

DEHYDRATION OF A SOLID COORDINATION NETWORK BASED ON $\text{Cu}^{\text{II}}\text{-(py)}_2\text{C(OH)}_2$ TRIMERS

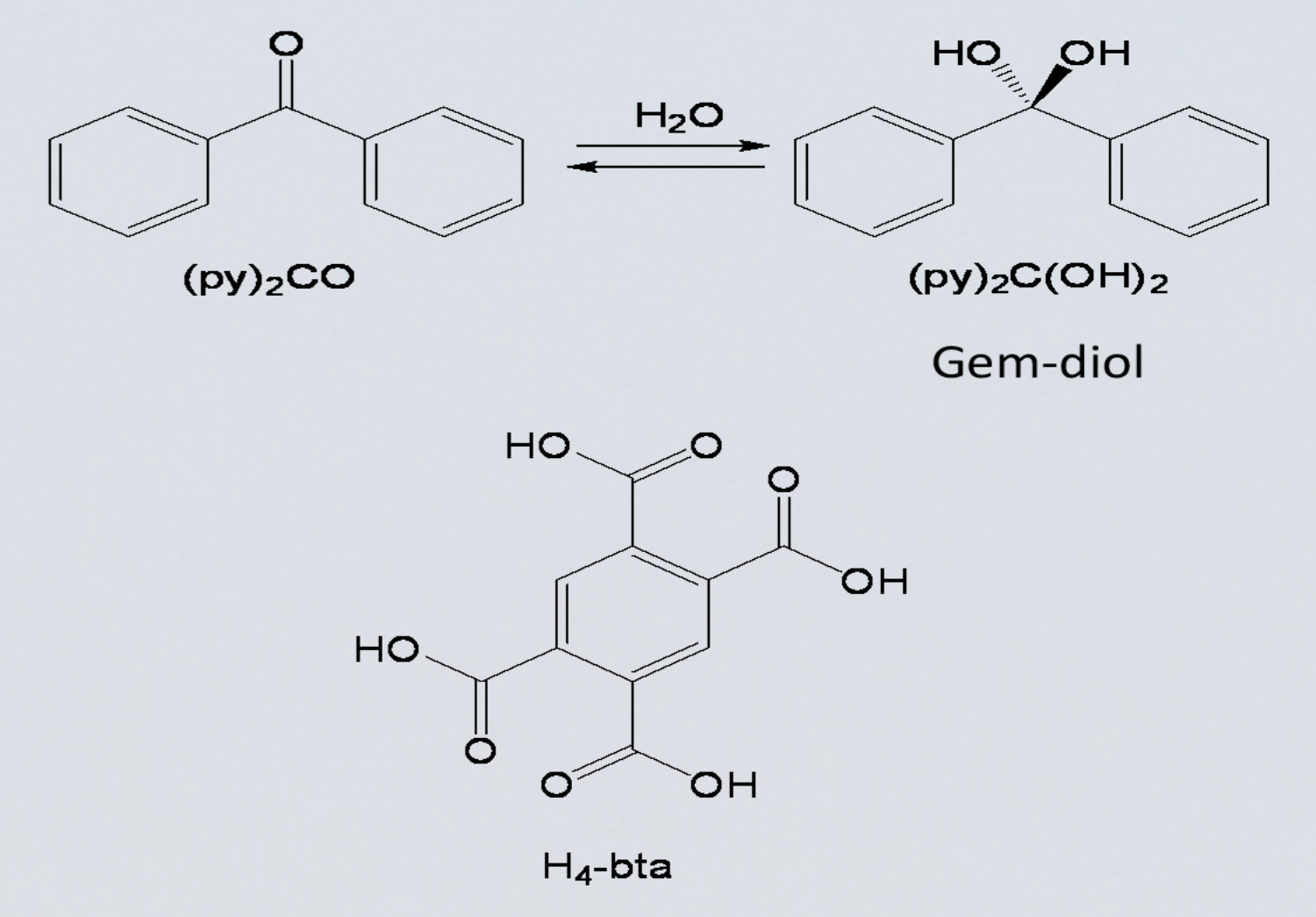
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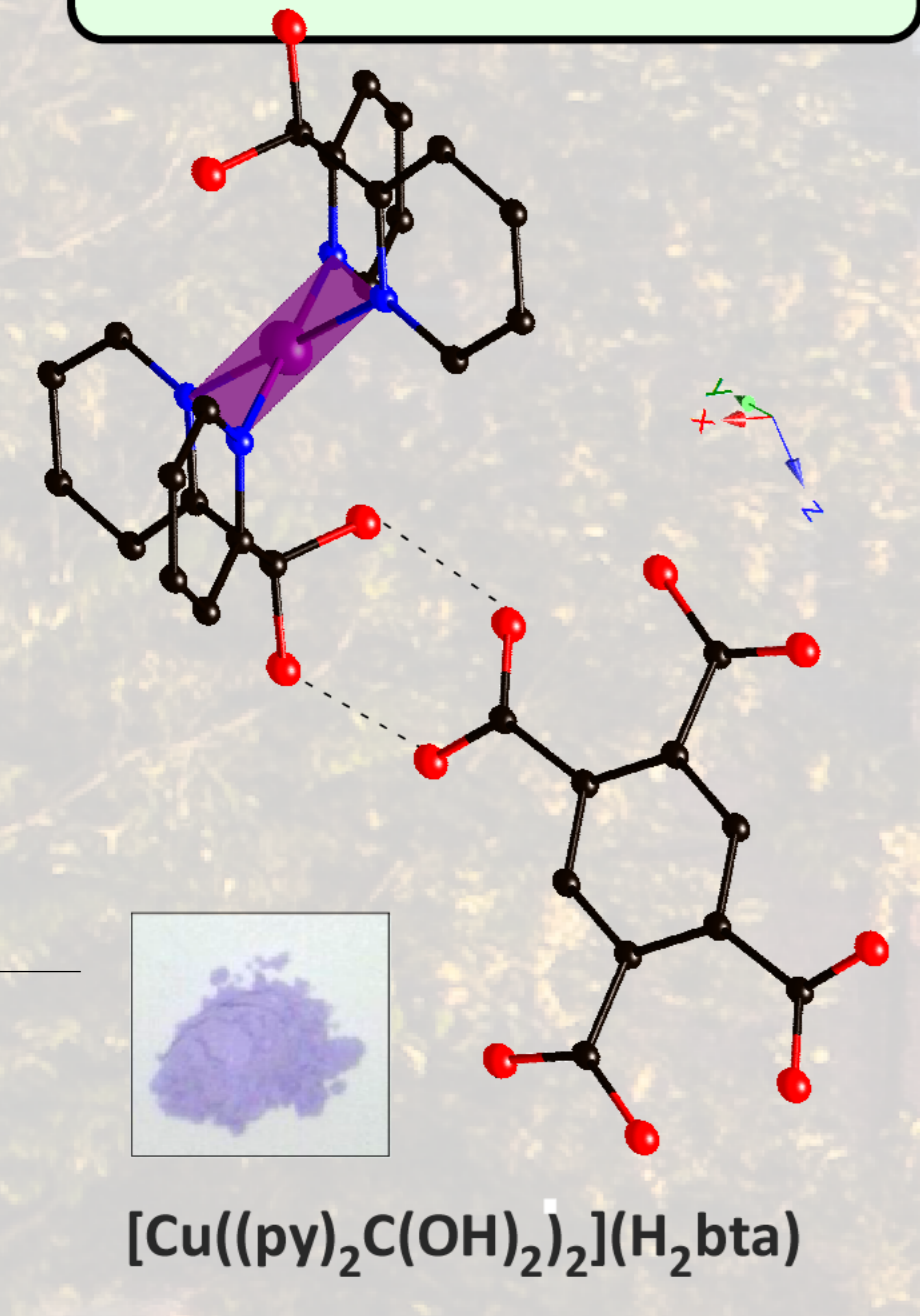
INTRODUCTION

