



Synthesis, Spectroscopic Characterization, and X-ray Structure of the Co-crystal Copper(II) Complex of the Dissymmetrical 1-(2 hydroxy-3-methoxybenzylidene)-5-(pyridin-2 ylmethylene) Carbnohydrazide Ligand

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Abstract: In the pentanuclear title complex, bis{ μ_2 -1-(2-oxido-3-methoxybenzylidene)-5-(pyridin-2-ylmethylene)carbonohydrazide}- $1\kappa^4O,N,N',N''$: $2\kappa^2O,N$; $2\kappa^2O,N$: $3\kappa^4O,N,N',N''$ -1,2,3-tricopper(II) bis{[1-(2-oxido-3-methoxybenzylidene)-5-(pyridin-2-ylmethylene)carbonohydrazide]- κ^4O,N,N',N'' -copper(II)} tetraperchlorate tetrahydrate (1), two monocationic mononuclear units and one dianionic trinuclear unit co-exist. The Cu^{II} centers in the mononuclear units as well as the two terminal Cu^{II} centers in the trinuclear unit are located in the N₃O cavity of the ligand and are coordinated to a phenolate oxygen atom, to a pyridine nitrogen atom, to an imino nitrogen atom and to a hydrazinyl nitrogen atom. The third central Cu(II) atom in the trinuclear unit, which is hexacoordinated, is located in N₂O₄. The metal center is coordinated to two ligand molecule through one imino nitrogen atom one oxygen atom of a carbonyl moiety per ligand and two oxygen atom of water molecules. The tetracoordinated copper(II) ions are situated in distorted square planar environments, while the hexacoordinated copper(II) is located in octahedral geometry. In the mononuclear units, as well as in the trinuclear units, the methoxy oxygen atoms remain uncoordinated. Each atom of the uncoordinated perchlorate anions is disordered over two sets of sites in a 0.5 ratio. Four free water molecules are also present. In the crystal, the trinuclear cationic unit and the mononuclear cationic units are assembled into infinite layers. These layers are held together via electrostatic interactions, forming a three-dimensional structure.

Keywords: O-vanillin, Carbonohydrazide, Schiff Bases, Copper, Mononuclear, Trinuclear

1. Introduction

Since the beginning of the 2000s, interest in asymmetric Schiff base ligands has greatly increased due to the interesting properties generated by the complexes formed [1–8]. Asymmetric Schiff bases associated with transition metals and lanthanides have been widely investigated by chemists. Both mononuclear [9, 10], homobinuclear [11, 12], heterobinuclear [13–15] and polynuclear [16, 17] complexes

have been prepared. A wide range of physico-chemical properties of these metal complexes have been reported in the literature. Some transition metal complexes have shown impressive catalytic capabilities [18–20]. Compounds with anticorrosive [21], electroluminescent [22], photovoltaic [23], biological [24, 25], magnetic [24, 26] or optical [24, 27] properties have been reported. With lanthanides these types of Schiff Base have provided complexes which are exploited in the field of photoluminescence [28] or medical [29].

Polynuclear complexes of transition metal cation with asymmetrical ligand have been studied with increasing interest by chemists [30, 31]. The large variety of structures [32–34], the physicochemical properties [35, 36], and the potential application [29, 37] have made this chemistry very attractive.

Symmetrical as well as unsymmetrical dicarbonohydrazide Schiff bases possess two cavities which can encapsulate metal ion with different size. Depending on the coordination reaction conditions, one or both inner of this kind of ligand can be occupied by a metal ion. In fact, the structure of the ligand present amidic bond which allows the keto-enol tautomer equilibrium. So, the ligand can act in neutral or deprotonated forms. The presence of the moiety —HC=N—NH—C(O)—NH—N=CH— in the structure of the ligand allows two different configurations, such *S*-cis or *S*-trans, yielding different structures with the same metal cation. According to the configuration adopted, the ligand can act in pentadentate or hexadentate fashion [38, 39], as well as in the ketonic or enolic form [40]. When the ligand adopt the *S*-trans it acts in hexadentate fashion and yield generally a dinuclear complex in which the metal ions are μ -*N,N* bridged [41]. When the *S*-cis-enol configuration is adopted by the ligand, square-grid complexes [42–44], in which metal ions are μ -*O* and μ -*N,N* bridged [40, 43] are produced.

