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Synthesis, spectroscopic studies and X-ray structure determination of two mononuclear copper complexes derived from the Schiff base ligand *N,N*-dimethyl-*N'*-((5-methyl-1*H*-imidazol-4-yl)methylene)ethane-1,2-diamine

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ABSTRACT



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Reactions of the Schiff base *N,N*-dimethyl-*N'*-((5-methyl-1*H*-imidazol-4-yl)methylene)ethane-1,2-diamine (HL), synthesised *in situ*, with chloride or thiocyanate copper (II) salt; afforded two new mononuclear complexes, [Cu(HL)Cl₂·H₂O] (1) and [Cu(HL)(SCN)₂] (2). These compounds have been studied and characterized by elemental analysis, IR and UV-Vis spectroscopies, electrochemistry, molar conductivity and room temperature magnetic measurements. Single crystal X-ray structure determination of the complexes revealed the presence of neutral moieties in the asymmetric unit. The mononuclear (1) crystallises in the monoclinic space group P2₁/c with the following unit cell parameters *a* = 7.4355(3) Å, *b* = 7.2952(3) Å, *c* = 26.2729(11) Å, β = 93.461(4)°, *V* = 1422.52(10) Å³, *Z* = 4, *R*₁ = 0.033 and *wR*₂ = 0.082 and the mononuclear complex (2) crystallises in the monoclinic space group C2/c with the following unit cell parameters *a* = 26.2578(7) Å, *b* = 7.4334(2) Å, *c* = 16.6237(5) Å, β = 99.089(3)°, *V* = 3203.95(16) Å³, *Z* = 8, *R*₁ = 0.037 and *wR*₂ = 0.104. In both complexes the ligand acts in tridentate fashion and the coordination environment of the copper atom can be described as distorted square pyramidal. The crystal lattice of the complex 1 is stabilized by electrostatic forces of attraction and O-H...Cl, C-H...O, N-H...Cl, and C-H...Cl, hydrogen bonding interactions while the crystal lattice of the complex 2 is stabilized by N-H...S and C-H...N.

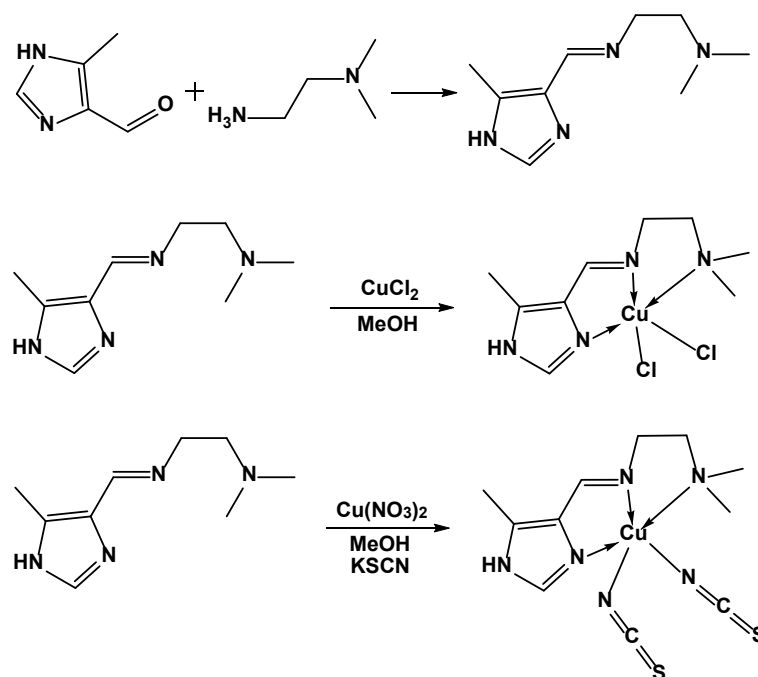
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1. Introduction

Schiff bases are organic ligands widely used in transition metal coordination chemistry [1-4]. The combination of these Schiff bases with the transition metals of the first row has made it possible to synthesize a very large number of complexes having very diverse structures and properties [5-8]. Among these copper compounds occupy a place of choice. These complexes can be used in various fields such as molecular magnetism [9,10], catalysis [11,12], materials chemistry [13,14] and biology [15,16]. A potent inhibitor of DNA synthesis and cell growth has been reported in the literature *ie.* the copper complex obtained from the tridentate ligand salicylaldehyde benzoylhydrazone [17]. It is known that the synthesis of Schiff bases from aromatic amine and

aromatic carbonyl compounds gives better yields with better purity than when one or both precursors are aliphatic [18]. This is due to the relative stability of the azomethine groups induced by the electron richness of aromatics. Schiff bases derived from a precursor having an imidazole moiety and their transition metal complexes have interested chemists in recent years because of their antimicrobial activities and the possibility of using them as bio-mimes for certain metallo-enzymes since we find often metal ions bound to the nitrogen atom of imidazole in the active metallo-enzymes [19]. Investigations were conducted for studied the influence on the properties of the ligand synthesized from substituted imidazole ring [20,21]. The combination of a linear amine and a heterocyclic ring via an azomethine moiety can lead to complexes having biological activity.



