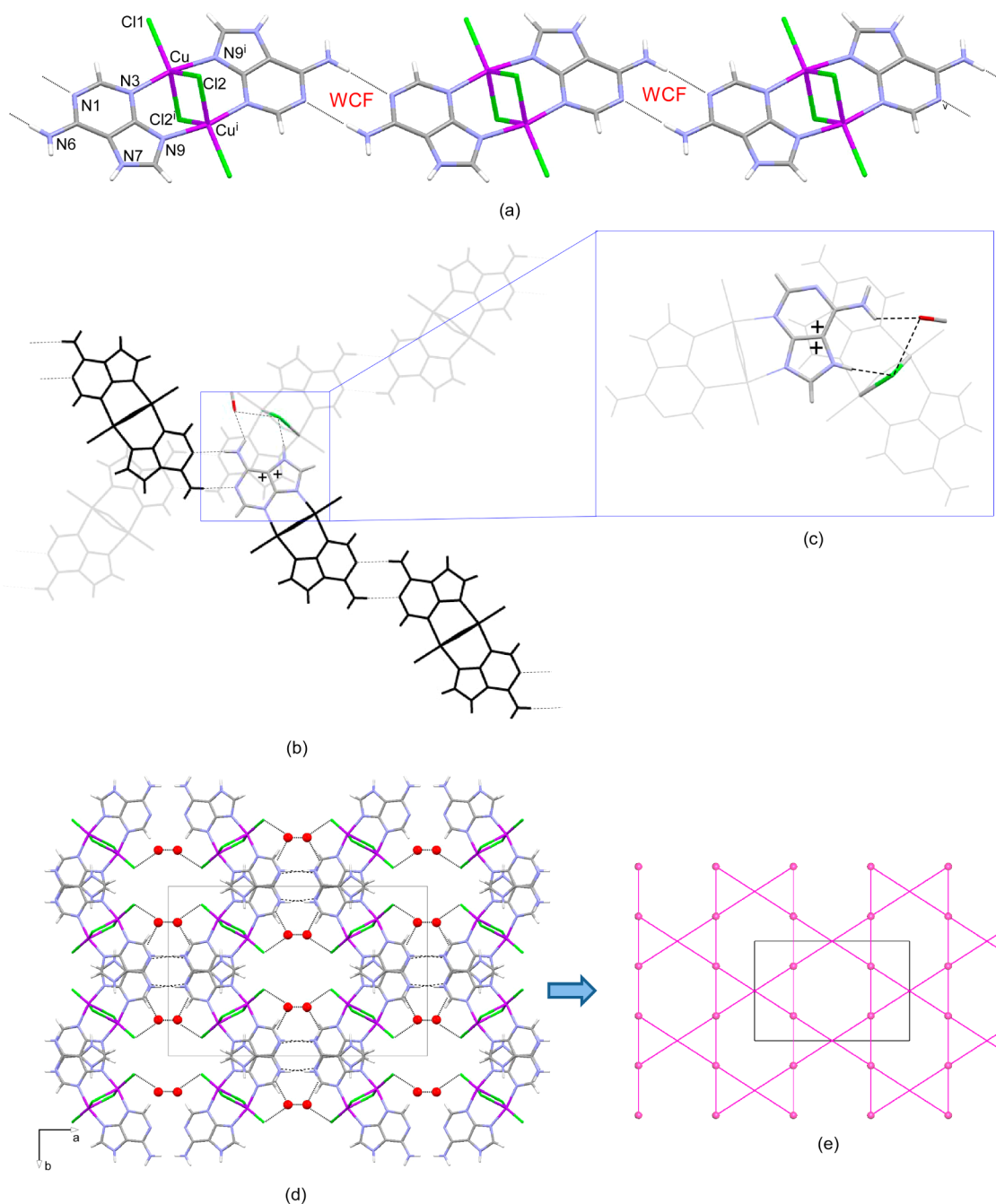
Figure 2. Crystal packing features in **SMOF-3**: (a) Strips of $[Cu_2(\mu\text{-adenine})_2(\mu\text{-Cl})_2Cl_2]$ dinuclear complexes grown by Watson−Crick base pairing interactions. (b, c) Dinuclear entities interacting through Cl···Hoogsteen face and $\pi-\pi$ interactions and the methanol hydrogen bonding mediating role. (d, e) View of the crystal packing along $[1\,0\,0]$ direction and overall supramolecular conectivity. Dashed lines indicate hydrogen bonds, while double plus signals represent $\pi-\pi$ interactions.

paddle-wheel like $[Cu_2(\mu\text{-adenine})_4Br_2]^{2+}$ complexes, bromide counterions, and disordered methanol molecules. Figure 1 shows a perspective view of the dimeric entity together with the labeling scheme which is conventionally accepted for the adenine nucleobase for chemical and biological purposes, while coordination bonds and angles are gathered in Table 2. Four bridging adenine molecules are linked to the copper(II) atoms through their N3 and N9 nitrogen atoms to provide the core of the paddle-wheel shaped dinuclear entity. Two bromide anions occupy the apical positions resulting in an elongated square pyramidal coordination environment of the metal centers. The dimeric complex is sited on a $2/m$ crystallographic position and

shows a UUDD conformation, referring the terms U(up) or D(down) to the coordination of each pyrimidinic N3 atoms to the upper or lower metal center.

The $[Cu_2(\mu\text{-adenine})_4Br_2]^{2+}$ dinuclear entities are cross-linked together by pairs of symmetry-related N6−H···N1 hydrogen bonding interactions between the Watson−Crick faces of two adjacent nucleobases to give a $R_2^2(8)$ ring. It deserves mentioning that this hydrogen bonding interaction scheme is a well-known structural synthon between self-assembling adenines.[5f,18] In the present compound the geometry and rigidity of the $[Cu_2(\mu\text{-adenine})_4Br_2]^{2+}$ entity (Figure 1) and the rigidity of the previously described hydrogen

bonding synthon make it suitable to assemble in such a way that it generates an open-supramolecular-framework because of the inefficient occupation of the space. This synthon involving the Watson−Crick faces yields by itself a four-connected uninodal 3D net with **nbo** topology and $(6^4.8^2)$ point symbol (Figure 1d).[19] However, the cohesion of the structure is further strengthen by $R_2^1(7)$ type hydrogen bonding interaction established among the free bromide counterions and the Hoogsteen faces of two adenine of neighboring complexes. Considering both types of interactions (Watson−Crick base pairing and Hoogsteen···bromide) the supramolecular network can be alternatively described as an eight-connected uninodal with **reo** topology and $(3^8.4^8.5^8.6^4)$ point symbol.

The resulting porous structure consists of 1D tubular channels that run along the crystallographic c axis with a diameter of 6.0 Å (distance among van der Waals surfaces of opposite chloride anions). These channels represent the 30% of crystal total volume,[20] and they are occupied by solvent methanol molecules in a highly disordered manner. Due to the greater size of bromide anion, these values are somewhat lower than those found in the chloride derivative (**SMOF-1**; pore diameter: 6.3 Å; accessible volume: 36%).

Structural Description of $[Cu_2(\mu$-adenine$)_2(\mu$-Cl$)_2$(Cl$)_2]\cdot$ 2MeOH (3, SMOF-3) and $[Cu_2(\mu$-adenine$)_2(\mu$-Br$)_2$(Br$)_2]\cdot$ 2PrOH (4). Both compounds are comprised of neutral centrosymmetric dimeric $[Cu_2(\mu$-adenine$)_2(\mu$-X$)_2$(X$)_2]$ entities (X: Cl$^-$, Br$^-$) (Figure 2). It shows some resemblances to the previously described $[Cu_2(\mu$-adenine$)_4$X$_2]^{2+}$ dimeric entity of **SMOF-1** and **SMOF-2**. The overall paddle-wheel shape is retained, but two opposite adenine ligands have been replaced by two bridging halide anions giving rise to a neutral dimeric entity showing an UD conformation with regard to the adenine bridges and two capping halide anions. The intradimeric Cu···Cu distances (2.942(1) and 2.902(1) Å, for chloride and bromide analogues) are slightly shorter than that of **SMOF-1** and **-2** (3.064(1) and 3.082(1) Å). Each copper atom is pentacoordinated by a N$_2$X$_3$ donor set which resembles a compressed trigonal bipyramid. The equatorial plane consists of three halide atoms implying longer bond distances than the apical ones (Table 2) and X−Cu−X angles within the range of 106−144° and a deviation of ca. 0.05 Å for the Cu(II) atom. The apical positions are occupied by the N3 and N9 donor sites of two symmetry related adenine molecules with a N−Cu−N angle of ca. 165° and an angle between equatorial plane and Cu−N bond of 83−86°. The coordination bond distances of the bridging halide anions are slightly longer than those of the terminal one as usually happens.

Obviously, the coplanar arrangement of adenines in the dimeric $[Cu_2(\mu$-adenine$)_2(\mu$-X$)_2$(X$)_2]$ entity although does not preclude the polymerization through direct complementary hydrogen bonding interactions between the nucleobases reduces the dimensionality of the resulting supramolecular network. In the case of **SMOF-3**, the base pairing interaction between the Watson−Crick faces of $[Cu_2(\mu$-adenine$)_2(\mu$-Cl$)_2$(Cl$)_2]$ units gives rise to linear 1D supramolecular ribbons (Figure 2a) that spread along two different crystallographic directions [1 1 0] and [1 $\bar{1}$ 0]. These supramolecular ribbons are further cross-linked by means of both the hydrogen-bonding interactions between the Hoogsteen face and the bridging chloride and π−π stacking interactions between adjacent adenines. The combination of the latter two types of interactions leads also to a relatively rigid synthon that extends the connectivity toward a robust supramolecular 3D one and, at

the same time, precludes an efficient occupation of the space (Figure 2d). Considering both types of synthons (Watson−Crick base pairing and Hoogsteen···chloride/π−π stacking) the supramolecular network can be described as a six-connected uninodal net with **rob** topology and $(4^8.6^6.8)$ point symbol (Figure 2e). This packing generates 1D channels along the crystallographic c axis with an elliptical cross-section of ca. 5.5 × 7.5 Å, that are filled by solvation water molecules that represent a 21% of the total volume. Again, the combination of rigid metal-nucleobase building unit and geometrically restricted supramolecular synthons leads to an ineffective space occupation providing accessible space within the crystal structure of this material. It is worthy to mention that the hydrogen bonding interaction between the Hoogsteen side of the adenine and the chloride anion is reinforced by an indirect hydrogen bonded interaction mediated by a solvation methanol molecule that will involve, as it is discussed later, a relatively significant unit cell change upon the removal of the solvent molecules.

