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Syntheses, Characterization, and X-Ray Crystal Structure of a Co-Crystal Containing One Neutral Mononuclear Copper (II) Unit and One Cationic Dinuclear Copper (II) Unit Assembled with Schiff Base and Perchlorate Copper(II) Salt

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Abstract

The use of 2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl}phenol (H_2L) in metal transition chemistry has yielded a co-crystal which is composed by one neutral mononuclear, one cationic dinuclear and one perchlorate anion. During the formation of the complex, one of the salicylaldimine groups of one of the molecules of the H_2L ligand hydrolyzed to form an asymmetrical ligand with an amino group leading to the molecule (2-((2-aminophenylimino)methyl)phenol (HL'). The complex was formulated as $\{[Cu(L)]\cdot[Cu_2(L)(L')]\}\cdot(ClO_4)$. The structure of the complex was solved by single crystal X-ray crystallography. In the mononuclear unit, the Cu^{2+} atom is coordinated by one dideprotonated molecule of the ligand acting in tetradentate fashion. In the dinuclear unit, one the Cu^{2+} atom is coordinated by one dideprotonated molecule of the ligand acting in tetradentate fashion and the other Cu^{2+} is coordinated by the monodeprotonated (2-((2-aminophenylimino)methyl)phenol (HL') acting in tridentate fashion. The two Cu^{2+} are bridged by the two phenoxo oxygen atoms of the dideprotonated molecule of the ligand. The complex crystallizes in the triclinic space group $P\bar{1}$ with the following parameters: a = 13.8864 (3) Å, b = 14.2078 (4) Å, c = 14.5007 (4)) Å, α = 64.593 (3), β =

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71.353 (2), γ = 71.707 (2)°, V = 2395.80 (13) Å^3, Z = 2, R_1 = 0.037, wR_2 = 0.041. The supramolecular structures are consolidated by multiple hydrogen bonds.

1. Introduction

Schiff base ligands with multiple coordination sites are the best choices for building multinuclear metal complexes. Bridged mononuclear and dinuclear copper(II) complexes have attracted much interest from chemists due to their original structures and their physical properties [1-7]. Much works have been published in recent years to investigate the relationship between structure and physical properties in dinuclear complexes in which the metal centers are bridged by phenoxo oxygen atoms [8-10]. The value of the angle the Cu-O-Cu moiety, strongly influence the magnetic interaction between the metal centers [11-13]. Several compounds exhibiting a Cu-O-Cu double bridge with antiferromagnetic properties are listed in the literature [11, 14-16]. Schiff bases having several salicylaldimine groups are effective in obtaining this type of complexes. Due to the bridging capacity of the phenoxo group, these ligands always show coordination capacity with both transition metal ions and lanthanide ions [17-21]. They can make it possible to obtain mononuclear which can be used as bricks to build other molecular buildings blocks [22-24]. Therefore, ligands with salicylaldimine moieties are effective for the construction of hetero-metallic complexes with d-block and f-block elements [25-27]. These ligands have also made it possible to prepare molecular species containing both s-block and d- or f-block elements [28-30]. Several compounds with magnetic [23,24], catalytic [31,32], and bioactivity [22] properties are listed in the literature. Our research group have already used salicylaldimine derivatives to prepare metalloligands and use them to prepare multinuclear complexes [29,30].

In this present work, we used a symmetric ligand having two salicylaldimine moieties (2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl}phenol (H_2L)) to prepare a complex which is formed of a neutral mononuclear unit, a cationic dinuclear unit and a perchlorate anion. It should be noted that during the formation of the complex, one of the salicylaldimine groups of one of the molecules of the H_2L ligand hydrolyzed to form an asymmetrical ligand with an amino group leading to the molecule (2-((2-aminophenylimino)methyl)phenol (HL'). The complex formulated as $[Cu(L)]\cdot[Cu_2(L)(L')\}]\cdot(ClO_4)$ is characterized by different spectroscopic studies. The differences in stoichiometry and in the structures of the units mononuclear and dinuclear were confirmed by X-ray diffraction.