Continuing our interest in carbonohydrazide derivatives, we have synthesized and characterized a new pentanuclear copper (II) complex formulated as $\{[\text{Cu}(\text{H}_3\text{L})]_2[\text{Cu}_3(\text{HL})_2(\text{H}_2\text{O})_2]\} \cdot (\text{ClO}_4)_4 \cdot (\text{H}_2\text{O})_2$ where H_3L is 1-(2-hydroxy-3-methoxybenzylidene)-5-(pyridin-2-ylmethylene)carbonohydrazide.

2. Experimental Section

2.1. Starting Materials and Instrumentations

All chemicals and solvents were of analytical reagent grade and were used directly without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000–400 cm^{-1} region. The UV-Visible spectra were recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The molar conductance of 1×10^{-3} M in DMF solution of the metal complex was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibility of the powdered sample was measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: $\text{Hg}[\text{Co}(\text{SCN})_4]$).

2.2. Synthesis of the H_3L Ligand

The ligand is synthesized according to the procedure reported in literature with slight modification [45]. Carbonohydrazide (2 g, 22.2 mmol) was introduced into a

100 mL flask containing 20 mL of methanol. To the resulting suspension was added a methanolic solution containing 2-pyridinecarbaldehyde (2.3785 g, 22.2 mmol) and two drops of glacial acetic acid. The mixture was stirred under reflux for 2 h. A methanolic solution containing *o*-vanillin (3.3807 g, 22.2 mmol) was added and the mixture was refluxed during 4 h. After being kept for two days at 277 K, the resulting solution yielded a white precipitate, which was recovered by filtration. The solid was washed successively with cold methanol (2 x 10 mL) and diethyl ether (2 x 10 mL) before being dried under P_2O_5 ; m.p. 146°C, yield 52%. Analysis calculated for $[\text{C}_{15}\text{H}_{15}\text{N}_5\text{O}_3]$ C, 57.50; H, 4.83; N, 22.35. Found: C, 57.45; H, 4.80; N, 22.30. IR (cm^{-1}): 3407, 3200, 1677, 1609, 1542, 1469, 1252, 1200, 1113. ^1H NMR (DMSO- d_6 , δ (ppm)): 3.82 (s, 3H, —O CH₃); 6.84–7.37 (m, 3H, H_{Ph}); 7.80–8.60 (m, 4H, H_{Py}); 7.3 (s, 1H, H—N); 8.12 (s, 1H, H—C=N); 8.22 (s, 1H, H—C=N); 10.89 (s, 1H, H—N); 11.2 (s, 1H, —OH). ^{13}C NMR (DMSO- d_6 , δ (ppm)): 153.39 (C=O); 151.39 (C_{Ar}); 149.08 (C_{Ar}); 147.77 (C=N); 146.90 (C=N); 142.43 (C_{Ar}); 136.51 (C_{Ar}); 123.55 (C_{Ar}); 119.95 (C_{Ar}); 119.94 (C_{Ar}); 118.8 (C_{Ar}); 113.12 (C_{Ar}); 113.84 (C_{Ar}); 55.78 (—O—CH₃).