The weaker hydrogen bond acceptor nature of the bromide anion in comparison to chloride makes the crystal packing features of compound **4**, $[Cu_2(\mu$-adenine$)_2(\mu$-Br$)_2$(Br$)_2]\cdot$ 2PrOH (Figure 3), to be essentially different from that of its

(a)

(b)
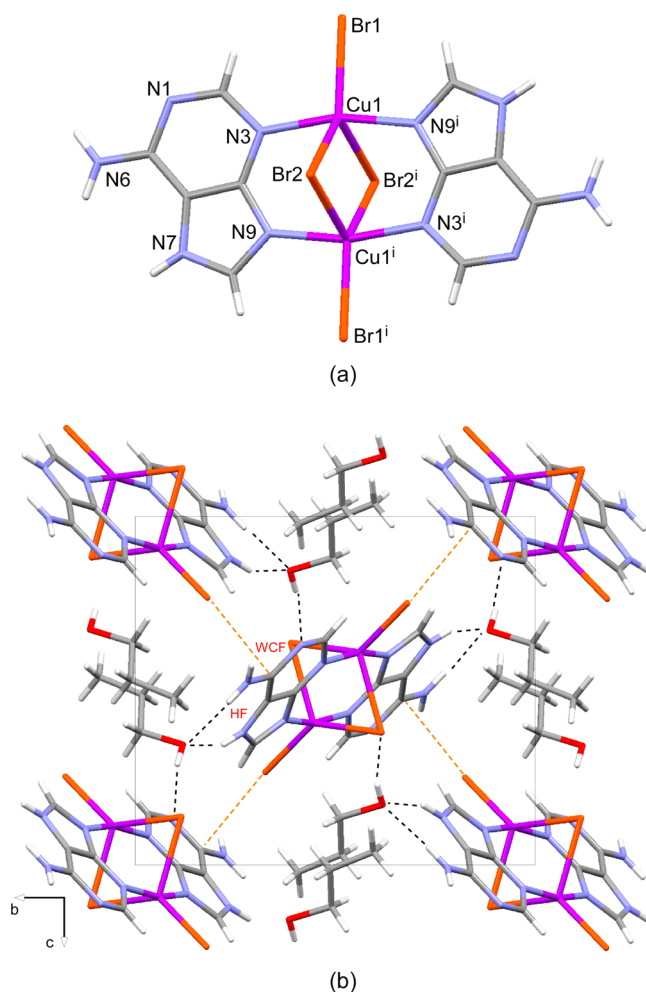
Figure 3. Dimeric unit (a) and view of the crystal packing along [1 0 0] direction (b) in compound **4**. Black dotted lines indicate hydrogen bonding interactions, while orange dashed lines indicate halide···π contacts.

chloride analogue (**SMOF-3**). It does not present base pairing interaction nor any other direct hydrogen bonding interaction between the adenine moieties and coordinated halides. In fact, the dinuclear entities are held together by the hydrogen bonding interactions mediated through the entrapped propan-1-ol molecules with the Hoogsteen and Watson–Crick faces of adjacent paddle-wheel entities. The Hoogsteen face of the nucleobase forms hydrogen bonding with the oxygen atom of the propan-1-ol molecule ($R_2^1(7)$ hydrogen bonded ring), while the Watson–Crick face of the adenine establishes a single hydrogen bond by means of the interaction of N1 with H atom of the alcohol group. The supramolecular interaction network of compound **4** is further reinforced by halide⋯π type interactions established between the terminal Br1 atoms and C6 carbon of the adenine (Br1⋯C6:3.489 Å). The lack of direct hydrogen bonding interactions among the rigid adenine moieties and the solvent mediated disruption of the hydrogen bonding network result in a nonporous crystal structure which collapses at temperatures close to 50 °C rendering an amorphous product, according to the thermogravimetric and variable temperature PXRD measurements.

Gas Adsorption Experiments on $[Cu_2(\mu$-adenine$)_2(Cl)_2]Cl_2\cdot\sim$2MeOH (SMOF-1) and $[Cu_2(\mu$-adenine$)_2(Br)_2]Br_2\cdot\sim$2MeOH (SMOF-2). Prior to gas adsorption experiments, thermal stability of both SMOFs was assessed by means of thermogravimetric and variable temperature PXRD experiments (see Supporting Information). According to the thermogravimetric data of both compounds, release of the solvent molecules hosted in the channels takes place between room temperature and 100 °C. In both cases the resulting compound remains stable up to 220 °C and the PXRD patterns at different temperatures (Figure 4a,b) do not differ substantially from that of the starting material, suggesting that the 3D open framework is retained after the removal of the methanol molecules. Above this temperature, it undergoes successive exothermic processes leading to CuO as final residue above 500 °C.

Freshly synthesized single crystals of **SMOF-1** and **-2** were used for gas adsorption experiments, and they were activated under a vacuum at temperatures ranging from 100 to 180 °C during 6–24 h to eliminate solvent guest molecules prior to measurements. Different outgassing conditions did not exert significant changes in N_2 uptake capacity. For clarity only the results of samples outgassed at 150 °C during 12 h are shown in subsequent figures. The adsorption curve collected at 77 K exhibits features resulting from multilayer adsorption. The fitting of the adsorption area to BET equation leads to surface area values of 26 and 14 m²/g, respectively. These values are substantially smaller than the surface area calculated from the BET fittings on GCMC simulated N_2 adsorption isotherms (767 and 654 m²/g, respectively), see details at the Supporting Information. Thereafter, H_2 adsorption experiments were also carried out by collecting isotherms at 77 K. Similarly to N_2, a negligible adsorption is observed for both compounds. A common explanation to such a difference between the experimental and expected porosity includes incomplete solvent removal, crystal collapse, or a massive presence of impurities. However, the weight loss of the outgassed sample fits the one expected from the compound formula, which suggests a quantitative removal of the solvent. The PXRD data confirms that the outgassed sample retains its crystallinity and, therefore, its bulk porous framework. Finally, the comparison of PXRD patterns, chemical analysis, and scanning electron

(a)

(b)

(c)

T (°C)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)
30	22.962(1)	13.668(1)	7.184(1)	90	108.47(1)	90	2138.5(1)
60	21.657(1)	13.393(1)	7.096(1)	90	90	107.65(1)	1961.3(1)
90	21.643(1)	12.859(1)	7.391(1)	90	90	101.16(1)	2018.0(1)
120	21.631(1)	12.935(1)	7.440(1)	90	90	101.51(1)	2040.0(1)
150	21.559(1)	12.915(1)	7.135(1)	90	90	101.69(1)	1945.4(1)
180	21.639(1)	12.764(1)	7.725(1)	90	90	100.95(1)	2094.8(1)
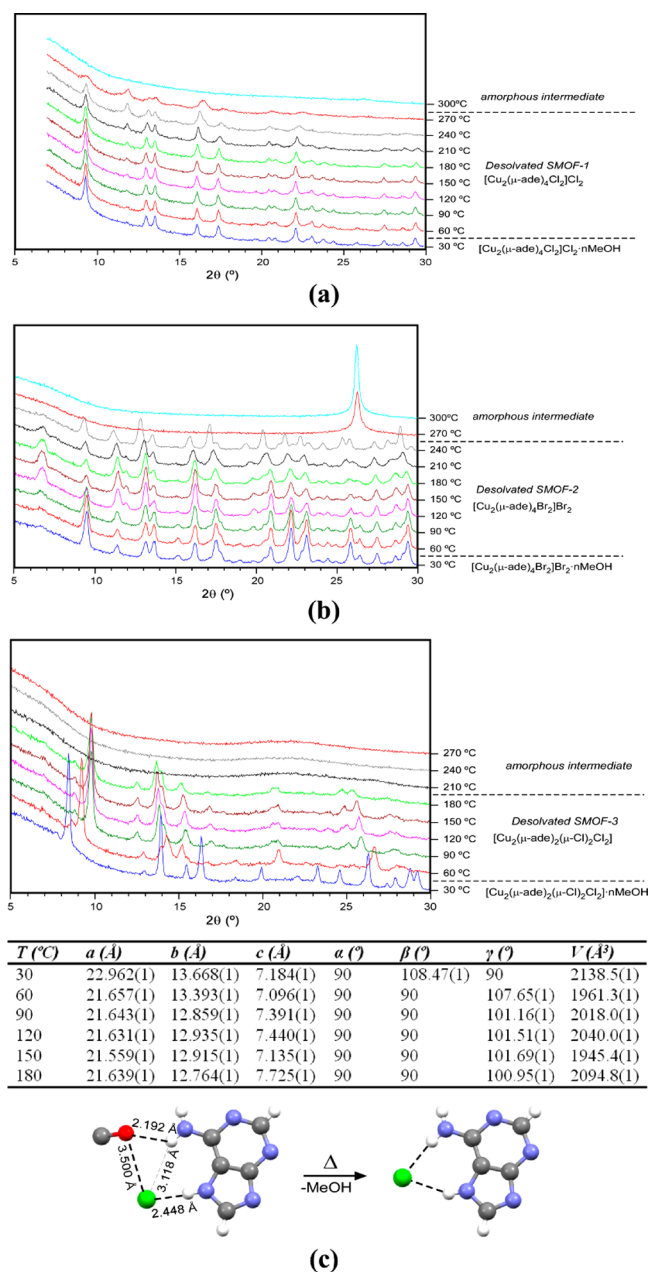
Figure 4. Thermodiffractometric data of (a) **SMOF-1**, (b) **SMOF-2**, and (c) **SMOF-3**.

microscopy data on the fresh and outgassed samples allowed to rule out the presence of a substantial amount of impurities.

In a recent work Matzger and co-workers explained the discrepancies between crystallographic porosity and experimental gas uptake for Zn-HKUST-1 based on positron annihilation lifetime spectroscopy.[21] The authors state that the lack of gas uptake is due to the inherent surface instability after solvent removal which renders the material impermeable to molecular guests irrespective of the handling and activation methods used in the gas adsorption experiments. However, according to the latter work, the surface collapse is overcome when the sample is immersed in a solvent, and thus the porous network is well accessible.

Nonetheless, the present SMOFs have been shown to behave as an adsorbent when they were exposed to the vapors of methanol, acetone, dichloromethane, tetrachloromethane, and

water.[11] Thus, it seems that the above-described diffusion barrier resulting from the surface instability is not only overcome in solution but also when adsorbate molecules in the gas phase have enough interaction energy to pass through. In order to get further evidence on the latter statement herein we have carried gas adsorption measurements at higher temperatures by collecting the isotherms for CO_2 at 273 K and CH_4 at 298 K (Figure 5). Similarly to the previous
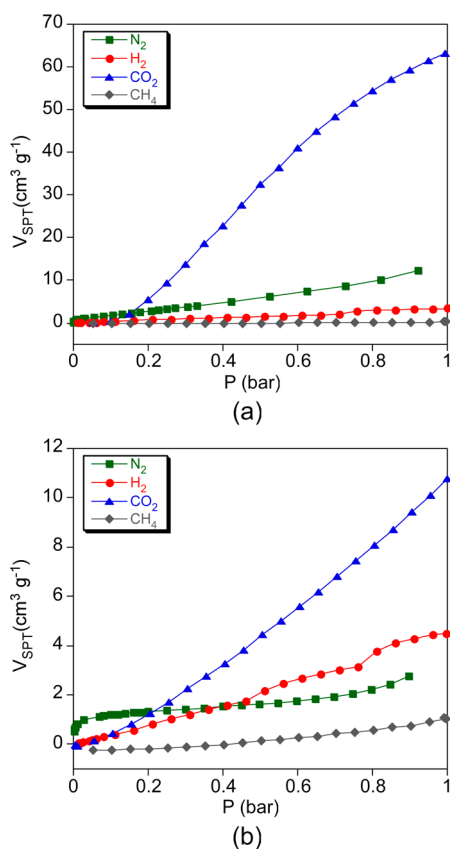
Figure 5. Adsorption isotherms for N_2 (77K), H_2 (77K), CO_2 (273 K), and CH_4 (298 K) for fresh samples of **SMOF-1** (a) and **-2** (b).