2. Materials and Methods

2.1. Starting materials and instrumentations

Salicylaldehyde, 1,2-diaminobenzene and $Cu(ClO_4)_2{\cdot}6H_2O$ were of analytical reagent grade and were obtained from Sigma-Aldrich Company. All used 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 an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm^{-1} region. The UV-Visible spectrum was recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker 500 MHz spectrometer at room temperature using TMS as an internal reference.

2.2. Synthesis of 2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl}phenol (H_2L)

To a solution of 4.84 g (40 mmol) of salicylaldehyde in 15 mL of ethanol was added dropwise a solution of 2.16 g (20 mmol) of 1,2-diaminobenzene in 15 ml of EtOH. Orange precipitate appears progressively. Two drops of glacial acetic acid were added, and the mixture was refluxed for 2 hours. On cooling to room temperature, the orange precipitate was recovered by filtration and washed with 5 mL of ethanol before dried under vacuum. Yield 35 %. m.p. > 260 °C. Anal. Calc for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.90; H, 5.06; N, 8.88. NMR ^1H (300 MHz, DMSO-d_6) 6.97-7.66 (mult, 12H, H_{Ar}); 8.94 (S, 2H, HC=N); 12.93 (S, 2H, OH). IR (cm^{-1}): 3254, 1610, 1596.8, 1557.95, 1479.96, 1361.32, 1275.35, 909, 787, 639.

2.3. Synthesis of the complex {[Cu(L)].[Cu_2(L)(L')]}·(ClO_4)

To a solution of 0.3 g (0.9482 mmol) of H_2L in 10 mL of methanol, was added a solution of 0.7g (1.8963 mmol) of $Cu(ClO_4)_2.6H_2O$ in 10 mL of methanol. The mixture is heated at reflux for 1 hour. The resulting green solution was filtered and then left for slow evaporation. Black single crystals, suitable for X-ray diffraction, were recovered after 4 days. Calc for $C_{53}H_{39}ClCu_3N_6O_9$: C, 56.33; H, 3.48; N, 7.44. Found: C, C, 56.30; H, 3.46; N, 7.41.

2.4. Crystal structure determination

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku XtaLAB PRO diffractometer with graphite monochromatized Mo *K*α radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [33]. 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 [34]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [35].

Table 1. Crystal data and structure refinement for $\{[Cu(L)]\cdot[Cu_2(L)(L')]\}\cdot(ClO_4)$.

Empirical formula	$C_{53}H_{39}ClCu_3N_6O_9$
Formula weight (g/mol)	1129.97
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	0.20 × 0.10 × 0.10
Mo *K*α (Å)	0.71073
Temperature (K)	293
a (Å)	13.8864 (3)
b (Å)	14.2078 (4)
c (Å)	14.5007 (4)
α (°)	64.593 (3)
β (°)	71.353 (2)
γ (°)	71.707 (2)
V (Å^3)	2395.80 (13)
Z	2
D_{calc} (g.cm^{-3})	1.566

F(000)	1150
μ (mm^{-1})	1.44
θ_{max} (°)	27.877
h, k, l ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-18 \leq l \leq 19$
Measured reflections	54980
Independent reflections	11323
Reflections [$I > 2\sigma(I)$]	8922
R_{int}	0.037
$R[I > 2\sigma(I)]$	0.041
wR_2	0.118
Data/parameters/restraints	11323/657/0
Goodness-of-Fit	1.05
$\Delta\rho$max, $\Delta\rho$min (e Å^{-3})	0.68, −0.45

3. Results and Discussion

3.1. General study

The IR spectrum of the 2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl} phenol (H_2L) ligand shows an absorption band around 1610 cm^{-1} which is attributed to the $\nu_{C=N}$ vibration of the imine. The bands due to vibrations $\nu_{C=C}$ of the aromatic ring are in the range 1475 and 1600 cm^{-1}. The intense and sharp band at *ca.* 758 cm^{-1} is due to the $\nu_{C\text{-}H}$ deformation of the aromatic ring. Additional band pointed at 3254 cm^{-1} due the $\nu_{O\text{-}H}$ of the phenol ring is observed.