2.3. Synthesis of the Title Complex (1)

The title complex was prepared by mixing a solution of H_3L (156.56 mg, 0.5 mmol) in 10 mL of methanol and a methanolic solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (92.63 mg, 0.25 mmol). A green solution was obtained after stirring for 1 h at room temperature. The solution was filtered, and the filtrate left for slow evaporation. After two weeks, green crystals suitable for X-ray diffraction were collected, yield 74.8%. Analysis calculated for $[\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{Cu}_2.67\text{N}_{10}\text{O}_{16.67}]$ C, 34.66; H, 3.10; N, 13.47; Cl, 6.82. Found: C, 34.63; H, 3.07; N, 13.44; Cl, 6.79. Λ ($\text{S cm}^2 \text{ mol}^{-1}$): 167. IR (cm^{-1}): 3500, 3200, 1681, 1609, 1542, 1469, 1252. UV-vis (Solution, DMF, λ (nm)): 257, 372, 481, 607. μ_{eff} (μ_{B}) = 2.93.

2.4. Crystal Structure Determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound (1), were grown by slow evaporation of MeOH solution of the complex. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku FRE+ equipped with Varimax confocal mirrors and UG2 Universal goniometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. Complex scattering factors were taken from the program package SHELXTL [46]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [47]. H atoms (NH, OH, CH and CH₃ groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP [48].

Table 1. Crystallographic data and refinement parameter for the complex (1).

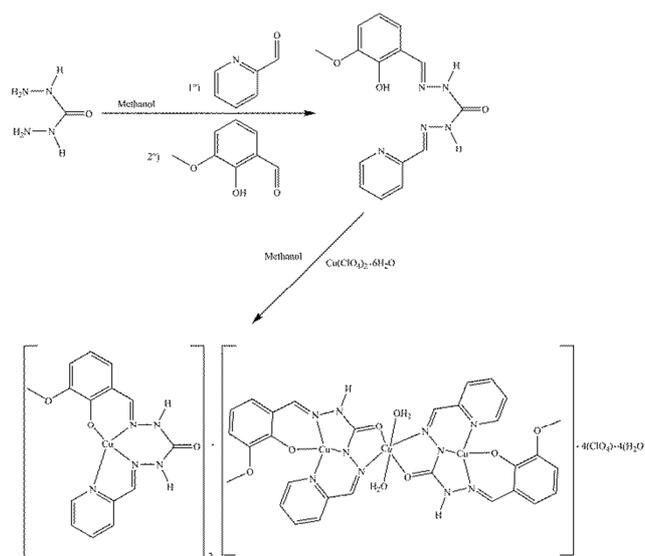
Chemical formula	C ₃₀ H ₃₂ Cu _{2.667} N ₁₀ O _{16.667} Cl ₂
Mr	1039.53
Crystal system, space group	Monoclinic, <i>P2₁/n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.7659 (8), 6.9371 (4), 22.3798 (16)
β (°)	105.947 (7)
<i>V</i> (Å ³)	1905.6 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.71
Crystal size (mm)	0.15 × 0.08 × 0.03
Tmin, Tmax	0.875, 0.963
No. of measured reflections	21060
No. of independent reflections	4353
No. of observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3485
<i>R</i> _{int}	0.032
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.063
w <i>R</i> (<i>F</i> ²)	0.163
GOF	1.12
No. of reflections	4353
No. of parameters	536
No. of restraints	216
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.74, -0.70