Figure 6. (a) CO_2 adsorption/desorption isotherms measured at 273 K showing the aging of **SMOF-1**. (b) CO_2 isotherms at 273 and 298 K. The onset pressure value is indicated for each case.

adsorbates methane adsorption is not observed. However, the CO_2 uptake shows a notable increase in both compounds. In fact while at pressures close to saturation, the N_2 uptake is 0.54 and 0.12 mmol/g for compounds **SMOF-1** and **-2**, and the CO_2 uptake increases about four times to reach values of 2.81 and 0.48 mmol/g, respectively. Considering the latter results this behavior can be rationalized on the basis of the thermal energy and of the polar nature of the adsorbate. The apolar CH_4 lacks of quadrupole moment, while CO_2 presents a relatively strong quadrupole moment (-0.8908 e·Å^2), sustantially greater than that for N_2 or H_2 (-0.2946 and $+0.1288$ e·Å^2, respectively).[22] Methane has not been able to permeate the surface although the increase of the adsorption temperature. Nonetheless, the higher measurement temperature and the stronger quadrupole moment of CO_2 confer the ability to diffuse through the surface barrier and permeate the porous network.

An additional proof that supports the hypothesis of the surface instability of these compounds is obtained from the gas adsorption study of the sample aging. In this regard, CO_2 measurements were carried out periodically during a month on samples of **SMOF-1** stored at room conditions (Figure 6a). It

becomes clear that the CO_2 uptake capacity decreases progressively as the sample becomes older, and after a month the uptake at $P = 1$ bar is depleted in a ca. 60% when compared to its initial value ($V_{STP} = 63.3$ and 24.4 cm^{3}g^{-1} for the initial and one month aged sample). A second phenomenon related with the sample aging is the adsorption onset pressure calculated from the intersection between the tangents at the low pressure region and at the region of maximum slope of the adsorption branch (see Supporting Information). The adsorption of the initial sample shows a plateau with a negligible CO_2 uptake at pressures below 0.1 bar, and it requires a minimum breakthrough pressure (P_{onset}: 0.15 bar) to permeate the surface and reach the porous network. Moreover, the breakthrough pressure is shift to higher values as the sample gets older, to reach an onset value of $P_{onset} = 0.38$ bar for the sample aged during 1 month. This progressive increase of the breakthrough pressure is related with increase of the thickness of the collapsed surface which acts as a surface permeation barrier. Another feature that supports the presence of a surface barrier that hinders the diffusion of the molecules is related to the hysteresis cycle enclosed by desorption branch and its trend with the aging of the sample (Figure 6a). It is noteworthy that even though different equilibration times were used the hysteresis cycle was not affected, and as consequence, this hysteresis seems to be induced by structural features of the

sample. In fact, the hysteresis becomes more acute as the sample is aged, and its end-pressure is delayed also progressively (P_{end}: 0.05 and 0.02 bar for fresh and one month aged samples, respectively). This behavior is also congruent with an increasing thickness of the collapsed surface (or diffusion barrier) as the storage time goes on, which would also obstruct the release of the adsorbed molecules during the desorption process.

On the other hand, comparison between adsorption experiments carried out at 273 and 298 K samples similarly aged (Figure 6b) shows that the onset pressure (0.35 and 0.31 bar, respectively) is reduced with the increase of the experiment temperature, as the potential energy of the molecules to permeate the surface is increased.

In order to analyze the bulk crystal stability during CO_2 adsorption PXRD patterns where collected in a sample subjected to a CO_2 atmosphere with pressure ranging between 0.5 and 6 bar. Prior to the experiment the sample was outgassed at 150 °C during several hours. As it can be observed (Figure 7)
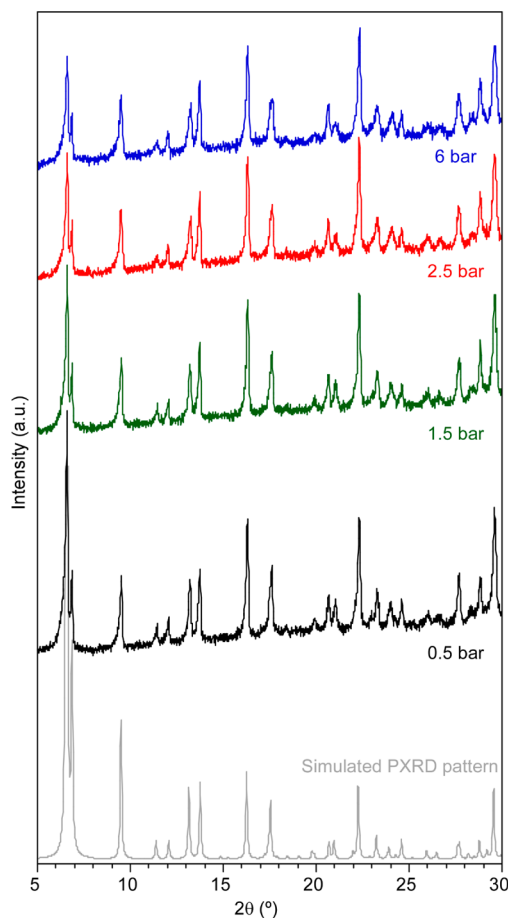
Figure 7. Comparison between experimental PXRD patterns collected at different CO_2 pressures and simulated PXRD pattern for the pristine crystal structure of **SMOF-1**.

all the experimental reflections match the ones corresponding to the simulated patterns of **SMOF-2**, and in any case no shift in 2θ positions is observed which stands for stability of the bulk crystallinity and for the bulk framework rigidity during the CO_2 adsorption process (i.e., reversible structural changes caused by CO_2 uptake can be disregarded, as for example, the so-called breathing effect).[23]

Regarding to the peak intensity, even though most of the peaks show no changes, the intensity of certain reflections is significantly affected. Figure 8a shows the trend of three
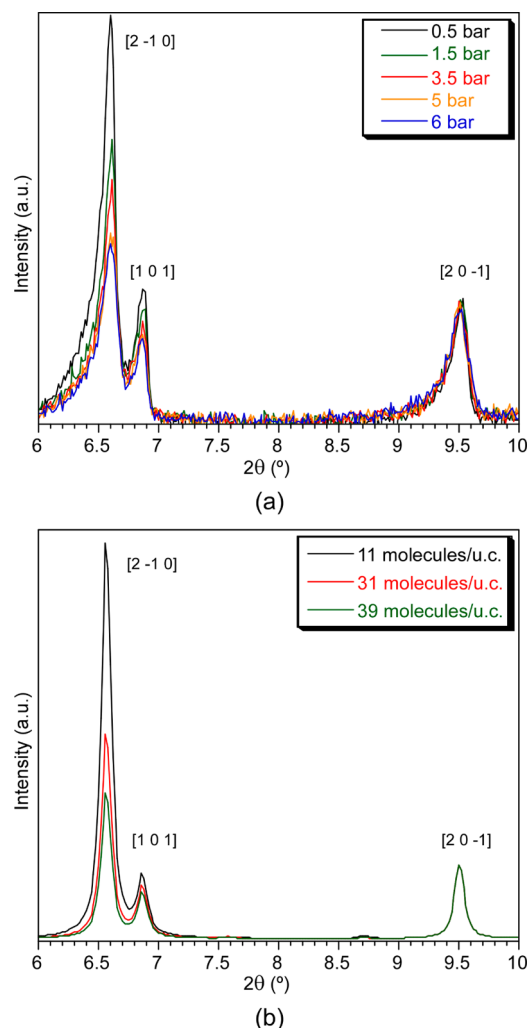
Figure 8. PXRD data for **SMOF-1** within 6−10°: (a) experimental patterns with increasing CO_2 pressure. (b) Simulated PXRD patterns from GCMC low energy configurations with increasing CO_2 uptake per unit cell.

reflections within the 6−10° 2θ range. As it can be observed [2 0 $\overline{1}$] reflection remains unvarying, while the intensity of [2 $\overline{1}$ 0] and [1 0 1] decays continuously with the increasing CO_2 pressure, which seems to be related to the CO_2 uptake within the structural pores. In order to confirm the latter proposal Grand Canonical Monte Carlo (GCMC) calculations were carried out in which the porous framework of **SMOF-1** was loaded with different amounts of CO_2 (see Supporting Information). Low energy configurations of the adsorbed molecules were used to model how the PXRD patterns are affected by the CO_2 (Figure 8b). The trend derived from the GCMC simulations matches the observed for experimental PXRD patterns, which allows us to state that intensity decay of the cited of reflections ([2 $\overline{1}$ 0] and [1 0 1]) is due the CO_2 presence within the 1D pores. When coordinates of CO_2 molecules are considered, no symmetry relation is found in any of the GCMC calculations. However, there is a periodicity of the preferential sites of adsorption (most sites derived from

probability density distribution for the center of mass of CO_2 molecule) in which electron density coming from adsorbed gas is accumulated (see Figure S5 in the Supporting Information). As a consequence, the decay of the mentioned reflections can be attributed to this periodically distributed averaged electron density of the adsorbed molecules.

Gas Adsorption Experiments of [Cu$_2$(μ-adenine)$_2$(μ-Cl)$_2$(Cl)$_2$]·2MeOH (3, SMOF-3). In order to assess the stability of the unsolvated **SMOF-3** thermogravimetric and variable temperature PXRD experiments were carried out (see Supporting Information). Thermogravimetric analysis (TGA) shows that the solvent molecules are released easily at temperatures below 100 °C. Afterward the TGA curve shows a stability plateau that extends up to 245 °C. At higher temperatures the compound decomposes in successive steps to yield CuO as the final residue at temperatures above 475 °C. The thermodiffractometric measurements show a significant difference between the diffractogram performed at 30 °C and those performed between 90 and 180 °C (Figure 4c). The cell parameters indexed for the PXRD pattern collected at 30 °C match the ones corresponding to the single crystal structure. However, the PXRD pattern change observed at temperatures above 60 °C lead to new unit cell parameters closely related to the previous ones but with a significant change in the unit cell transforming it to a nonstandard monoclinic setting with $\gamma \neq 90°$, but maintaining the cell volume nearly constant. This transformation is related to a rearrangement of the synthon established between the Hoogsteen face and the chloride anion once the methanol molecule is released. All this indicates that although the supramolecular structure presents a moderate change its overall supramolecular crystal structure remains essentially stable up to 180 °C.