Materials consisting of metal ions or clusters that are linked by polyfunctional organic ligands can form networks of different dimensionalities.[1] Their structural features have opened a wide range of applications in fields [2] like gas storage and separation, drug delivery, chemical sensing, heterogeneous catalysis, biomedical imaging and others referred to their host-guest chemistry like water sorption for heat transformation. In this sense, the use of dipyridyl ligands is an effective strategy to produce extended structures. However, this strategy not always results in 3D networks, as occurred in the case herein presented.

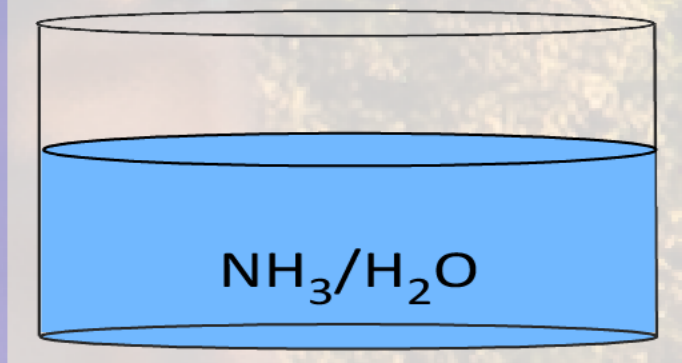
A novel compound, $[\text{Cu}_3(\text{py})_2\text{C(OH)}_2)_4] \cdot 6\text{H}_2\text{O}$ (**1**), has been synthesized from compound $[\text{Cu}(\text{py})_2\text{C(OH)}_2)_2](\text{H}_2\text{bta})$ [3], where $(\text{py})_2\text{C(OH)}_2$ is the gem-diol of di-2-pyridyl ketone ((py) CO) and $\text{H}_4\text{-Bta}$ is 1,2,4,5-benzenetetracarboxylic acid. Additionally the dehydrated phase, $[\text{Cu}_3(\text{py})_2\text{C(OH)}_2)_4]$ (**1-deh.**), has been obtained after a heating treatment.