3. Results and Discussion

3.1. General Studies

Reaction of copper(II) perchlorate and H₃L produces the pentanuclear copper(II) complex $\{[\text{Cu}(\text{H}_2\text{L})]_2 \cdot [\text{Cu}_3(\text{HL})_2(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_4 \cdot (\text{H}_2\text{O})_2\}$ (Figure 1). The infrared spectra of the ligand and the complex show bands characteristic of the functions of the ligand and those relating to water molecules. Among the vibrations of the free ligand, we present those due to functions involved in the complexation through the donor atoms such as N and O. The vibrations relative to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ imine and $\nu(\text{C}=\text{N})_{\text{py}}$ appear, respectively, at 1677 cm⁻¹, 1609 cm⁻¹ and 1542 cm⁻¹. After reaction of the ligand with copper perchlorate tetrahydrate bands at 1681 cm⁻¹, 1601 cm⁻¹, and 1552 cm⁻¹ are assigned to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})_{\text{imine}}$ and $\nu(\text{C}=\text{N})_{\text{py}}$, respectively. We notice a displacement of all these bands with respect to the free ligand, indicating the involvement of the azomethine nitrogen atom, the pyridine nitrogen atom, and the carbonyl oxygen atom in the coordination with copper. The bands with medium intensity present in all the spectra at *ca.* 3036 cm⁻¹ and 3400 cm⁻¹ are attributed, respectively, to N—H stretching of the ligand and $\nu(\text{O}—\text{H})$ of the free water molecules. After coordination, the ligand remains in its amide form as shown by the $\nu(\text{C}=\text{O})$ band at 1681 cm⁻¹. The presence of the $\delta(\text{H}_2\text{O})$ band at 855 cm⁻¹ indicates the presence of coordinated water molecules. Additionally, the infrared spectrum of the complex (1) presents an intense band approximately around 1070 cm⁻¹ as well as a weak band around 621 cm⁻¹ which are characteristic of tetrahedral free perchlorate ion (ClO₄⁻) [49]. The molar conductivity of complex (1) which was carried out in a millimolar solution of (1) in DMF gives a value of 94 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, indicating 1:2 electrolyte nature [50]. The

electronic spectrum of the complex (1) recorded with millimolar DMF solution reveals, an absorption band centered at 481 nm attributed to the ligand \rightarrow metal charge transfer. Two other absorption bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand are pointed, respectively, at 257 nm and 372 nm. The absorption band pointed at 607 nm is attributed to the d-d transitions of the Cu(II) ion. The effective magnetic moment value of complex (1) of 2.82 MB is far from the value of 1.73 MB expected for a mononuclear complex indicating the presence of two or more Cu(II) ions in the structure [51].

**Figure 1.** Chemical diagrams for the ligand and the compound (1).

3.2. Structure Description of the Complex

The title compound (1) crystallizes in the monoclinic space group *P2₁/n*. The asymmetric unit consists of a co-crystal of two isotype monocationic dinuclear units, $[\text{Cu}(\text{H}_2\text{L})]^+$, one dicationic trinuclear unit, $[\text{Cu}_3(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$, four perchlorate anions and four uncoordinated water molecules. The structure of complex 1 is shown in Figure 2. Owing to the complexity of the structure represented in Figure 2, the structure is depicted in two figures representing respectively the mononuclear unit (Figure 3) and the trinuclear unit (Figure 4). In the mononuclear units (Figure 3), the copper(II) ion is surrounded by one phenolate oxygen atom, one pyridine nitrogen atom and two imino nitrogen atoms. Since the tetragonality parameter $\tau_4 = (360 - \beta - \alpha) / 141$, is evaluated by the two largest angle values in four-coordinated geometry, the τ_4 value of 0.1057 which can be compared with the ideal value of 0 for the square-planar environment and 1 for the tetrahedral environment indicates that the CuON₃ chromophore is best described as a distorted square-planar geometry. The *cisoid* bond angles formed between the copper(II) cation and the coordinated sites are in the range [82.7(6)—94.7(9) °] while the *transoid* bond angles values are 170.9(12)° and 174.2(7)°. The ligand acts in tridentate fashion yielding two six membered rings Cu1B/N2B/N3B/C7B/N4B/N5B and

Cu1B/O1B/C14B/C9B/C8B/N5B with bite angles of 91.7(6)° and 94.7(9)° and one five membered ring Cu/N2B/C6B/C5B/N1B with bite angle of 82.7(6)°. The mean planes of the two six membered ring are slightly twisted with dihedral angle of 2.140(5)°. They are, respectively, twisted relative to the mean plane of the five membered ring with dihedral angles of 3.545(4)° and 4.914(3)°.