In order to assess the permanent porosity inferred from thermodiffractometric measurement we proceeded to measure gas adsorption isotherms on freshly synthesized sample of **SMOF-3** which was activated under a vacuum at 140 °C during 12 h to eliminate solvent guest molecules. The results and conclusions derived from the study of the gas adsorption behavior of **SMOF-1** and **SMOF-2** suggest that the surface weakness of this kind of supramolecular compounds can make routine nitrogen adsorption isotherms not suitable for the study their porous features. In fact, **SMOF-3** presents a computed surface area of 361 m^2 g^{-1}, but the experimental N$_2$ adsorption isotherm corresponds to a nonporous material. **SMOF-3** adsorbs a significant amount of CO_2 as depicted by Figure 9, but comparatively smaller than **SMOF-1** and **SMOF-2**, due to the greater free volume and surface area of the latter ones. Similarly to the precedent supramolecular microporous compounds, **SMOF-3** presents a breakthrough pressure close to $P = 0.31$ bar.

CONCLUSIONS

It becomes clear how a combination of rigid tectons with rigid synthons spreading at least in three noncoplanar directions is a well-suited route to obtain porous supramolecular networks. In this context, the metal-nucleobase complexes can be good candidates to fulfill both requirements when the nucleobase is anchored to the discrete entity by at least two positions. This anchorage and the aromatic nature of the nucleobase provide rigid supramolecular building units. On the other hand, the well-known complementary hydrogen bonding established between the nucleobases ensures the necessary rigidity of these synthons. Therefore, as it has been probed here the
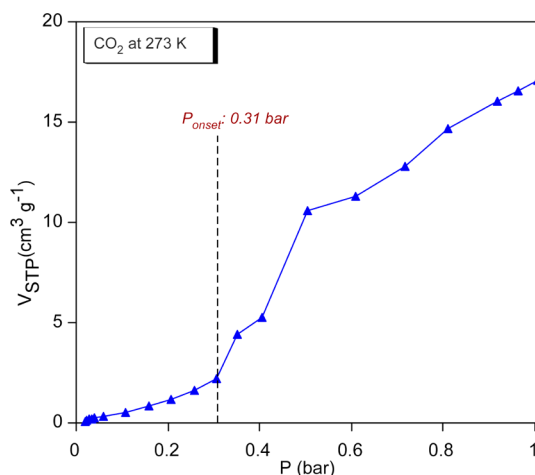
Figure 9. CO$_2$ adsorption isotherm **SMOF-3** at 273 K.

chances to obtain 3D supramolecular metal–organic frameworks based on metal-nucleobase systems are high. However, it is necessary to take care of the synthetic conditions in order to ensure the presence of the required direct hydrogen bonding interactions between the nucleobases. Related to this latter issue, the presence of water molecules can disrupt these direct adenine···adenine hydrogen bonding interactions, leading to nonporous materials as evidenced by the crystal structure of [Cu$_2$(μ-adenine)$_4$Cl$_2$]Cl$_2$·8H$_2$O.[24] The direct hydrogen bonding disrupting capacity of the water molecule seems also to be responsible of the surface instability observed in **SMOF-1, -2** and **-3**.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Hydrogen bonding interaction tables, thermogravimetric measurements, thermodiffractometric analysis, onset pressure calculation on SMOFs, details on GCMC calculations, and cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Unravelling the Growth of Supramolecular Metal−Organic Frameworks Based on Metal-Nucleobase Entities

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S *Supporting Information*

ABSTRACT: The present work provides the basis to obtain three-dimensional (3D) extended porous supramolecular assemblies named supramolecular metal−organic frameworks (SMOFs). This goal can be achieved by considering three key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units, and (iii) the non-coplanarity of functional groups involved in the predictable synthons. Throughout this report we demonstrate the suitability of this synthetic strategy supported by six new SMOFs based on metal-nucleobase entities which fulfill the stated requirements: $[Co(ThioG)_3]$ (**SMOF-4**; ThioG = thioguaninato), $[Co(Hade)_2X_2]$ (**SMOF-5**, **SMOF-6**; Hade = adenine and X = $Cl^−$, $Br^−$), $[Cu_8(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)_4(ade)_4(\mu\text{-}ade)_4(\mu\text{-}Hade)_2]$ (**SMOF-7**; ade = adeninato), $[Cu_4(\mu_3\text{-}ade)_4(\mu\text{-}ade)_2(pentylNH_2)_2(CH_3OH)_2(CO_3)_2(H_2O)_2]$ (**SMOF-8**; pentylNH$_2$ = 1-pentylamine), and $[Cu_2(\mu\text{-}ade)_2(ade)(\mu\text{-}OH)(H_2O)(CH_3OH)]_n$ (**SMOF-9**). **SMOF-4** is built up from monomeric entities in which bidentate thioguaninato ligands establish complementary hydrogen bonding interactions in non-coplanar directions leading to supramolecular layers that are further connected resulting in a porous structure with one-dimensional (1D) channels. The hydrogen bonding interactions among Watson−Crick and sugar edges of monomeric entities in **SMOF-5** give rise to a triply interpenetrated supramolecular framework. Octameric clusters in **SMOF-7** are self-assembled by hydrogen bonding to yield a porous 3D network. **SMOF-8** is built up from tetranuclear units that are linked via base pairing interactions involving Watson−Crick faces to afford layers whose assembly generates a two-dimensional pore system. **SMOF-9** is in between pure MOFs and SMOFs since it consists of 1D infinite coordination polymers held together by complementary hydrogen bonding interactions into a 3D supramolecular porous structure.
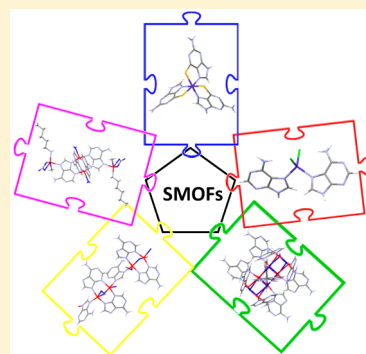
INTRODUCTION

Metal−organic frameworks (MOFs) encompass an area of chemistry that has experienced impressive growth during the last decades because of their various potential applications in catalysis, gas storage, chemical separations, sensing, ion exchange, drug delivery, and optics.[1] Regarding the adsorption field, it is worth mentioning that their large surface areas, adjustable pore sizes, and controllable functionalities are key factors that make MOFs promising candidates for adsorptive separations and purification purposes.[2,3] Taking into account the great potential of MOFs, we decided to explore a related type of material, in which the coordination bonds are replaced with hydrogen bonds as connectors, which are also directional and predictable interactions, to sustain the three-dimensional (3D) crystal building containing potentially accessible voids (Figure 1).[4,5] Although such kinds of alternative materials can arise a similar fascination to that of MOFs, the crystal engineering principles and the synthetic approach are not yet settled, and examples of this kind of material are rather scarce. In this sense a first clue to reach this goal can be inferred using the naive analogy of soft and rigid balls. Soft balls can adjust their shape to provide an efficient packing leaving almost no space in between. However, rigid balls do not have the option

Figure 1. Similarity between (a) coordination bonds and (b) hydrogen bonding interactions as structure directing agents.

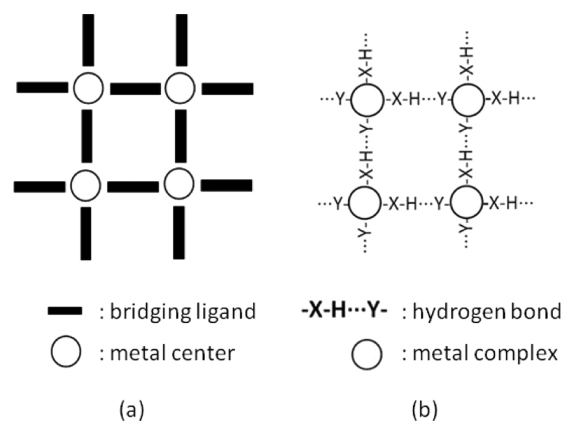of changing their shape, and, as a consequence, their packing is less effective giving rise to the presence of voids. In other words, flexible objects pack effectively, while rigid objects do not unless they present very specific and appropriate shape, such as cubes, triangular, rectangular and hexagonal prisms, etc.[6] This simple idea has helped us develop a synthetic strategy to obtain supramolecular metal−organic frameworks (SMOFs)[7,8] with potentially accessible voids as an alternative to more conventional metal−organic frameworks (MOFs).

The synthetic strategy is based on the following key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units, and (iii) the noncoplanarity of functional groups involved in the predictable synthons. The rigidity of the building units (discrete complexes) can be achieved using rigid ligands bonded through multiple positions. It means, in most common cases, a double anchoring of the ligand by means of two simultaneous coordination bonds or the combination of a coordination bond and an intramolecular hydrogen bond. The predictability and rigidity of the synthons require the presence of adjacent functional groups, incorporated into the rigid ligands, able to establish complementary hydrogen bonding interactions. Finally, the requisite of noncoplanar arrangement of the synthons comes from our objective of obtaining 3D extended systems that is achieved by the presence of at least three noncoplanar synthons. The use of nonplanar coordination geometries for the complexes makes this last condition easy to accomplish.

From previous studies we realized that a suitable system that would fulfill all of the above-described requirements for obtaining SMOFs are the discrete metal-nucleobase systems, especially those based on purine nucleobases.[9−11] These ligands provide, on the one hand, the advantage of increased rigidity of the supramolecular building block due to the coordination through multiple positions, and, on the other hand, they present many edges capable of establishing complementary hydrogen bonding interactions that provide rigid and predictable synthons (Scheme 1). Therefore, the adequate selection of the metal-nucleobase discrete entity that would afford a non-coplanar arrangement of the nucleobases could provide the desired supramolecular porous materials.