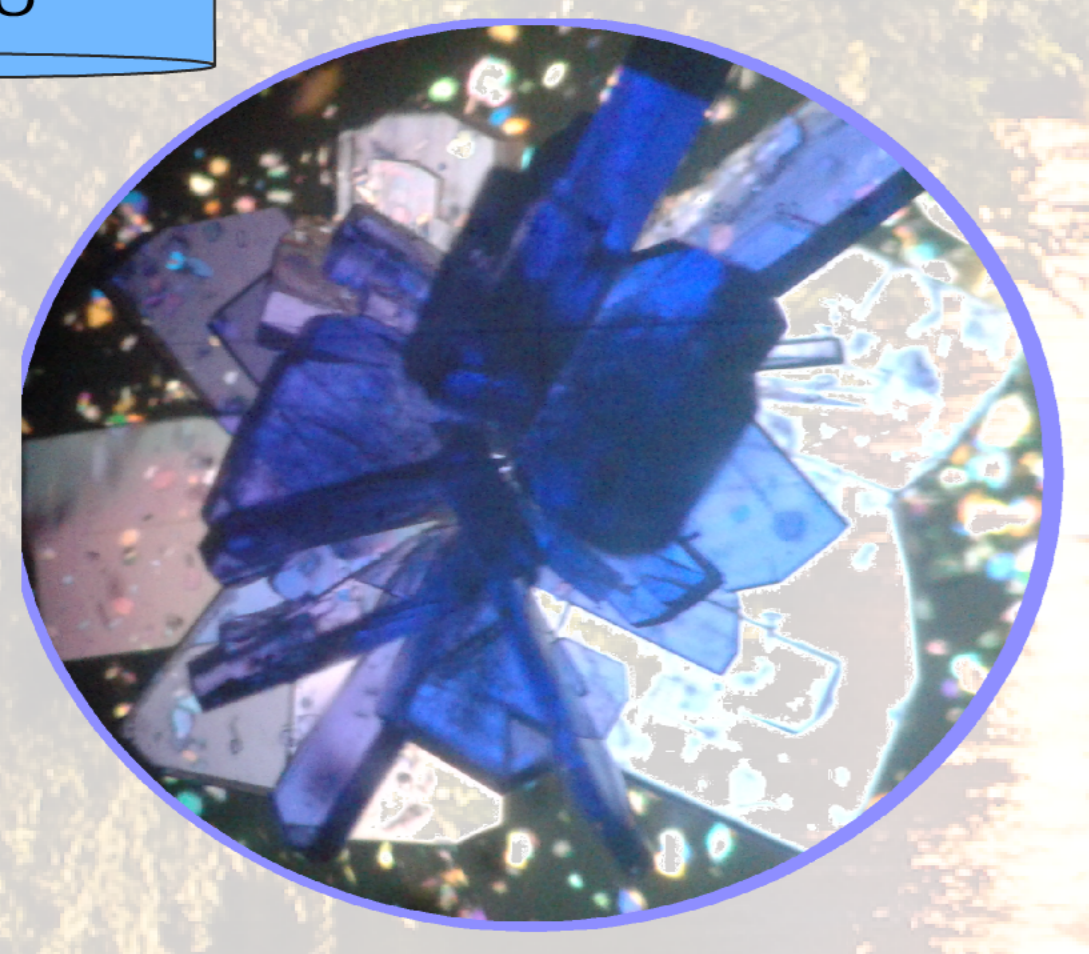
SYNTHESIS



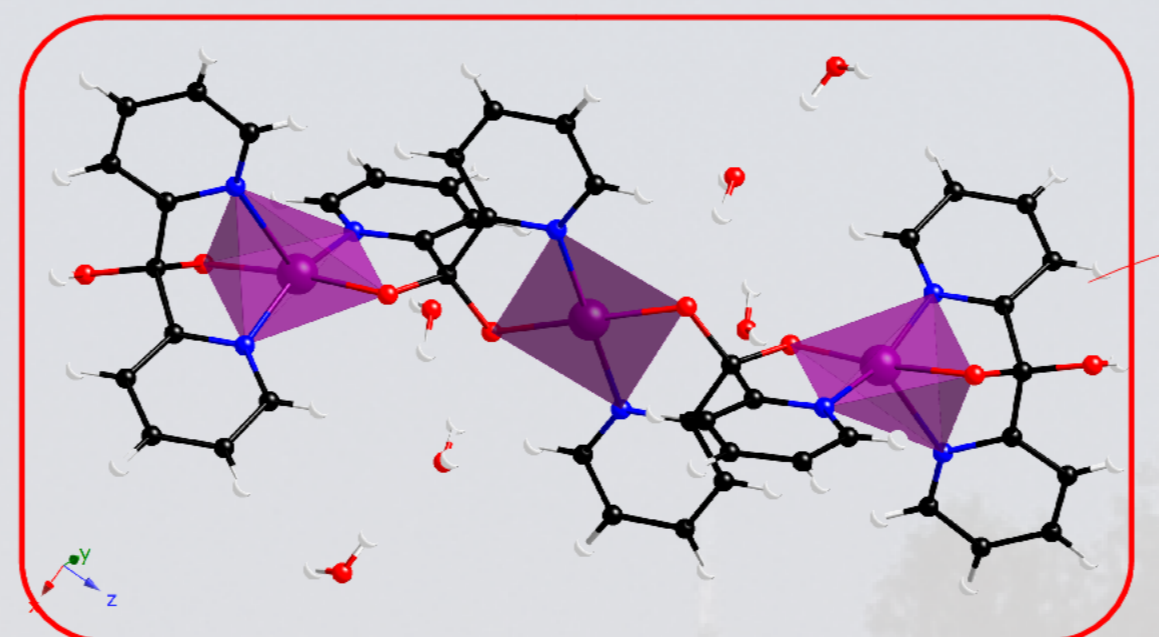
Compound $[\text{Cu}(\text{py})_2\text{C(OH)}_2)_2](\text{H}_2\text{bta})$ was previously synthesized under heating and stirring during 24 h.[3] Afterwards, the purple powered sample was dissolved in a basic aqueous solution ($\text{NH}_3(25\%) / \text{H}_2\text{O}$).