The reaction of the ligand H_2L with perchlorate copper (II) salt afforded back crystal complex. The infrared spectrum of the complex shows a band at 1604 cm^{-1} attributable to the $\nu_{C=N}$ elongation. The shift of this vibration band to low frequencies, comparatively to the free ligand spectrum, is indicative of the involvement of the azomethine nitrogen atom in the coordination to the metal center. The absence of the band at 3254 cm^{-1} attributed to the $\nu_{O\text{-}H}$ in the free ligand indicates that the ligand acts in its deprotonated form. The bands observed as doublets at *ca.* 3500 cm^{-1} suggest the presence of -NH_2

group in the molecule. These bands was not observed in the spectrum of the free ligand. These facts suggest hydrolysis of the azomethine function leading to the formation of amine group $-NH_2$. The sharp and strong band pointed at 1068 cm^{-1} is characteristic of a uncoordinated perchlorate group [36]. The electronic spectrum of the complex (Figure 1) shows two broad bands centered at 311 nm and 426 nm. The band at *ca.* 311 nm is due to the intraligand transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ while the band centered at 426 nm is attributed to LMCT [37]. The third band pointed at 605 nm is due to a d→d transition and is characteristic of a square pyramidal geometry around a Cu(II) center [38]. Conductance measurements were carried out at 25°C in a 10^{-3} M dmf solution. The conductance value of 90 $S.cm^2.mol^{-1}$ for the complex is indicative of a 1:1 electrolyte [39].

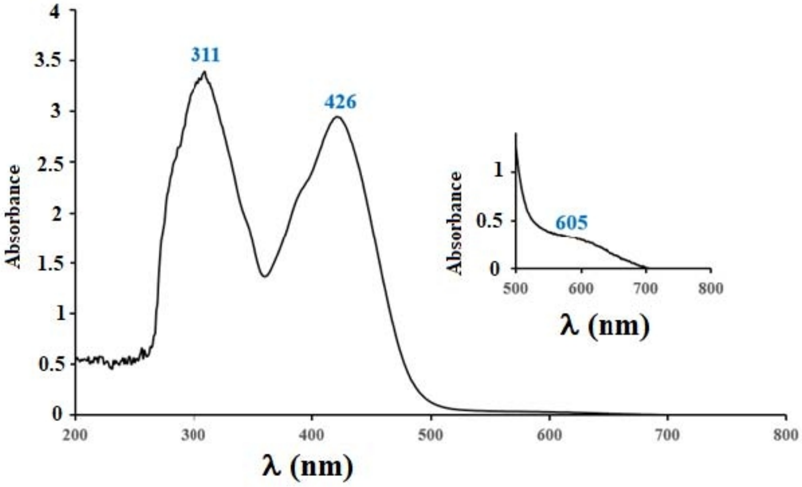

Figure 1. Electronic spectrum of the complex $\{[Cu(L)]\cdot[Cu_2(L)(L')]\}\cdot(ClO_4)$.