Scheme 1. Adenine Edges Capable of Establishing Rigid Complementary Double Hydrogen Bonding Synthons
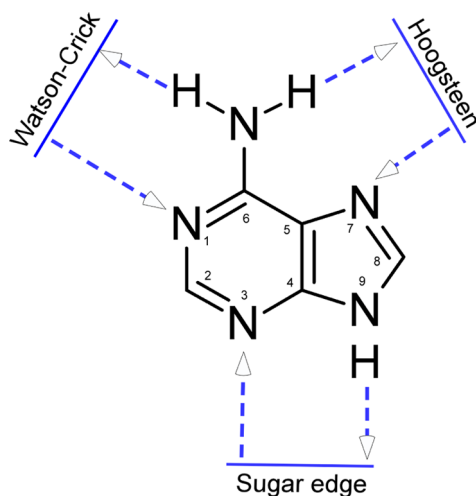
The preliminary results were achieved employing [Cu$_2$(μ-adenine)$_4$(X)$_2$]$^{2+}$ (**SMOF-1** and **SMOF-2**; X = Cl$^−$, Br$^−$) as supramolecular building blocks in which two or more nucleobases are tightly anchored to the metal centers by two donor positions (N3 and N9 sites), imposing a rigid building unit.[7,12] Moreover, this coordination motif imposes a rigid geometrical restraint among the nucleobases providing a set of noncoplanar synthons that otherwise would be very difficult to achieve. As many hydrogen donor/acceptor positions of the nucleobase remain free, these discrete entities are able to self-assemble among them by means of double hydrogen bonds to provide extended supramolecular solids in which great channels are present. These compounds present a surface instability that creates a diffusion barrier permeated only by strong interacting adsorbate molecules such as CO$_2$ but not N$_2$, H$_2$, and CH$_4$, which makes them attractive for selective gas adsorption and separation technologies. Zaworotko et al. reported an analogous compound, based on the [Cu$_2$(μ-adenine)$_4$(X)$_2$]$^{2+}$ dinuclear entity, replacing the halides by bulkier TiF$_6$$^{2−}$ anions improving the chemical stability of the supramolecular network toward humidity, thus avoiding the surface instability, and therefore, being able to adsorb CO$_2$, CH$_4$, and N$_2$.[13] These studies also pointed out the relevance of the solvent selection because strong hydrogen bond donor and acceptor solvents such as water molecules could disrupt the direct hydrogen bonding interactions between the nucleobases that are the key factors to achieve this type of compound.

In this report we demonstrate the suitability of this synthetic strategy to afford the self-assembly of rigid mono- or polynuclear entities by means of a set of non-coplanar synthons into supramolecular porous materials.

■ **EXPERIMENTAL SECTION**

Synthesis of SMOF-4, [Co(ThioG)$_3$]. 0.59 mL (0.4 mmol) of pentylamine was added dropwise to 0.0685 g (0.4 mmol) of 6-thioguanine dissolved in 20 mL of water, and the mixture was stirred in an ice bath for 1 h. To this mixture was added a 10 mL solution of 0.0291 g (0.1 mmol) of Co(NO$_3$)$_2$·6H$_2$O dissolved in water. The brown-colored solution was then stirred for 2 h in an ice bath and then left for evaporation. Brown-colored single-crystals were separated after 2 weeks. The compound was also obtained on replacing Co(NO$_3$)$_2$·6H$_2$O with CoSO$_4$·7H$_2$O. Yield: 60%. Anal. Calcd (found) for C$_{15}$H$_{12}$CoN$_{15}$S$_3$·6.7H$_2$O: C, 26.56 (26.68); H, 3.78 (3.70); N, 30.98 (31.29), S, 14.18 (14.21), Co, 8.69 (8.75). Main IR features (cm$^{−1}$; KBr pellets): 3422s, 1611m, 1498w, 1459w, 1385m, 1306sh, 1243vs, 1190m, 1146s, 983s, 933w, 893w, 836w, 803w, 743w, 716w, 680w, 630w, 523w.

Synthesis of SMOF-5, [Co(Hade)$_2$Cl$_2$]. This compound was obtained as deep blue polycrystalline form by the dropwise addition of a propanolic solution of adenine (0.0270 g, 0.2 mmol) into a stirring solution of 0.0238 g of CoCl$_2$·6H$_2$O (0.1 mmol). When the synthesis was performed in methanol bad quality crystals were obtained. Then, single crystals of good quality were obtained by using diffusion techniques. Yield: precipitate 70%, crystals 50%. Anal. Calcd (found) for C$_{10}$H$_{10}$Cl$_2$CoN$_{10}$: C, 30.02 (30.09); H, 2.52 (2.47); N, 35.01 (34.93); Co, 14.73 (14.82) %. Main IR features (cm$^{−1}$; KBr pellets): 3391vs, 3258vs, 3133vs, 3058vs, 2346w, 2280w, 2186w, 2016w, 1943w, 1790w, 1696vs, 1611s, 1498m, 1459w, 1397s, 1327m, 1237m, 1171m, 1105w, 1066w, 1016w, 942m, 895m, 856w, 778m, 712m, 631w, 610m, 530m.

Synthesis of SMOF-6, [Co(Hade)$_2$Br$_2$]. The synthesis is the same as for **SMOF-5** but replacing CoCl$_2$·6H$_2$O by CoBr$_2$. Yield: precipitate 60%. All the attempts to grow single-crystals were unsuccessful. Anal. Calcd (found) for C$_{10}$H$_{10}$Br$_2$CoN$_{10}$: C, 24.56 (24.49); H, 2.06 (2.15); N, 28.64 (28.57); Co, 12.05 (12.01) %. Main IR features (cm$^{−1}$; KBr pellets): 3450s, 3341s, 3066s, 2817w, 2671w, 2284w, 1951w, 1663vs,

Table 1. Crystallographic Data and Structure Refinement Details[a]

	SMOF-4	SMOF-5	SMOF-7	SMOF-8	SMOF-9
formula	$C_{15}H_{12}CoN_{15}S_3$	$C_{10}H_{10}Cl_2CoN_{10}$	$C_{50}H_{50}Cu_8N_{50}O_8$	$C_{30.85}H_{46.80}Cu_{3.55}N_{21.55}O_{8.20}$	$C_{16}H_{19}Cu_2N_{15}O_3$
MW (g mol^{-1})	557.51	400.11	1987.72	1076.37	596.54
crystal system	trigonal	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{3}$	$C2/c$	$Ccca$	$P\bar{1}$	$C2/c$
a (Å)	16.7297(14)	11.2442(18)	20.1899(5)	12.646(5)	23.472(7)
b (Å)	16.7297(14)	6.9401(7)	28.964(2)	13.136(5)	16.398(3)
c (Å)	6.5245(4)	18.760(2)	16.5403(5)	13.158(5)	18.803(5)
α (deg)	90	90	90	73.784(5)	90
β (deg)	90	95.000(13)	90	81.840(5)	112.30(3)
γ (deg)	120	90	90	62.368(5)	90
V (Å^3)	1581.4(2)	1458.4(3)	9672.6(8)	1859.2(12)	6696(3)
Z	2	4	4	1	8
ρ_{calcd} (g cm^{-3})	1.171	1.822	1.365	0.961	1.184
μ (mm^{-1})	0.769	12.758	1.790	1.047	1.899
reflections collected	4690	5201	33482	6909	5529
unique data/parameters	2300/103	1462/109	5277/272	6909/269	5529/325
R_{int}	0.1278	0.0656	0.0630	0.1840	0.0972
goodness of fit (S)[b]	1.033	1.045	1.092	0.773	0.741
R_1[c]/wR_2[d] [all data]	0.0924/0.1673	0.0664/0.1606	0.0872/0.2221	0.2330/0.2882	0.1519/0.2091
R_1[c]/wR_2[d] [$I > 2\sigma(I)$]	0.0646/0.1585	0.0606/0.1560	0.0721/0.2115	0.1044/0.2691	0.0800/0.1840

[a]Reported data do not include the variable amount of solvent molecules present in the channels. [b]$S = [\sum w(F_0^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$. [c]$R_1 = \sum\|\|F_0\| - \|F_c\|\|/\sum\|F_0\|$. [d]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum wF_0^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2Fc^2)/3$ with $a = 0.0691$ (**1**), 0.0897 (**2**), 0.1440 (**3**), 0.1283 (**4**), 0.0584 (**5**) and $b = 4.8645$ (**2**), 1.6779 (**3**).

1596vs, 1513w, 1480s, 1416s, 1360w, 1343s, 1306s, 1246s, 1170w, 1120w, 1020w, 1063w, 1030w, 973m, 910m, 870w, 791m, 763m, 722s, 680w, 638m, 627m, 557s, 545m, 532s.

Synthesis of **SMOF-7**, [Cu$_8$(μ_3-OH)$_4$(μ_4-OH)$_4$(ade)$_4$(μ-ade)$_4$(μ-Hade)$_2$]. Twenty milliliters of an aqueous methanolic solution (1:1) containing adenine (0.8 mmol, 0.108 g) were added to 20 mL of an aqueous solution of CuSO$_4$·5H$_2$O (0.4 mmol, 0.0998 g) leading to a solution of pH = 3. Immediately a dark blue precipitate appeared. Then, sulfuric acid was added until complete dissolution of the precipitate (pH = 1.5). A glass vial with the resulting solution was placed in an Erlenmeyer flask containing triethylamine favoring the difussion of the base into the solution. A few days later a small amount of purple crystals appeared mixed with a major unknown phase.

Synthesis of **SMOF-8**, [Cu$_4$(μ_3-ade)$_4$(μ-ade)$_2$(pentylNH$_2$)$_2$-(CH$_3$OH)$_2$(CO$_3$)$_2$(H$_2$O)$_2$]. Single crystals of this compound were obtained by adding a 10 mL methanolic solution of 0.0198 g of Cu(OOCCH$_3$)$_2$·H$_2$O (0.1 mmol) to a methanolic solution (20 mL) of 0.0206 g of adenine (0.15 mmol) mixed with 0.59 mL of pentylamine. The green-colored solution was stirred for 1 h and left evaporating at room temperature. On evaporating the color of the solution started changing to blue-violet. After 2 weeks, violet-colored prismatic shaped crystals appeared. The crystals are unstable out from the mother liquid.

Synthesis of **SMOF-9**, [Cu$_2$(μ-ade)$_2$(ade)(μ-OH)(H$_2$O)-(CH$_3$OH)]$_n$. Single crystals of this compound were obtained by the slow addition of a 10 mL methanolic solution of 0.0199 g of Cu(OOCCH$_3$)$_2$·H$_2$O (0.1 mmol) into a methanolic solution (50 mL) of 0.0546 g of adenine (0.4 mmol) mixed with 0.59 mL of pentylamine. The green-colored solution was stirred for 1 h and left evaporating at room temperature. Few blue needle like crystals that correspond to **SMOF-9** appeared in a time period of 1 week, mixed with violet crystals of **SMOF-8**. Yield: 5%. Anal. Calcd (found) for C$_{16}$H$_{19}$Cu$_2$N$_{15}$O$_3$·8.5(CH$_3$OH): C, 33.87 (33.77); H, 6.15 (6.08); N, 24.18 (24.09); Cu, 14.63 (14.74) %. Main IR features (cm^{-1}; KBr pellets): 3446s, 3356vs, 3123s, 1671s, 1418m, 1398m, 1385m, 1333m, 1308s, 1268m, 1251w, 1191m, 1149m, 1123w, 1022w, 979w, 939m, 910w, 875w, 845w, 797m, 738w, 723s, 641m, 620w, 570w, 541m.

Physical Measurements. Elemental analyses (C, H, N, S) were performed on an Euro EA elemental analyzer, whereas the metal content was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) from Horiba Yobin Yvon Activa.