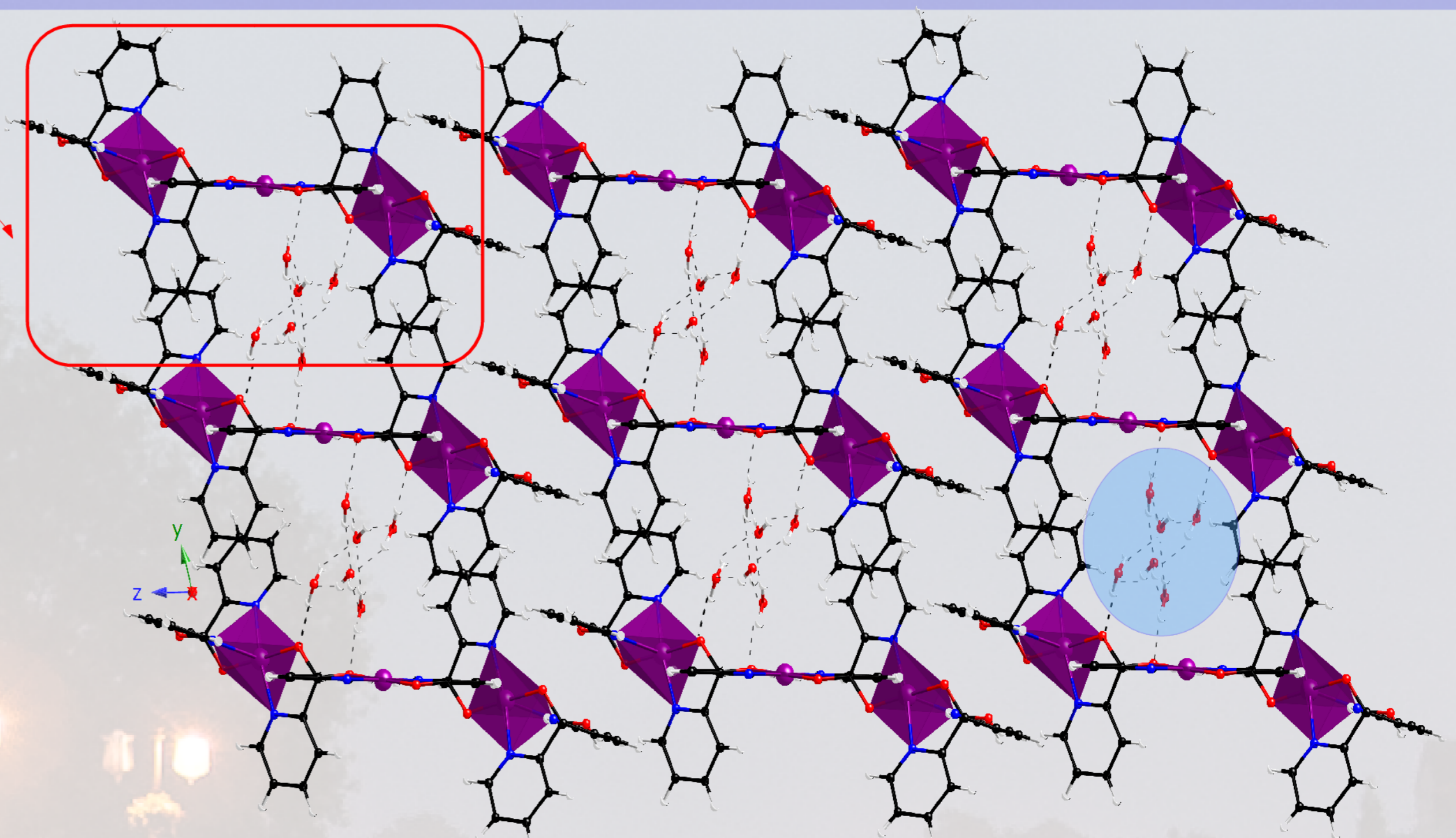
Compound **1**
 $[\text{Cu}_3(\text{py})_2\text{C(OH)}_2)_4] \cdot 6\text{H}_2\text{O}$