3.2. Structure description of the complex $\{[Cu(L)]\cdot[Cu_2(L)(L')]\}\cdot(ClO_4)$

The complex crystallizes as a co-crystal in the triclinic system with a P$\bar{1}$ space group. The asymmetric unit is composed of a cationic dinuclear copper (II) complex and a neutral mononuclear copper (II) complex. Neutrality is ensured by uncoordinated perchlorate anion (Figure 2). Selected bond lengths and angles are listed in Table 2. The mononuclear unit is composed of the symmetrical ligand 2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl}phenol (H_2L) which coordinates to the copper (II) through two phenoxo oxygen atoms and two azomethine nitrogen atoms yielding a N_2O_2 core. The complex is formulated as $\{[Cu(L)]\cdot[Cu_2(L)(L')]\}\cdot(ClO_4)$. In the dinuclear unit the two copper(II) are bridged by two phenoxo oxygen atom and are differently coordinated (Figure 3). Two different ligand molecules issued from the o-phenylene diamine are present: one dissymmetrical ligand in which one of the diamine arms is mono condensed with one salicylaldehyde molecule (2-((2-aminophenylimino)methyl)phenol (HL')) and a second symmetrical ligand molecule in which the diamine is doubly condensed with two salicylaldehyde molecules (2-{[2-(2-hydroxybenzylideneamino)phenylimino]methyl}phenol (H_2L)). The unsymmetrical ligand acts as a tridentate fashion and coordinates to one Cu(II) cation through one phenoxo oxygen atom, one azomethine nitrogen atom and one amino nitrogen atom. The symmetrical ligand acts in tetradentate manner and coordinates via two azomethine nitrogen atoms and two phenoxo oxygen atoms. These two phenoxo oxygen atoms are coordinated to the Copper(II) cation which is coordinated to the unsymmetrical ligand. Thus, in the dinuclear unit one copper(II) cation is situated in a N_2O_2 inner while the second is situated in a N_2O_3 environment.

In the dinuclear unit the Cu3 ion is pentacoordinated while the Cu2 is tetracoordinated. According to the Addison index [40] ($\tau = (\beta - \alpha)/60$ where β and α are the largest values of the bond angles around the central atom the coordination geometry around a pentacoordinated metal center can be discussed: $\tau = 0$ describes a perfect square pyramidal while $\tau = 1$ describes a perfect trigonal bipyramidal geometry. The τ value of 0.155 (Cu3) is indicative of a distorted square pyramidal geometry around the metal center. The best equatorial plane of the polyhedron around the Cu3 ion is constituted by one azomethine nitrogen atom (N5), one amino nitrogen atom (N6), one monocoordinated phenoxo oxygen atom (O5) and one bridged phenoxo oxygen atom (O3) (rms 0.0997) with the metal ion 0.0900 (1) Å out of this plane. The sum of the angles subtended by the atom in equatorial plane is 359.84°. The apical position is occupied by one bridged phenoxo oxygen atom (O4). The Cu2 atom which is tetracoordinated is linked to two azomethine nitrogen atoms (N3 and N4) of the bis-condensed ligand and two phenolate oxygen atoms (O3 and O4) which act as bridged between Cu2 and Cu3. The atoms of the ligand which are coordinated to Cu2 form a plane (rms 0.0221) with the Cu2 -0.0102 (1) Å out of the plane defined by these O3/O4/N3/N4. The sum of the angles subtended by the coordinated atoms to Cu2 is 360.03°. The Cu2/O3/Cu3/O4 are quasi planar (rms 0.0631) with a maximum deviation from the least-squares plane of 0.0700 (1) Å for Cu2 ion. The slight deformation of the coordination sphere around each Cu(II) center is confirmed by the values of the angles around the metal centers which differ with the ideal values. For Cu2 the *transoid* angles are 177.69 (9)° and 179.28 (9)° while the cissoid angle are in the range [84.74 (9)-95.54 (8)°]. For Cu3 the *transoid* angles are 167.43 (10)° and 176.73 (8)° while the cissoid angle are in the range [84.60 (9)-93.92 (9)°]. For the pentacoordinated Cu3 center, the angles between the O4 atom in apical position and each of the four atoms in the basal plane are largely different from the ideal value of 90° and fall in the range [71.28 (7)-109.21 (8)°]. The Cu2 and Cu3 are bridged by the two phenoxo O3 and O4 atoms. The two Cu(di-μ-phenoxo)Cu bridging fragments show a difference between the Cu—O lengths [Cu2—O3 = 1.9179 (17) Å; Cu3—O3 = 2.0110 (18) Å] and [Cu2—O4 = 1.8859 (19) Å; Cu3—O4 = 2.3787 (18) Å]. The angles Cu2—O3—Cu3 and Cu2—O4—Cu3 have different values with average of 107.38 (8)° and 95.19 (7)°, respectively. These observations are indicative of an asymmetry in the Cu(di-μ-phenoxo)Cu bridging fragments [41]. The dihedral angles between the mean planes Cu2—O3—O4 and Cu2—O3—O4 is equal to 9.341 (1)°, which is indicative of a twisting in the structure. The two equatorial planes around Cu2 and Cu3 are quite perpendicular with dihedral angle of 88.640 (1)°. The sum of the angles at the phenoxo oxygen atoms O3 and O4 are respectively 359.79° and 359.76° and are quite equal to the ideal value of 360°, indicating no pyramidal oxygen distortion as observed in the complex [$Cu_2L(OAc)_2$] (L is 2,4-di-tert-butyl-6-{[(2-dimethylaminoethyl)-(2-hydroxybenzyl)-amino]-methyl}-phenol) [41,42]. The Cu2—Cu3 distances of 3.1666 (3) Å is longer than those found for similar complexes [41,43] and suggests no interaction between the metal centers. The distances of Cu3—N5 [1.947 (2) Å], Cu3—N6 [2.008 (2) Å], Cu3—O3 [2 .0110 (18) Å] and Cu3—O5 [1.896 (2) Å] in the equatorial plane are shorter than the distance of Cu3—O4 [2.3787 (18) Å] of the apical position as expected for the Jahn Teller effect [44].