The IR spectra (KBr pellets) were recorded on a FTIR 8400S Shimadzu spectrometer in the 4000−400 cm^{-1} spectral region. Dinitrogen (77 K) and carbon dioxide (273 K) physisorption data were recorded on activated samples (vacuum at 100 °C for 4 h) with a Quantachrome QUADRASORB-SI-MP and a Quantachrome Autosorb-iQ-MP, respectively. The specific surface area was calculated from the adsorption branch in the relative pressure interval from 0.01 to 0.10 using the Brunauer−Emmett−Teller (BET) method.

X-ray Diffraction Data Collection and Structure Determination. Single-crystal X-ray diffraction data were collected on an Oxford Diffraction Xcalibur diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(2) K for **SMOF-4** and **SMOF-7**, and at 293 K for **SMOF-8**, and on an Agilent Technologies SuperNova diffractometer with Cu Kα radiation (1.54185 Å) for **SMOF-5** and **SMOF-9**. Data reduction was done with the CrysAlisPro program.[14] All the structures were solved by direct methods using the SIR92 program[15] and refined by full-matrix least-squares on F^2 including all reflections (SHELXL97).[16] All calculations for these structures were performed using the WINGX crystallographic software package.[17] After the initial structure solution was completed, the difference Fourier map for **SMOF-4**, -**7**, -**8**, and -**9** showed the presence of substantial electron density at the voids of the crystal structure that was impossible to model. Therefore, its contribution was subtracted from the reflection data by the SQUEEZE method[18] as implemented in PLATON.[19] During the data reduction process it became clear that the crystal specimen of **SMOF-8** was a nonmerohedral twin with a twin law: (1.026 −0.077 0.038/0.070 0.963 0.012/−0.023 −0.000 1.003). The final result showed a percentage of twinned component of 24.3%. Additionally, one of the metal centers (Cu2) and its coordinated ligands present a partial occupation of 0.78. Relevant data adquisition and refinement parameters are gathered in Table 1. CCDC 1038651−1038655 contain the supplementary crystallographic data for this paper.

■ RESULTS AND DISCUSSION

Structural Description of [Co(ThioG)$_3$] (SMOF-4). The basic media of the reaction favored the oxidation to Co(III), as ensured by its diamagnetic nature, giving rise to neutral monomeric [Co(ThioG)$_3$] entities. Three thioguaninato

ligands, in its 9*H*-tautomeric form, are coordinated in a bidentate chelating mode to the Co(III) atoms by their N7 and S6 atoms affording an octahedral coordination environment. Coordination bonds lengths and angles are gathered in the Supporting Information. The coordination mode of the nucleobase analogue renders a rigid metal-complex and, at the same time, exposes its Watson−Crick (N1, N2) and sugar edges (N3, N9) providing a set of non-coplanar synthons with dihedral angles of 87° (Figure 2a). Therefore, this discrete
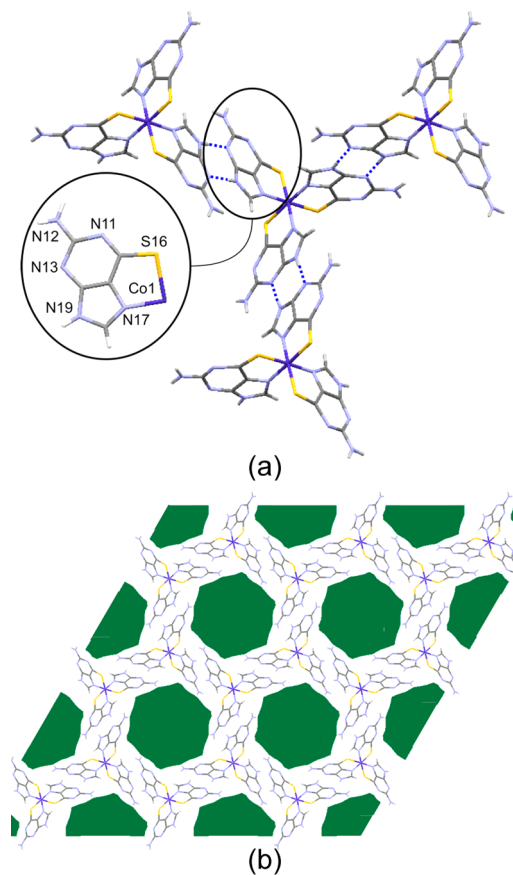

Figure 2. (a) Interactions among the monomeric entities and numbering scheme. (b) Projection of the crystal packing of **SMOF-4** along the crystallographic *c* axis. Green-colored regions represent the solvent accessible void.

complex entity fulfils the previously stated requirements for the success in obtaining a supramolecular porous material. In fact, there is a previous work based on similar discrete entities but using 6-thioguanosine that provides a complementary hydrogen bonding interaction involving only the Watson−Crick face (N1, N2) as the sugar edge is blocked by the sugar residue. It affords a supramolecular assembly containing great voids that are occupied by the sugar residue of the thioguanosine.[20] In **SMOF-4** both sides of the 6-thioguaninato are available to contribute to the supramolecular assembly. The sugar edge (N3, N9) of the nucleobases establishes a double hydrogen bonding interaction with the nucleobases of three neighboring entities to give a $R_2^2(8)$ ring (Table 2). This rigid synthon, based on direct thioguaninato⋯thioguaninato pairing interactions, leads to layers in the *ab* plane in which Δ and Λ isomers of the trischelate complex are sequentially arranged similarly to what happens in layered $[M(ox)_3]^{n-}$ based compounds.[21,22] The resulting arrangement corresponds to

Table 2. Structural Parameters (Å, °) of Noncovalent Interactions in SMOF-4[a]

Hydrogen Bonding Interactions			
D−H⋯A[b]	H⋯A	D⋯A	D−H⋯A
N19−H19⋯N13[i]	2.03	2.875(5)	167
N12−H12⋯S16[ii]	2.69	3.467(4)	151
C18−H18⋯S16[iii]	2.67	3.415(4)	138
$\pi-\pi$ Interactions[c]			
ring⋯ring[d]	angle	DC	α	DZ	DXY
h⋯h[iv]	0.0	3.46	18.5	3.28	1.10

[a]Symmetry codes: (i) −x, −y + 1, −z + 2; (ii) x − y, x, −z + 1; (iii) −x + y, −x + 1, z + 1; (iv) −x, −y + 1, −z + 1. [b]D: donor; A: acceptor. [c]Angle: dihedral angle between the planes (deg), DC: distance between the centroids of the rings (Å), α: angle between the normal to the first ring and the DC vector (deg), DZ: interplanar distance (Å), DXY: lateral displacement (Å). [d]h: hexagonal ring of the thioguanine.

the Shubnikov hexagonal **hcb** topology with a (6^3) point symbol.[23−25] The interactions among the three-connected uninodal two-dimensional (2D) nets are linked via weaker hydrogen bonds (N2−H⋯S6 and C8−H⋯S6) and reinforced with $\pi-\pi$ interactions, (Table 2) leading to an **acs** topology and $(4^9.6^6)$ point symbol that corresponds to a porous crystal structure with an estimated surface area of 887 m^2/g and 43% of void space based on theoretical calculations.[26,19] The resulting porous structure consists of one-dimensional (1D) channels that run along the crystallographic *c* axis with a diameter of 8.2−9.4 Å (Figure 2b). It is worth mentioning the template effect exerted by the pentylamine. This molecule provides the basic media that this reaction requires, and, at the same time, the tendency of the aliphatic tails to form aggregates in water promotes the growth of the supramolecular structure around them. In fact, the same synthesis but using different amines with shorter aliphatic tails does not provide this compound.

According to N$_2$ (77 K) and CO$_2$ (273 K) adsorption studies, this compound is highly selective toward CO$_2$ adsorption (Figure 3). The N$_2$ adsorption curve exhibits features of a nonporous material, and, accordingly, the fitting of the adsorption area to BET equation leads to a negligible value. However, it shows a significant CO$_2$ uptake with a non-saturating curve reaching a value of 1.4 mmol/g at 1 bar. This behavior has been described in the introduction section for
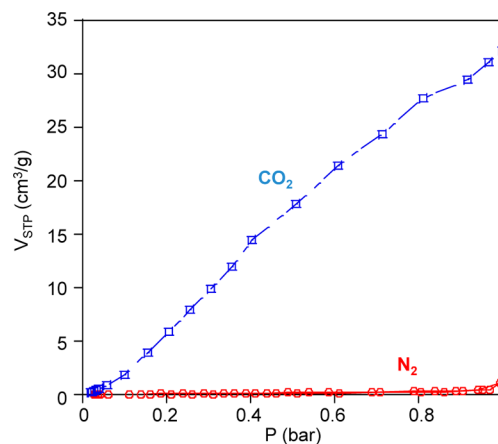

Figure 3. Adsorption isotherms for N$_2$ (77 K) and CO$_2$ (273 K), of a fresh sample of **SMOF-4**.

SMOF-1 and **SMOF-2**, and its explanation for **SMOF-4** probably would also be related to a crystal surface instability.

Structural Description of [Co(Hade)₂Cl₂] (SMOF-5). **SMOF-5** contains neutral monomeric [Co(Hade)₂Cl₂] units. 9*H*-Adenine acts as a monodentate ligand, and it is coordinated to the Co(II) metal center through the N7 position that it is very usual for unsubstituted adenine moieties, but it requires a second anchoring position of the nucleobase to be stiff enough to meet our requirements. Such stiffness is achieved by the presence of intramolecular hydrogen bonding interactions between the amino hydrogen atom and the chloride one. The adenine also exposes its Watson−Crick and sugar-edges to establish intermolecular complementary hydrogen bonding interactions with adjacent adenine molecules (Figure 4a).
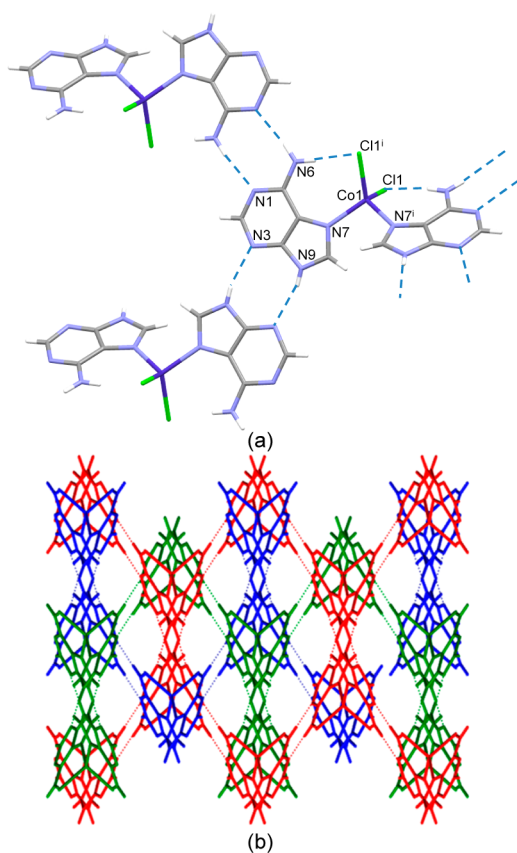

Figure 4. (a) Rigid synthon formed by direct supramolecular interactions in **SMOF-5**. (b) Triple interpenetrated crystal structure of **SMOF-5**. Each subnet is represented using a different color.