The bonds lengths Cu—O is 1.960(4) Å while the distances between the copper atom and the nitrogen atoms of the ligand are slightly different being 1.935(12), 1.938(13) and 1.9995(13) Å. These distances are comparable to those reported for analogous complexes [34, 52].

Table 2. Selected geometric parameters (Å, °).

Atom – Atom	Length	Atom – Atom – Atom	Angle
Cu1A—N1A	1.994 (7)	N3A—Cu1A—N1A	92.6 (2)
Cu1A—N3A	1.894 (6)	N3A—Cu1A—N5A	80.7 (3)
Cu1A—N5A	1.963 (8)	N5A—Cu1A—N1A	173.2 (3)
Cu1A—O2A	1.825 (16)	O2A—Cu1A—N1A	94.0 (4)
Cu1B—N1B	1.995 (13)	O2A—Cu1A—N3A	172.2 (5)
Cu1B—N2B	1.935 (12)	O2A—Cu1A—N5A	92.8 (4)
Cu1B—N5B	1.938 (13)	N2B—Cu1B—N1B	82.7 (6)
Cu1B—O2B	1.96 (4)	N2B—Cu1B—N5B	91.7 (6)
Cu2A—N2A	1.973 (7)	N2B—Cu1B—O2B	170.9 (12)
Cu2A—N2A ⁱ	1.973 (7)	N5B—Cu1B—N1B	174.2 (7)
Cu2A—O1A ⁱ	1.941 (9)	N5B—Cu1B—O2B	94.7 (9)
Cu2A—O1A	1.941 (9)	O2B—Cu1B—N1B	90.6 (9)
Cu2A—O4A	2.455 (8)	N2A—Cu2A—N2A ⁱ	180.0 (4)
Cu2A—O4A ⁱ	2.455 (8)	N2A ⁱ —Cu2A—O4A	93.8 (3)
		O1A ⁱ —Cu2A—N2A	97.4 (3)
		O1A ⁱ —Cu2A—N2A ⁱ	82.6 (3)
		O1A—Cu2A—N2A	82.6 (3)
		O1A—Cu2A—O1A ⁱ	180.0 (3)
		O1A ⁱ —Cu2A—O4A	98.0 (4)
		O1A—Cu2A—O4A	82.0 (4)

Symmetry code: (i) -x, -y, -z+1.

In the trinuclear unit (Figure 4), the cation [Cu₃(HL)₂(H₂O)₂]²⁺ lies on a crystallographic twofold axis. The coordination spheres of the terminal copper(II) cations are distorted square planar geometries with τ_4 value of 0.1035. Cu1A and his related symmetry adopt N₃O coordination spheres with *cisoid* bond angles varying in the range 80.7(3)°—94.0(4)°. The Cu1A/O2A/N5A/N3A/N1A atoms are quite coplanar (rms 0.0376) with the Cu1A situated at 0.0182(6) Å out of the mean plane. The *transoid* bonds angle are O2A—Cu1A—N3A = 172.2(5)° and N5A—Cu1A—N1A = 173.2(3)°. The central Cu2A is situated in a N₂O₄ environment which is best described as a distorted octahedral geometry. The basal plane is occupied by the atoms from the ligand, the axial positions being occupied by two oxygen atoms from coordinated water molecules. The atoms in the equatorial plane are perfectly coplanar (rms 0.000) with the Cu2A at 0.000 Å out of the mean plane. The distortion can be seen from the *cisoid* bonds angle formed by the atoms occupying the basal plane [O1A—Cu2A—N2Aⁱ = 97.4(3)°; O1A—Cu2A—N2A = 82.6(3)°]. All the *transoid* bonds angle around Cu2A are equal to 180°. The two terminal Cu atoms and the central Cu atom are perfectly