CRYSTALLOGRAPHIC STUDY

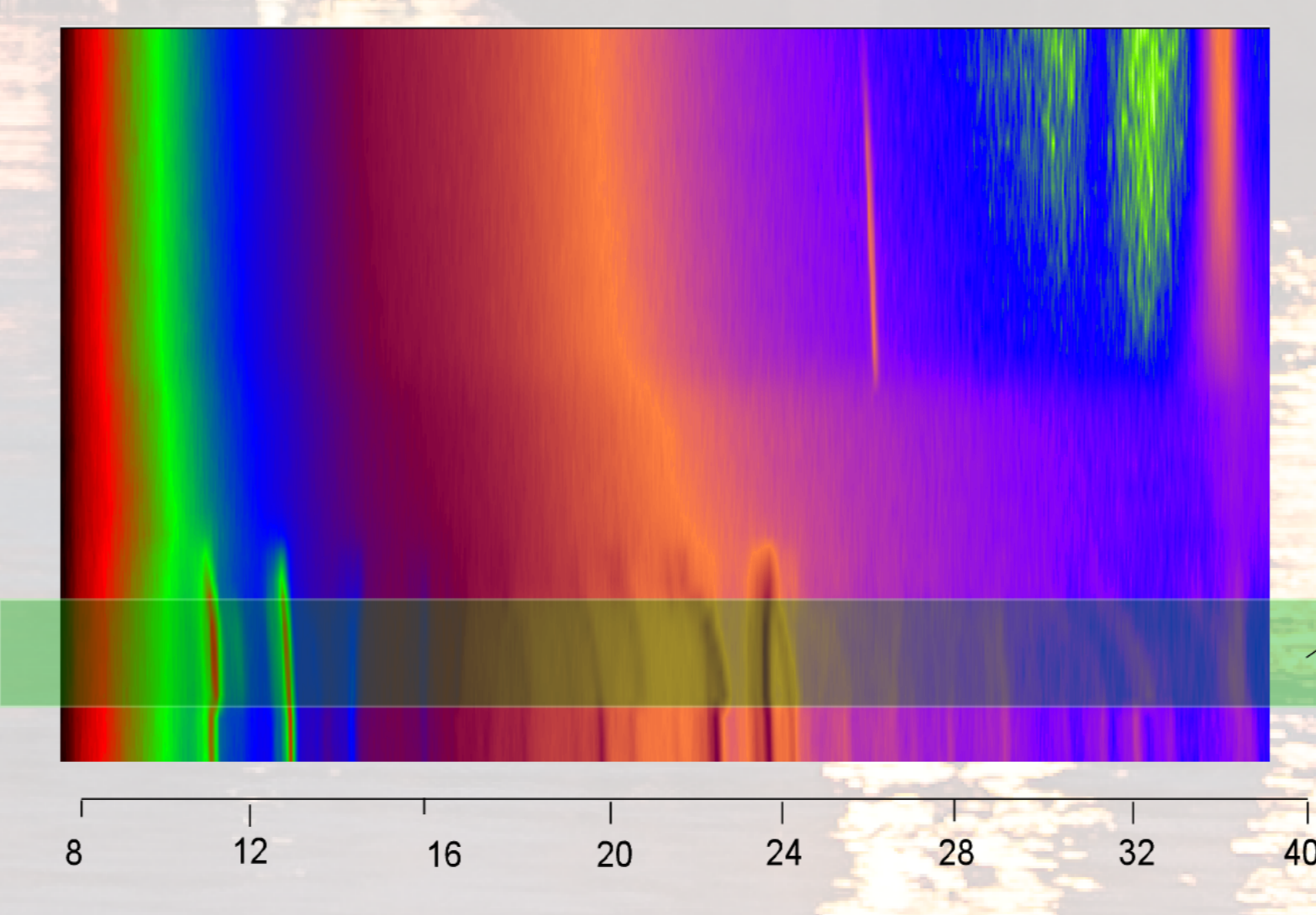


	Compound 1	Compound 1-deh.
Formula	$\text{C}_{44}\text{H}_{46}\text{Cu}_3\text{N}_8\text{O}_{14}$	$\text{C}_{44}\text{H}_{34}\text{Cu}_3\text{N}_8\text{O}_2$
FW, g mol ⁻¹	1100.15	992.15
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a, Å	8.1821(4)	8.226(5)
b, Å	8.9076(5)	8.865(1)
c, Å	16.5299(8)	16.608(1)
α , °	74.586(4)	77.002(8)
β , °	88.111(4)	87.246(5)
γ , °	80.684(4)	80.149(7)
V, Å ³	1146.1(1)	1162.7(2)
Z	1	1
Final R index	R=0.0565	R=0.0475
[I2 σ (I)]a	wR=0.1337	wR=0.1226