The rigid synthons involving WC···WC and sugar···sugar edges interactions give rise in both cases to $R_2^2(8)$ hydrogen bonding rings, that are well-known structural synthons between self-assembling adenine fragments.[27−33] These interactions build up a four-connected uninodal 3D supramolecular net with **dia** topology and (6^6) point symbol that would represent a new porous material with an estimated internal surface area of 3600 m²/g and 67% of void space.

Nevertheless, it would contain such huge channels that the real crystal structure involves three interpenetrated networks that occupy all the available space providing a nonporous material. This entanglement problem is also common in MOFs.[34] Porous materials try to minimize the system energy through optimal filling of void space, but structural inter-penetration may occur only if the pore space of an individual net is sufficiently large to accommodate an additional net. In addition to this, various weak supramolecular forces such as H-bonding, π−π aromatic stacking interactions, and van der Waals forces are believed to play vital roles in the formation of interpenetrated structures. **SMOF-5** follows the same pattern, provided that it contains such a huge percentage of void. Thus, the resulting structure can be described as a 3-fold inter-penetrated network as shown in Figure 4b. The attempt to avoid this interpenetration using the more voluminous bromide anion instead of chloride did not succeed, providing the same triple interpenetrated supramolecular structure (**SMOF-6**, see Supporting Information).

Table 3. Hydrogen Bonding Interactions (Å, °) in SMOF-5[a]

D−H···A[b]	H···A	D···A	D−H···A
N6−H6A···N1[ii]	2.06	2.912(6)	173
N6−H6B···Cl1[i]	2.39	3.237(4)	167
N9−H9···N3[iii]	2.11	2.833(6)	165

[a]Symmetry codes: (i) −*x*, *y*, −*z* + 1/2; (ii) −*x* + 1/2, −*y* + 1/2, −*z* + 1; (iii) −*x*, −*y* − 1, −*z* + 1. [b]D: donor; A: acceptor.

Structural Description of [Cu₈(μ₄-OH)₄(μ₃-OH)₄(ade)₄-(μ-ade)₄(μ-Hade)₂] (SMOF-7). This compound consists of [Cu₈(μ₄-OH)₄(μ₃-OH)₄(adeninato-κN9)₄(μ-adeninato-κN3:κN9)₄(μ-adenine-κN3:κN9)₂] octameric clusters formed by the stacking of four Cu₂(μ-OH)₂ dimers that are 90° rotated and linked by a semicoordination to the neighboring Cu(II) atoms through the hydroxide bridges (Figure 5a). The resulting aggregate can be described as the stacking of three cubanes (cubes with the vertices alternatively occupied by the metal and the bridging ligand). The surface of each octamer is occupied by eight adeninate and two neutral adenine ligands. Four adeninato and the neutral adenine entities act as bidentate *N3,N9*-bridging ligands. These bridging ligands are disordered into two coplanar arrangements with inverted orientation regarding the coordination mode (μ-κN3:κN9/μ-κN9:κN3).[35,36] The remaining adeninato ligands are anchored to the corners of the cluster as terminal ligands through N9, and their stiffness is reinforced by intramolecular hydrogen bonds involving the hydroxide bridges and the N3 positions of the nucleobases. All the adenines, adeninates, and hydroxides are rigidly anchored to the octameric entity because of their multiple coordination bond (OH/adenine/adeninato) or the combination of a coordination bond and an intramolecular hydrogen bond (adeninato).

The interaction of each octamer with the adjacent ones is by means of a hydrogen bonding scheme involving the hydroxide anions and the N7 imidazolic atom of terminal adeninato ligands giving rise to a bidimensional network. Moreover, the bridging adeninato ligands direct their Watson−Crick and Hoogsteen faces outward in those supramolecular layers in such a way that they establish complementary hydrogen bonding interactions with neighboring tectons. As in previous compounds the Watson−Crick faces establish a $R_2^2(8)$ hydrogen bonding ring. The combination of the above-described interactions leads to a 3D 8c uninodal supra-molecular net with a **sqc3** topology, point symbol being $(4^4.6^2)$, where the geometrical requirements imposed by the rigidity of the octameric unit and the hydrogen bonding interactions avoid the full occupancy of the space. This is reflected by the presence of large monodimensional channels of ca. 4.9 Å
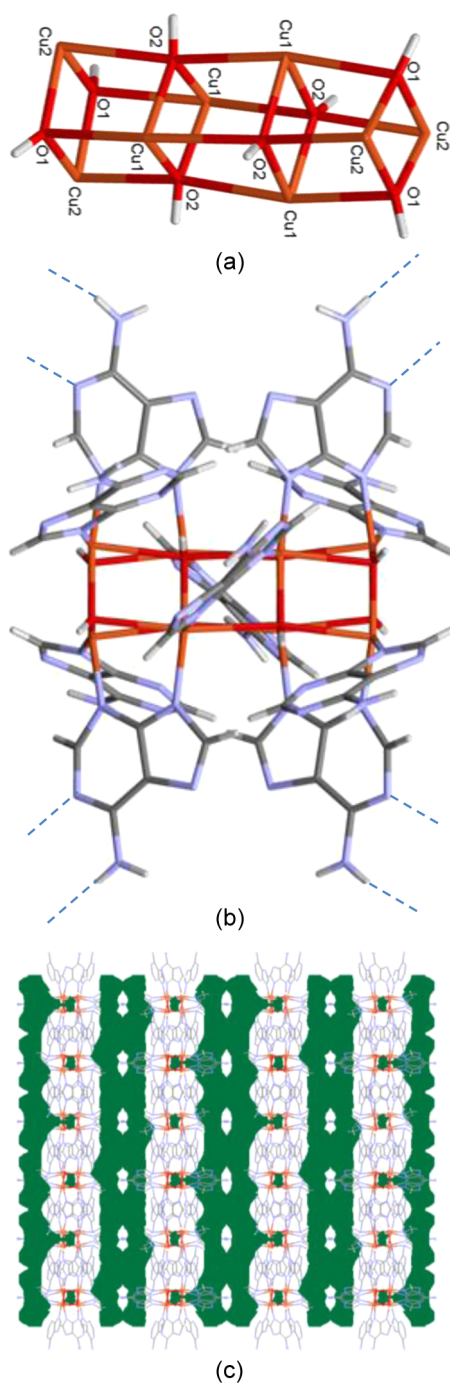
Figure 5. (a) $[Cu_8(\mu_4\text{-OH})_4(\mu_3\text{-OH})_4]$ unit, (b) whole octameric entity, and (c) three-dimensional packing of **SMOF-7**.

spreading along the [100] direction, which corresponds to a calculated surface area of 366 m²/g and a 30% of void space.

Structural Description of $[Cu_4(\mu_3\text{-ade})_4(\mu\text{-ade})_2$-(pentylNH$_2$)$_2$(CH$_3$OH)$_2$(CO$_3$)$_2$(H$_2$O)$_2]\cdot n$(solvent) (SMOF-8). **SMOF-8** is built up by tetranuclear $[Cu_4(\mu_3\text{-ade})_2(\mu\text{-ade})_2$-(pentylNH$_2$)$_2$(CH$_3$OH)$_2$(CO$_3$)$_2$(H$_2$O)$_2]$ units in which two types of neutral building units coexist: a dimeric $[Cu_2(\mu\text{-ade})_4(H_2O)_2]$ entity and two monomeric $[Cu(pentylNH_2)$-$(CH_3OH)(CO_3)]$ moieties (Figure 6).

The dimeric fragment is centrosymmetric and is made of two Cu(II) atoms bridged by four $\mu\text{-}N3,N9$-adeninate anions in a paddle-wheel shaped arrangement. The apical position of the

Table 4. Hydrogen Bonding Interactions (Å, °) in SMOF-7^a

D−H···A^b	H···A	D···A	D−H···A
N16−H16A···N11A^{iii}	2.51	3.34(3)	161
N36−H36B···N13^i	2.56	3.317(7)	148
O1−H1···N37^{iv}	2.09	2.947(5)	177
O2−H2···N33^v	2.18	3.015(6)	167

^{a}Symmetry codes: (i) x, $-y + 1/2$, $-z + 1/2$; (iii) $-x + 3/2$, y, $z - 1/2$; (iv) $-x + 3/2$, $-y + 1$, z; (v) $-x + 3/2$, y, $z + 1/2$. ^{b}D: donor; A: acceptor.
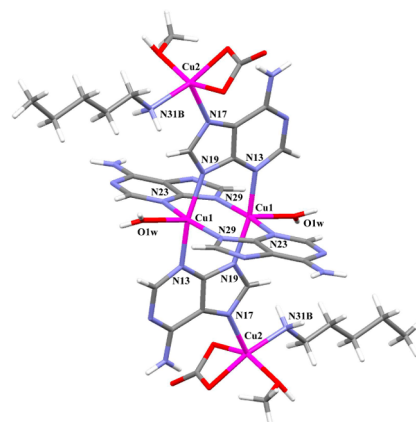

Figure 6. Structural unit of **SMOF-8** with the atomic numbering scheme.

distorted square pyramidal coordination around Cu1 atom is completed with a water molecule. Each dimeric entity is linked to two neighboring monomeric units via the N7 imidazolic atoms of two adeninato ligands. Therefore, two adeninate anions behave as tridentate $\mu_3\text{-}N3,N7,N9$ bridging ligands, whereas the other two act as bidentate $\mu\text{-}N3,N9$. The basal plane of the square pyramidal chromophore around Cu2 atom is completed with two oxygen atoms from a carbonato ligand, an oxygen atom of a methanol molecule, and the nitrogen atom of a pentylamine molecule.

Each tetranuclear entity is linked to four adjacent ones via double N6−H···N1 hydrogen bonding interactions between the Watson−Crick faces of neighboring entities to give a $R_2^2(8)$ ring. This assembling of tetrameric entities gives rise to layers that can be described as a four-connected uninodal net with Shubnikov tetragonal **sql** topology and $(4^4.6^2)$ point symbol. It is worth noting that the dinuclear paddle-wheel entity of **SMOF-1** and **SMOF-2** presents analogous four-connected nodes (using Watson−Crick base pairing interactions), but the absence of the bulky capping monomeric entities allows the growth of a 3D supramolecular network (**nbo**, $6^4.8^2$). However, in **SMOF-8** the 3D cohesion requires additional hydrogen bonding interactions involving the coordination water molecule, the carbonato ligand, and the pentylamine molecule (Figure 7, Table S4) leading to an α-Po **pcu** topology. The overall packing generates a 2D pore network with channels running along the b and c axes of 3−5 Å of diameter, that represents 43% of void space and a calculated surface area of 402 m²/g. However, the crystals decompose upon removal from the mother liquor and even when immersed in pure methanol. This fact is probably due to the loss of pentylamine that seems to play a key role stabilizing the crystal structure.