aligned with the bond angle Cu1A—Cu2A—Cu1Aⁱ = 180°, with equal distances between two adjacent atoms [4.655 Å (Cu1A...Cu2A) and 4.655 Å (Cu2A...Cu1Aⁱ)]. The Cu—O bonds involving the central Cu2A, and the oxygen atom of the ligand are comparable to those involving the terminal Cu1A and Cu1Aⁱ [Cu2A—O1A = 1.941(9) Å; Cu1A—O2A = 1.825(16) Å]. The Cu—N_{imine} [Cu2A—N2A = 1.973(7) Å and Cu1A—N5A = 1.963(8) Å], Cu—N_{hydrazinyl} [Cu1A—N3A = 1.894(6) Å] and Cu—N_{pyridine} [Cu1A—N1A = 1.994(7) Å] bond lengths are comparable to those reported for a similar complex [53]. The coordination of the ligand molecule acting in tridentate fashion with the Cu1A cation results in the formation of two six membered rings Cu1A/N1A/C5A/C6A/N2A/N3A and Cu1A/O2A/C14A/C9A/C8A/N5A with bite angle values of 92.6(2)° and 92.8(4)° and one five membered ring Cu1A/N3A/C7A/N4A/N5A with bite angle value of 80.7(3)°. The three mean planes formed by the two six-membered rings and the five-membered ring share a vertex occupied by the Cu1 atom. The mean planes of the two six membered ring are quite coplanar with dihedral angle of 1.644(3)°. They are, respectively, quite coplanar to the mean plane of the five membered ring with dihedral angles of 1.771(2)° and 0.735(2)°. The same ligand acts in bidentate fashion with Cu2A yielding a five membered ring Cu2A/N2A/N3A/C7A/O1A with bite angle of 82.6(3)°.

Each copper atom of a mononuclear unit is almost located in front of a copper atom in terminal position of the trinuclear. Thus, each ligand atom of a mononuclear complex is located opposite the analogue atom of the ligand in the trinuclear unit (Figure 2).

Table 3. Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C2B—H2B...O9B ⁱⁱ	0.95	2.15	3.050 (19)	158.1
C6A—H6A...O8A ⁱⁱⁱ	0.95	2.35	3.11 (3)	137.3
C11A—H11A...O9A ^{iv}	0.95	2.16	3.08 (4)	161.5
C12A—H12A...O4A ^v	0.95	2.36	3.074 (12)	131.8
N3B—H3BA...O1B ⁱ	0.88	1.80	2.67 (3)	169.4
N4A—H4AA...O6A	0.88	1.80	2.67 (4)	170.2
N4B—H4BA...O6B	0.88	2.11	2.98 (5)	166.6
O4A—H4AB...O9A	0.85	2.54	3.034 (12)	117.8
O6A—H...O7A ^{vi}	0.85	2.33	3.03 (4)	139.7
O6A—HA...O10A ^{vi}	0.85	2.46	3.12 (7)	135.1

Symmetry codes: (i) -x, -y, -z+1; (ii) -x+1/2, y-1/2, -z+1/2; (iii) x, y-1, z; (iv) -x+1, -y+1, -z+1; (v) x+1, y, z; (vi) x+1/2, -y+1/2, z+1/2.

The structure of the compound present intermolecular hydrogen bonding of type O—H...O involving coordinated water molecule and free perchlorate group: O4A—H4AB...O9A and N—H...O involving hydrazinyl group and free water molecule N4A—H4AA...O6A and N4B—H4BA...O6B. Numerous intra-molecular hydrogen bonding stabilized the structure. The packing of the molecules reveals that the sheets of the coordination polymer units are connected through intermolecular hydrogen bonding involving coordinated and uncoordinated water molecules as donor and perchlorate oxygen atoms as acceptor (*ie.* O6A—