In the mononuclear unit, the geometry around Cu1 which is tetracoordinated, is determined by the tetragonality parameter [45] $\tau4 = (360° - \alpha - \beta)/141°$ where α and β are the two largest angles around the latter. The expected values for $\tau4$ are zero for a perfect square plane and one for a perfect tetrahedron. The value of $\tau4$, which is 0.0335, suggests distorted square planar geometries around Cu1. The metal center Cu1 is coordinated by two phenoxo oxygen atom and two imino nitrogen atoms. The sum of the angles subtended by the coordinated atoms is 359.99°. These atoms are quasi co-planar (rms 0.0044) with the Cu1 ion -0.0087 (1) Å out of the plane. The *transoid* angles are 177.33 (12)° and 177.95 (10)° while the cissoid angle are in the range [84.10 (12)-93.95 (11)°]. The molecule is slightly twisted. The three benzene rings (C1/C6), (C8/C13) and (C15/C20) make dihedral angles with the coordination plane (O1, O2, N1, N2) of 6.613

(1)°, 3.845 (1)° and 8.732 (1)° respectively. The angle between the planes (O1, N1, C14, C15, C20) and (Cu1, O1, N1) is 6.621 (1)° whereas that between the corresponding planes in the other salicylaldimine residue (O2, N2, C1, C6, C7) and (Cu1, O2, N2) is smaller with a value of 4.604 (1)°. The angle between the (C15/C20) and (O1, N1, C14, C15, C20) moieties is 3.843 (1)°, while the angle between the (C1/C6) and (O2, N2, C1, C6, C7) residues is only 1.531 (1)°. The Cu1—O [1.902 (2) Å and 1.887 (2) Å] and Cu1—N [1.946 (3) Å and 1.944 (2) Å] bond lengths are comparable to those found in the dinuclear unit. All these values are compared to those reported for a complex of the same ligand in the form of a co-crystal [46].