Structural Description of $[Cu_2(\mu\text{-ade})_2(ade)(\mu\text{-OH})$-(H$_2$O)(CH$_3$OH)]$_n\cdot n$(solvent) (SMOF-9). The basic structural
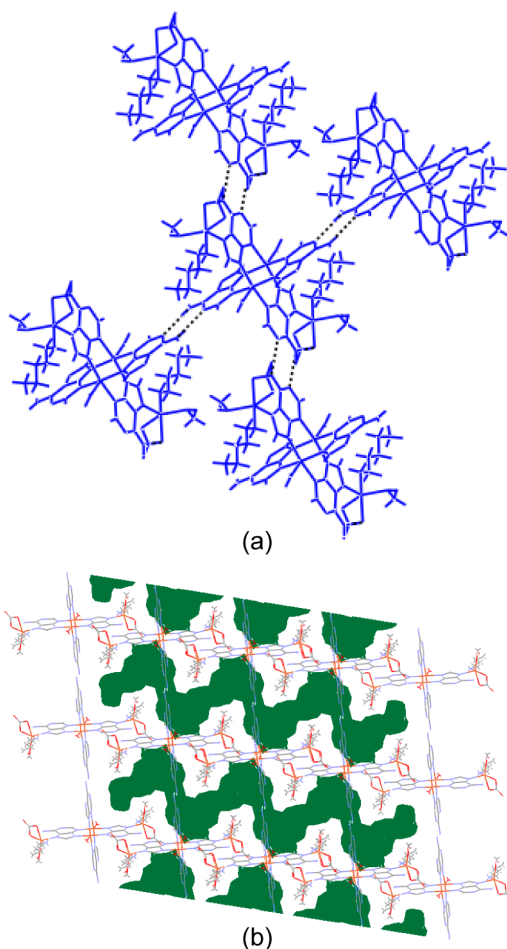
(a)

(b)

Figure 7. (a) Linkage of the tetranuclear entities by the Watson−Crick faces and (b) crystal packing along the *b* axis of **SMOF-8**, showing the generated voids.

Table 5. Hydrogen Bonding Interactions (Å, °) in SMOF-8^a

D−H···A^b	H···A	D···A	D−H···A
N6−H6A···N11^{ii}	2.13	2.978(11)	167
N6−H6B···O1	2.11	2.965(13)	175
N6−H26B···N21^{iii}	2.08	2.935(17)	172
O1w−H12w···O3^{iv}	1.94	2.790(13)	169
N31−H31A···O2^{v}	1.94	2.843(18)	176

^{a}Symmetry codes: (ii) −x + 2, −y + 1, −z + 1; (iii) −x + 2, −y, −z; (iv) x − 1, y, z; (v) −x + 3, −y, −z + 1. ^{b}D: donor; A: acceptor.

unit of this compound consists of 1D infinite coordination polymers held together by complementary hydrogen bonding interactions in a 3D supramolecular porous structure. The coordination polymer can be described as noncentrosymmetric dinuclear units (Figure 8) in which two Cu(II) atoms are bridged with two adeninate moieties by the N3 and N9 atoms and also by one hydroxyl group (Figure 9a). One of the metal centers is also coordinated to a water molecule while the other to the oxygen atom of a methanol molecule. These dinuclear units are connected by additional bridging adeninates that are coordinated to the Cu(II) centers by the N7 and N9 atoms to provide a 1D coordination chain. An interesting structural feature is that the bridging adeninates inside the dinuclear units are tilted by 22°, but they present wider tilt angle with respect to those connecting the dimeric units (56 and 78°, respectively)
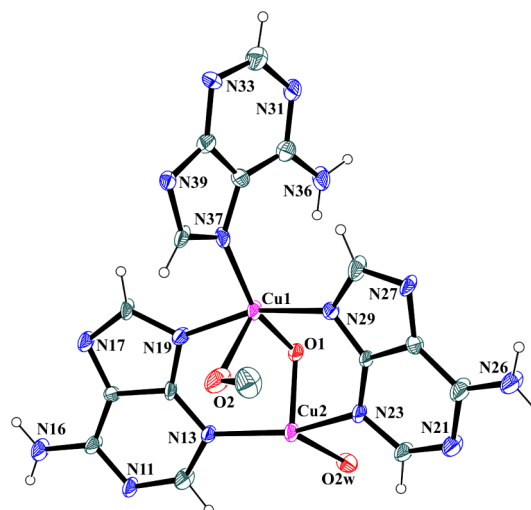

Figure 8. Ortep representation of the dimeric unit [Cu$_2$(μ-ade)$_2$(ade)(H$_2$O)(μ-OH)(CH$_3$OH)] together with the numbering scheme in **SMOF-9**.

in the polymeric chain. This fact together with the complementary double hydrogen bonding interactions of the nucleobases promotes a three-dimensional propagation of the supramolecular structure. The μ-$\kappa N3$:$\kappa N9$-adeninates are able to establish double WC···WC and H···H synthons leading to R$_2^2$(8) and R$_2^2$(10) hydrogen bonding rings, respectively. On the other hand, the μ-$\kappa N7$:$\kappa N9$-adeninates are hydrogen bonded to the bridging hydroxide and the coordinated water molecule of an adjacent polymeric chain through N1 and N6 positions of the Watson−Crick face. The resulting supramolecular crystal structure shows the presence of large channels along the *b* axis with a calculated surface area of 295 m^2/g and 44% of void space.

This compound is an interesting case because it is in between pure MOFs and SMOFs as it polymerizes into 1D through coordination bonds and further extends to supramolecular array through complementary hydrogen bonding interactions resulting in a 3D porous network (Figure 9c).

■ CONCLUSIONS

In this report we have paid special attention to the design prerequisites of SMOFs: (i) rigid building unit/complex, (ii) rigid and predictable synthons, and (iii) at least three non-coplanar synthons. This approach is supported by six new SMOFs based on different metal centers, nucleobases, and synthetic conditions. It also highlights the suitability of metal-nucleobase systems, specially purine based ones, to obtain SMOFs since many of them accomplish the above stated requirements: (i) the rigidity of the building unit is achieved using nucleobases because they can be coordinated through multiple positions, normally by a double anchoring (double coordination bonds or the combination of a coordination bond and an intramolecular hydrogen bond), (ii) the well-known complementary hydrogen bonding interactions between the nucleobases ensures the necessary rigidity of the predictable synthons, and (iii) the metal coordination geometries impose, in many cases, a non-coplanar arrangement of the nucleobases affording a non-coplanar disposition of the synthons that allows three-dimensional propagation of the nucleobase···nucleobase complementary hydrogen bonding assembly.
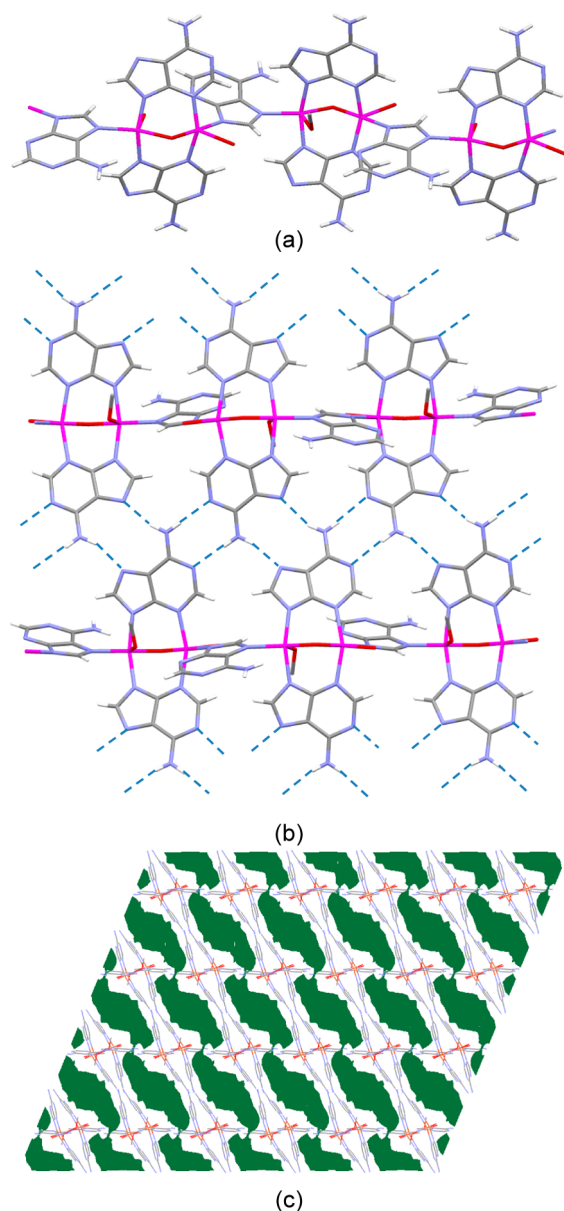
Figure 9. (a) Coordination polymeric chain. (b) Supramolecular complementary base pairing interactions among the adeninate entities. (c) Porous supramolecular architecture of **SMOF-9** along the *b* axis.

Table 6. Hydrogen Bonding Interactions (Å, °) in SMOF-9[a]

D−H···A[b]	H···A	D···A	D−H···A
N16−H16A···N11[ii]	2.23	3.075(10)	170
N26−H26A···N21[iii]	2.06	2.920(11)	179
N26−H26B···N17[iv]	2.08	2.904(11)	161
N36−H36B···O1[v]	2.12	2.884(9)	148

[a]Symmetry codes: (ii) −x + 1, −y + 2, −z + 1; (iii) −x, −y + 2, −z; (iv) x − 1/2, −y + 3/2, z − 1/2; (v) −x + 1/2, −y + 3/2, −z. [b]D: donor; A: acceptor.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of coordination bond lengths, figures of network topologies, XRPD patterns, and cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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This work reports a synthetic strategy to obtain supramolecular metal—organic frameworks (SupraMOFs) based on base pairing interactions with potentially accessible voids as an alternative to more conventional metal–organic frameworks (SupraMOFs) that are based on coordination bonds. This goal can be achieved by considering three key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units and (iii) the non-coplanarity of functional groups involved in the predictable synthons. Throughout this report we demonstrate the suitability of this synthetic strategy supported by several SupraMOFs based on metal—nucleobase entities which fulfill the above stated requirements. The crystal structures of these compounds are sustained through base pairing interactions taking place between nucleobases anchored to adjacent discrete metal complexes.

According to gas adsorption studies, most of these compounds present a surface instability that creates a diffusion barrier that can be permeated only by strong interacting adsorbate molecules with high kinetic energy such as CO_2 but not N_2, H_2, and CH_4. This feature makes them attractive for selective gas adsorption and separation technologies.