$\text{H}\cdots\text{O7A}^{\text{iv}}$; $\text{iv} = -x+1, -y+1, -z+1$ and hydrazinyl group as donor and carbonyl oxygen atom as acceptor ($\text{N3B}\cdots\text{H3B}\cdots\text{O1B}^{\text{i}}$; $\text{i} = -x, -y, -z+1$) (Table 2) leading to a three-dimensional supramolecular network (Figure 5). The

structure is consolidated by the presence of intermolecular hydrogen bonding type of $\text{C}\text{--}\text{H}\cdots\text{O}$. For the mononuclear units, dimerization due to hydrogen bonding $\text{N}\text{--}\text{H}\cdots\text{O}$ is observed resulting in a $R_2^2(8)$ loop as shown in Figure 3.

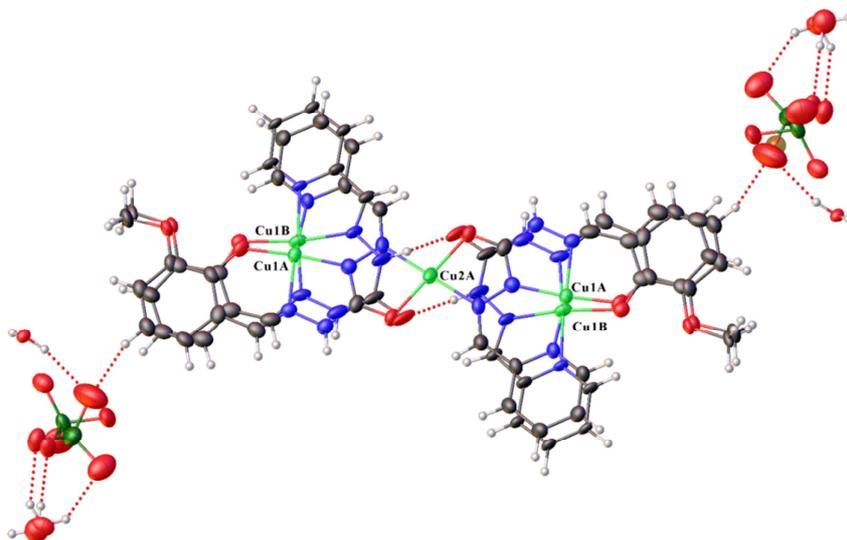


Figure 2. Crystal structure of the pentanuclear complex (1).

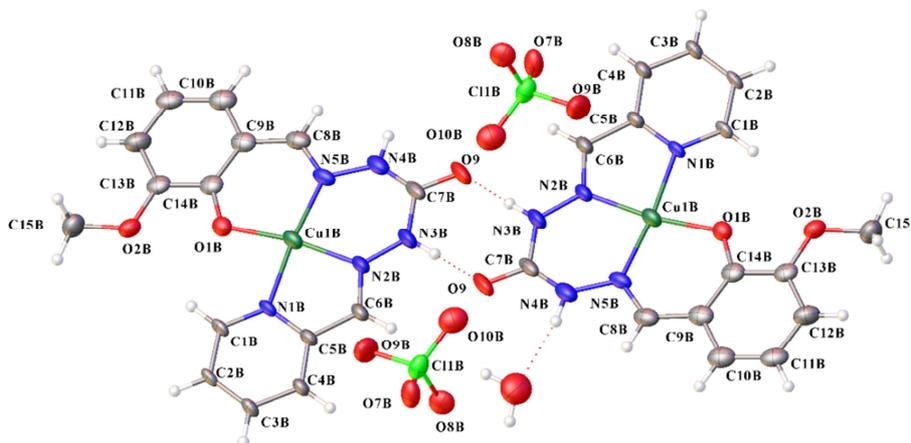


Figure 3. Part 1 of the co-crystal structure of the pentanuclear complex (1).