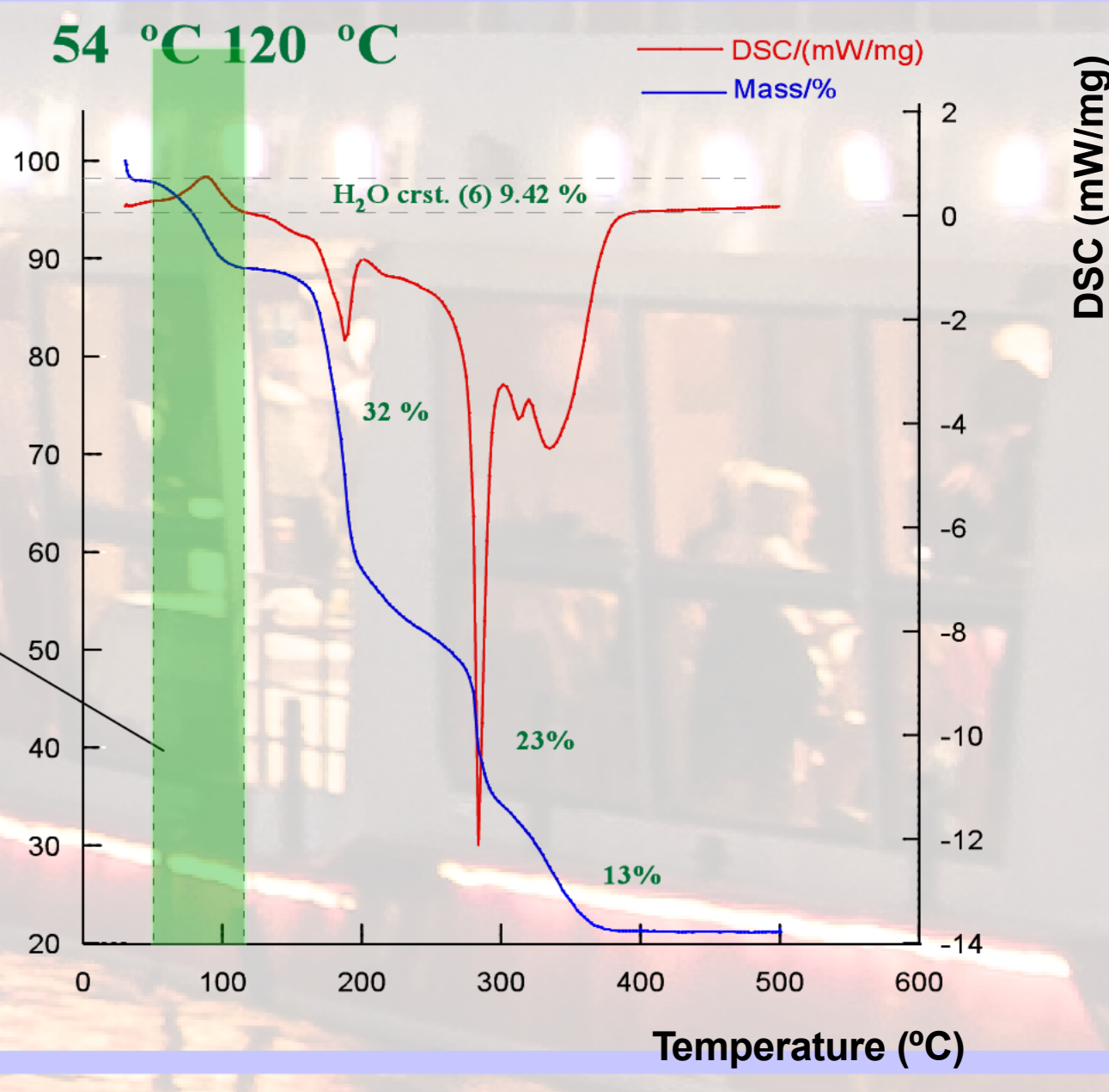


Both crystal structures consist of Cu^{II} -trimers. Two of them are pentacoordinated, whereas the central one is tetraordinated. Hydrogen bonding interactions are responsible for the 3D packing of these trimers.