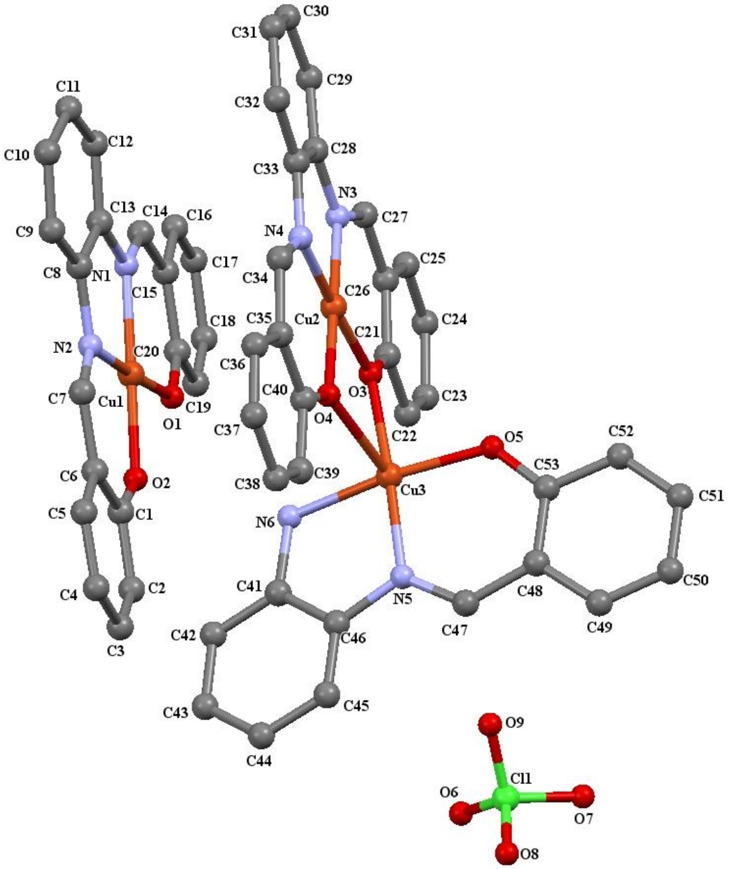

Figure 2. Crystal structure of the co-crystal complex. Displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.

The mononuclear unit, the dinuclear unit and the perchlorate anion of the asymmetric unit are connected by intramolecular hydrogen bonds of type N_{amino}-H…$O_{phenoxo}$ (N6-

H6A…O1) and C_{Ar}-H…$OClO_3$ (C45-H45…O6) (Figure 4, Table 3). Intermolecular hydrogen bond of type N_{amino}-H…$OClO_3$ (N6—H6B···O6^{i} ; i = −x+1, −y, −z+1) and weak intramolecular hydrogen bonds involving C_{Ar}-H…$OClO_3$ (C32—H32···O9^{ii} ; ii = −x+1, −y+1, −z+1) and C_{imino}-H…$O_{phenoxo}$ (C27—H27···O5^{iii} ; iii =−x+1, −y+1, −z) and C_{imino}-H…$OClO_3$ (C34—H34···O9^{ii} ; ii = −x+1, −y+1, −z+1) link mononuclear, dinuclear units and perchlorate anion belonging to different asymmetric units. The combined hydrogen bonds links give rise to a three-dimensional network architecture. It should be noted that the perchlorate ion is engaged in numerous interactions in the structure.

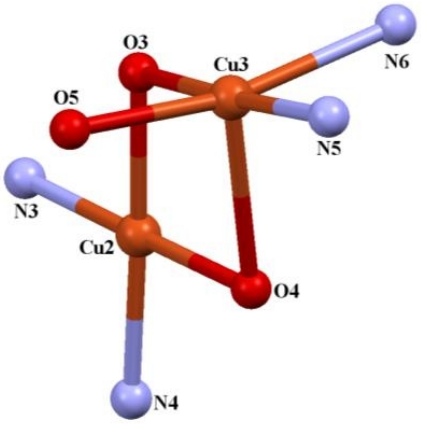

Figure 3. Plot showing the coordination sphere in the dinuclear unit of the co-crystal.

Table 2. Selected bond lengths (Å) and bond angles (°) for the co-crystal.