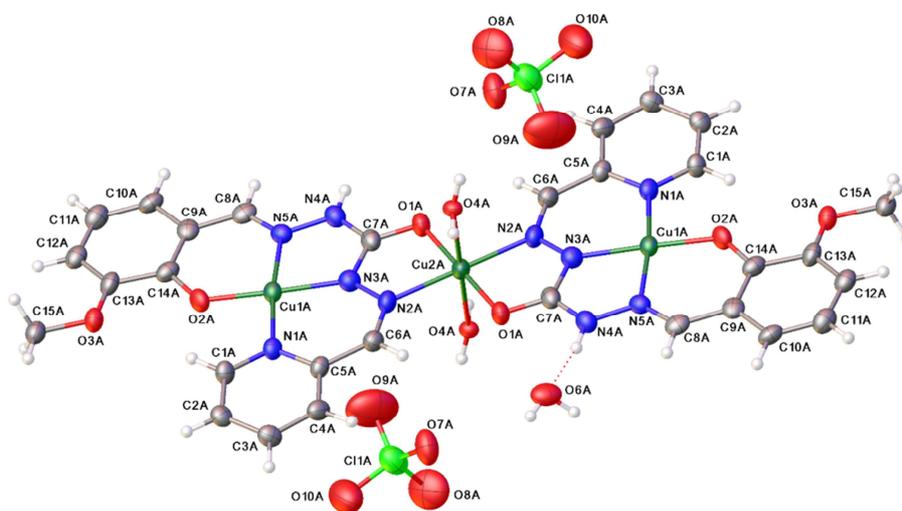


Figure 4. Part 2 of the co-crystal structure of the pentanuclear complex (1).

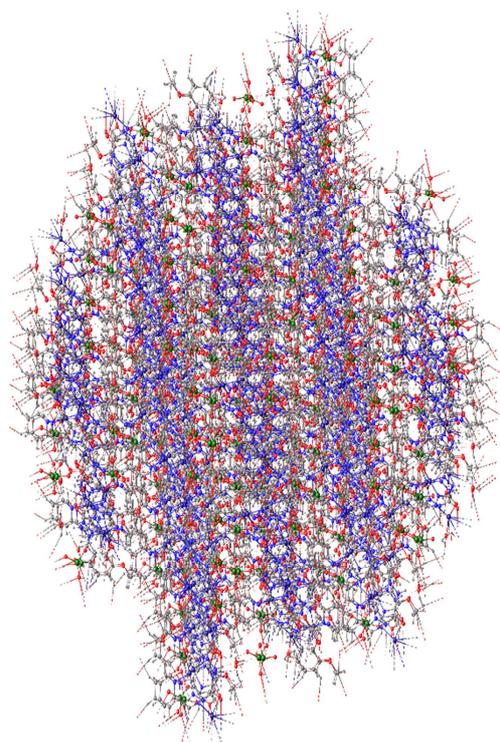


Figure 5. The packing of the complex in the crystal structure.

4. Conclusion

The *c* (H_3L) was synthesized and used to prepare the complex (1). The pentanuclear compound 1 is characterized by elemental analysis, magnetic moment, molar conductivity and FTIR spectroscopy. The X-ray diffraction technique reveals that two mononuclear units and one trinuclear unit coexist in the crystal. Both copper cations in the mononuclear unit are situated in a square planar environment. In the trinuclear unit the three copper cations are perfectly aligned. The two terminal copper (II) ions adopt a square planar geometry while the central copper(II) ion is situated in an octahedral environment. In the structure, each terminal copper ion of the trinuclear unit is opposite with a copper ion of a mononuclear unit.

Supplementary Materials

CCDC-2234018 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk (or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

In Memorium

Mouhamadou Moustapha SOW 1982–2022.

While preparing this work, we were shocked to hear of the death of Dr Mouhamadou Moustapha SOW. Dr Mouhamadou Moustapha SOW was a very talented young chemist working in inorganic chemistry. SOW has helped many PhD students over the years and his informed advice and support will be greatly missed by our team, both personally and professionally. This article is dedicated to his memory.

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