THERMAL ANALYSIS

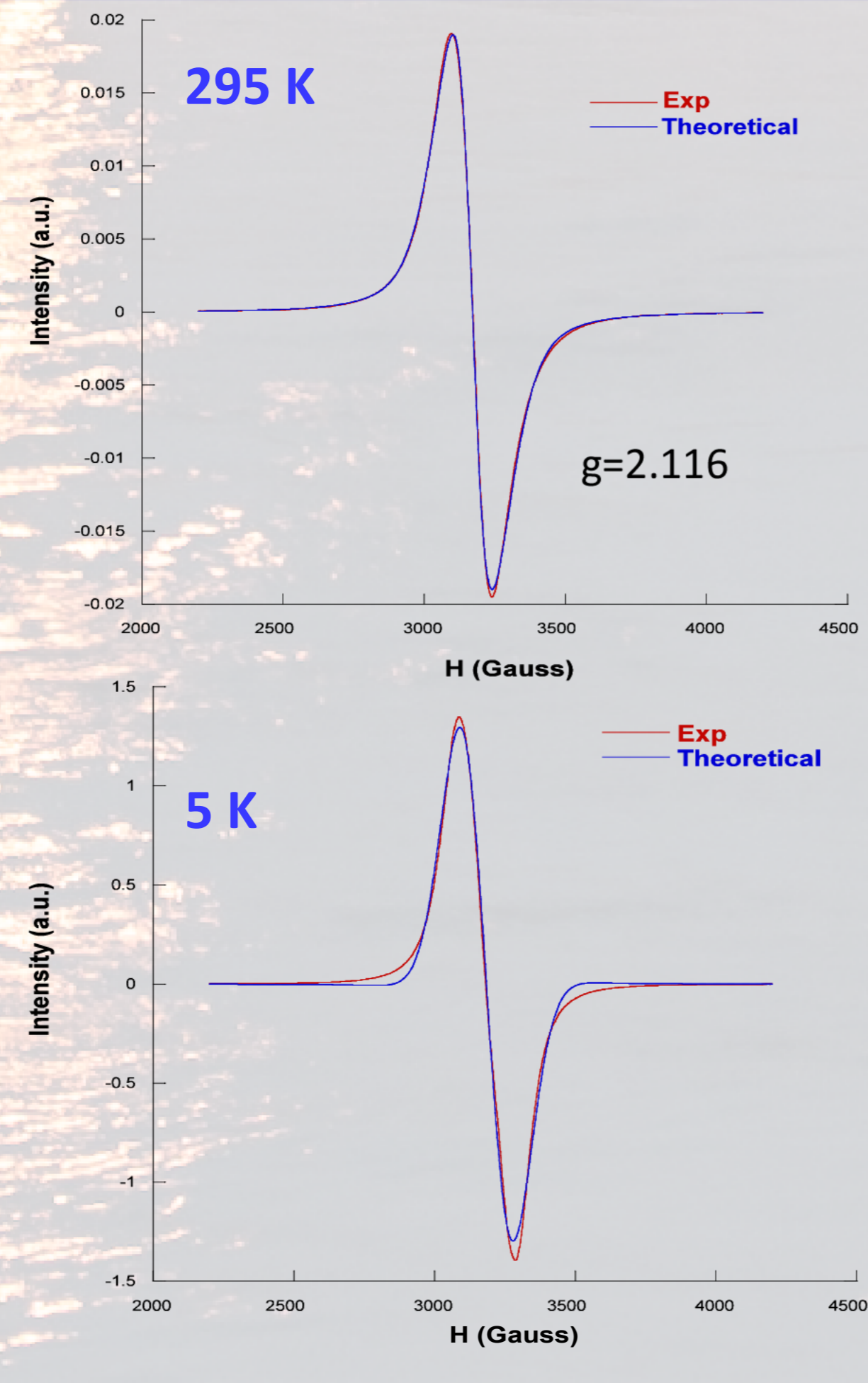
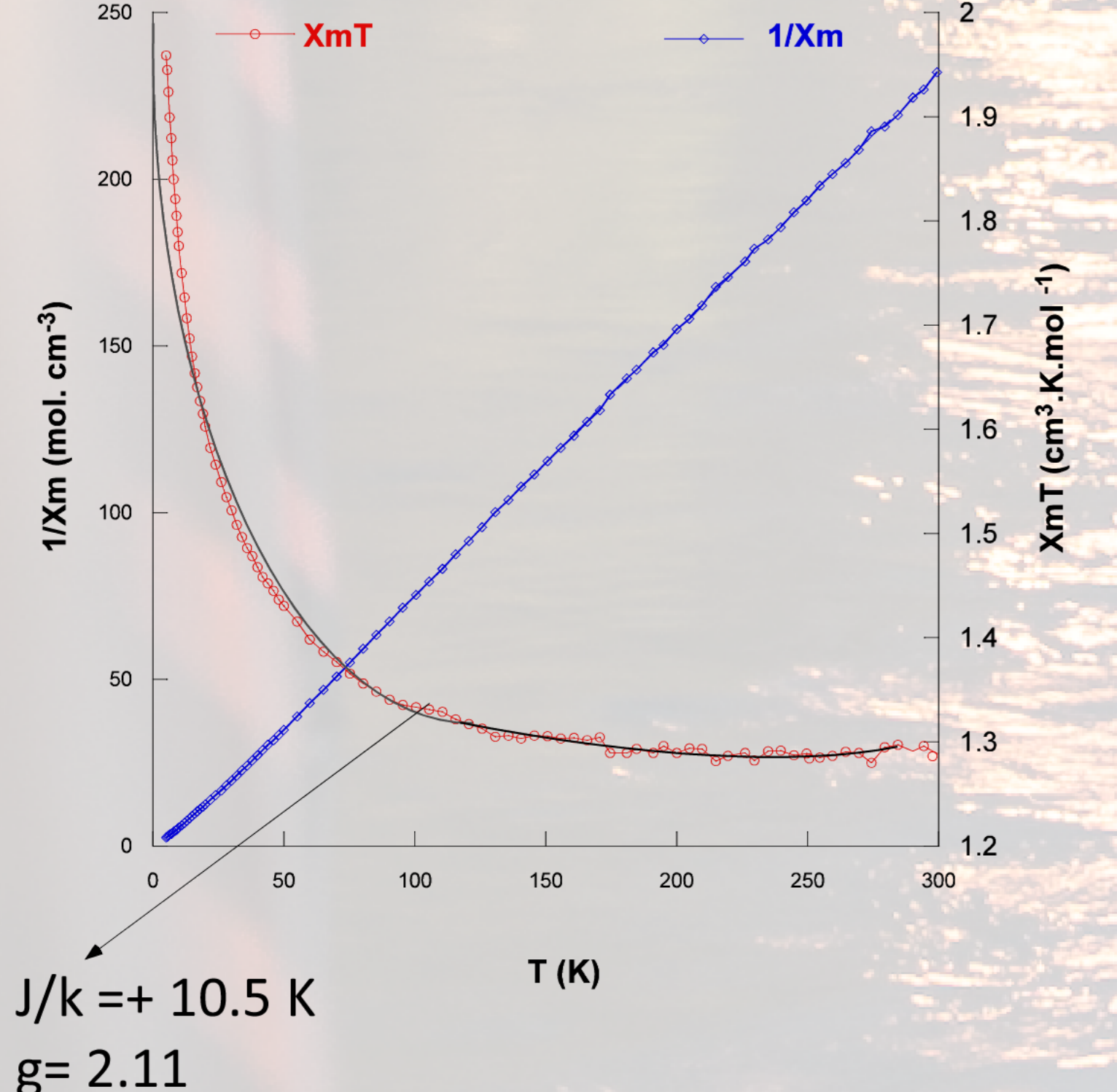


After heating compound **1** during 24 h at 74 °C the solvent molecules are removed.