Bond	Distance	Bond	Distance
O5—Cu3	1.896 (2)	Cu3—N5	1.947 (2)
Cu2—O4	1.8859 (19)	Cu3—O3	2.0110 (18)
Cu2—O3	1.9179 (17)	Cu3—O4	2.3787 (18)
Cu2—N4	1.925 (2)	Cu1—O2	1.887 (2)
Cu2—N3	1.930 (2)	Cu1—O1	1.902 (2)
N6—Cu3	2.008 (2)	Cu1—N2	1.944 (2)
N1—Cu1	1.946 (3)		

Bond	Angle	Bond	Angle
O4—Cu2—O3	85.22 (8)	N6—Cu3—O3	92.15 (8)
O4—Cu2—N4	95.53 (9)	O5—Cu3—O4	99.80 (8)
O3—Cu2—N4	177.69 (9)	N5—Cu3—O4	109.21 (8)
O4—Cu2—N3	179.28 (9)	N6—Cu3—O4	92.45 (8)
O3—Cu2—N3	94.54 (8)	O3—Cu3—O4	71.28 (7)
N4—Cu2—N3	84.74 (9)	O2—Cu1—O1	88.63 (10)
O5—Cu3—N5	93.92 (9)	O2—Cu1—N2	93.95 (11)
O5—Cu3—N6	167.43 (10)	O1—Cu1—N2	177.33 (12)
N5—Cu3—N6	84.60 (9)	O2—Cu1—N1	177.95 (10)
O5—Cu3—O3	89.16 (8)	O1—Cu1—N1	93.31 (10)
N5—Cu3—O3	176.73 (8)	N2—Cu1—N1	84.10 (12)

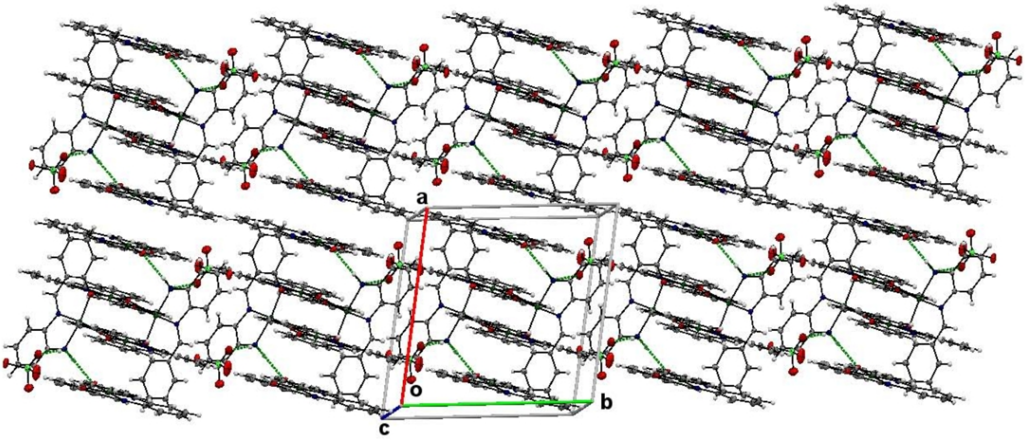

Figure 4. The packing of the compound in the crystal structure.

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

***D*—H···A**	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N6—H6A···O1	0.89	2.12	2.952 (3)	154.6
N6—H6B···O6^{i}	0.89	2.20	3.064 (4)	163.1
C45—H45···O6	0.93	2.48	3.327 (5)	151.6
C32—H32···O9^{ii}	0.93	2.55	3.476 (4)	176.7
C27—H27···O5^{iii}	0.93	2.39	3.258 (3)	154.8
C34—H34···O9^{ii}	0.93	2.58	3.486 (4)	165.9

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

4. Conclusion

Based on various physico-chemical techniques such as elemental analyses, FTIR, conductance measurements, electronic spectroscopy properties study, and single crystal X-ray diffraction analysis, the ligands and their complexes are characterized. In the co-crystal complex the Cu(II) ion of the mononuclear unit have square planar geometry. In the cationic dinuclear unit one of the Cu(II) square planar geometry while the second Cu(II) have square pyramidal environment. In the asymmetric unit, the mononuclear, the dinuclear unit and the perchlorate anion are linked through intramolecular hydrogen bonds. Numerous intermolecular hydrogen bonds link the molecule in three dimensional network.

5. Supporting Information

CCDC-2144297 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).

Conflicts of Interest

The authors declare that they have no conflict of interest.

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