MAGNETISM AND EPR

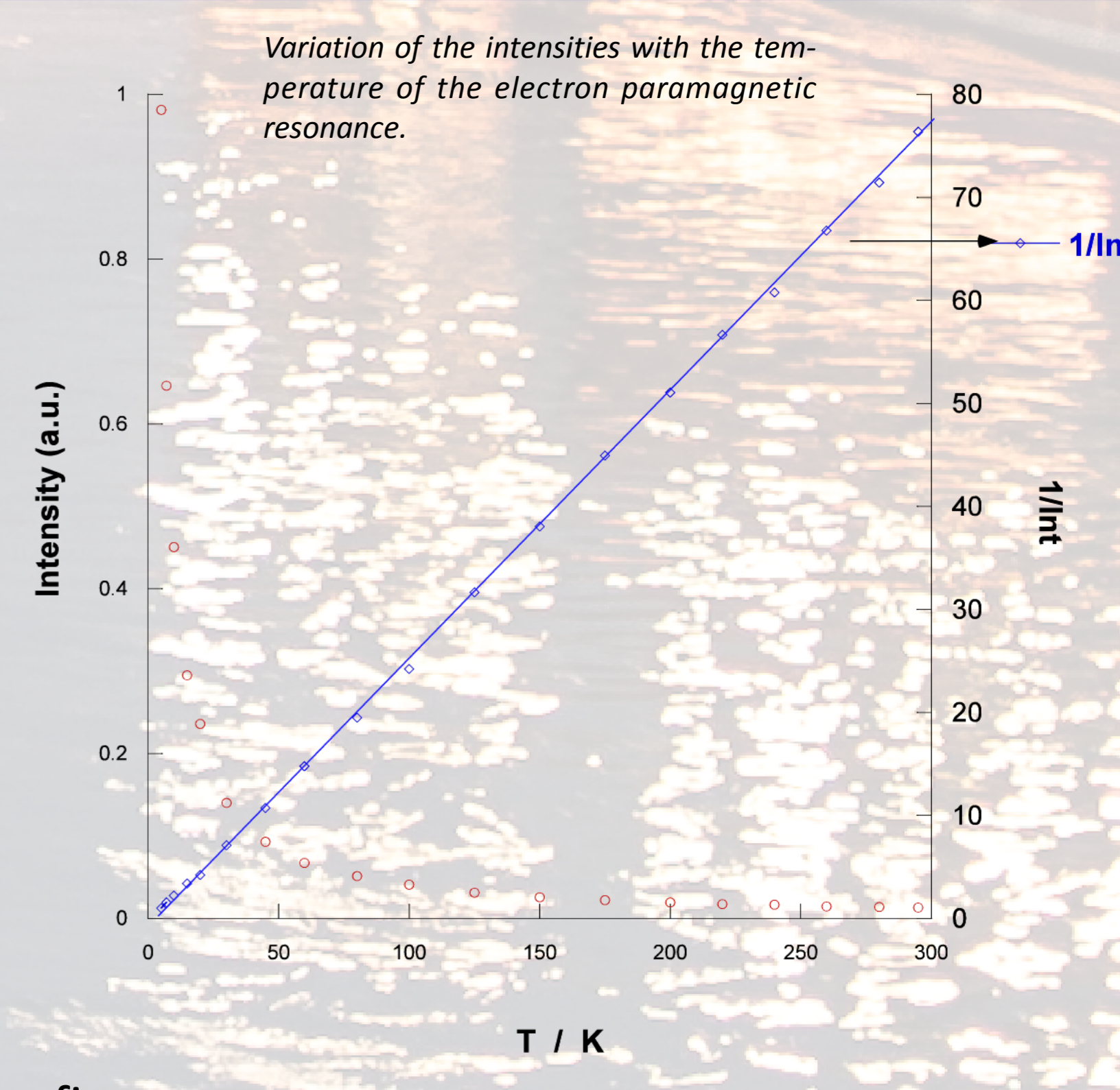
Compound **1** shows a weak ferromagnetic behavior. The magnetic susceptibility follows a Curie-Weiss law with positive temperature intercept ($\theta = +4\text{k}$)



The isotropic signal suggested a coupling among Cu^{II} ions with different orientations. At 295 K the signal can be fitted with a 66 % lorentzian contribution and 33 % Gaussian, which suggests a not totally effective exchange through the orbitals. The g value is about 2.116 that indicates the unpaired electrons in a $d_{x^2-y^2}$ orbital.

At 5 K the Gaussian contribution rise up to 92 % indicating strong increase of the dipolar coupling due to the net contraction.

The electron paramagnetic resonance confirm the weak ferromagnetic behavior of compound **1**.



CONCLUSIONS

The combination of $(\text{py})_2\text{CO}$ with $\text{H}_4\text{-Bta}$ and Cu^{II} produces a ionic precursor compound, $[\text{Cu}(\text{py})_2\text{C(OH)}_2)_2](\text{H}_2\text{bta})$. Using this precursor, $[\text{Cu}_3(\text{py})_2\text{C(OH)}_2)_4] \cdot 6\text{H}_2\text{O}$ (**1**) and its dehydrated phase (**1-deh.**) have been synthesized. The magnetic properties suggest a weak ferromagnetic behavior confirmed by EPR.

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