Scheme 1. The synthesis procedure of the ligand and the related complex.

Copper complex with Schiff base ligands has also been investigated as effective scavengers of superoxide radicals, acting as antioxidants [22,23]. Extensive studies have been carried out on the transition metal complexes with imidazole-based Schiff bases, but there is no reported copper complex with the *N,N*-dimethyl-*N'*-((5-methyl-1*H*-imidazol-4-yl)methylene)ethane-1,2-diamine (C₉H₁₆N₄). In this work, we described the synthesis, spectroscopic properties and crystal structure of two neutral copper complexes obtained by the complexation of the previous Schiff base with CuCl₂·2H₂O with or without the presence of KSCN.

2. Experimental

2.1. Materials and physical methods

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 an 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 DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: Hg[Co(SCN)₄]). The voltammetric measurements were recorded using a Palm Sens3 type potentiostat controlled by PSTrace software. A glassy carbon working electrode with a radius of 2±0.1 mm, a stainless steel wire as a counter-electrode and Ag/AgCl electrode as a reference were used. Cyclic voltammetry experiments were performed in acetonitrile solution 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHFP) as a supporting electrolyte.

2.2. Synthesis

2.2.1. Synthesis of [Cu(HL)Cl₂·H₂O (1)]

To a solution of 5-methyl-1*H*-imidazole-4-carbaldehyde (0.1100 g, 1 mmol) in 30 mL of methanol was added (0.0881 g, 1 mmol) of *N,N*-dimethylethane-1,2-diamine. The resulting yellowish mixture was stirred for 30 min. A solution of CuCl₂·2H₂O (0.171 g, 1 mmol) in 5 mL of methanol was added at room temperature. The initial yellow solution which turned immediately into a deep blue color upon addition of CuCl₂·2H₂O was stirred during 2 hours. The mixture was filtered off and the solution was evaporated near dryness. The solid was isolated by filtration and recrystallized from a minimum of methanol. On standing for one day crystals suitable for X-ray analysis were formed (Scheme 1).

{Dichlorido[*N,N*-dimethyl-*N'*-((5-methyl-1*H*-imidazol-4-yl)methylene)ethane-1,2-diamine-κ³N, N', N''}copper(II)} monohydrate: Color: Dark-brown. M.p.: 246-248 °C. Yield: 86.44 %. FT-IR (KBr, ν, cm⁻¹): 3534 (OH) (br, water), 1628 (C=N), 1423, 1343, 1245, 941, 816, 630. Anal. calcd. for C₉H₁₈N₄Cl₂O: C, 32.49; H, 5.45; N, 16.84. Found: C, 32.46; H, 5.48; N, 16.80%. UV (λ (nm), Abs): 241.25 (4.9954), 299.5 (4.7678), 677.15 (0.2981). μ_{eff} (μ_B): 1.75. Λ_M (S.cm².mol⁻¹): 70.

2.2.2. Synthesis of [Cu(HL)(SCN)₂] (2)

To a solution of 5-methyl-1*H*-imidazole-4-carbaldehyde (0.1100 g, 1 mmol) in 30 mL of methanol was added (0.0881 g, 1 mmol) of *N,N*-dimethylethane-1,2-diamine. The resulting yellowish mixture was stirred for 30 min. To a solution of Cu(NO₃)₂·3H₂O (0.240 g, 1 mmol) in 5 mL of methanol was added KSCN (0.194 g, 2 mmol). This mixture was filtered and the filtrate was added to the solution of the ligand at room temperature. The initial yellow solution which turned immediately into a deep blue color was refluxed during for 2 hours. On cooling the mixture was filtered off and the filtrate was left for slow evaporation. On standing for one week crystals suitable for X-ray analysis were isolated.

Table 1. Crystal data and structure refinement for [Cu(HL)Cl₂]-H₂O (**1**) and [Cu(HL)(SCN)₂] (**2**)

Compound	1	2
Formula	C ₉ H ₁₆ Cl ₂ CuN ₄ ·H ₂ O	C ₁₁ H ₁₆ CuN ₆ S ₂
FW	332.71	359.96
Crystal shape/color	Prismatic/dark-brown	Prismatic/blue
Crystal size (mm)	0.08 × 0.07 × 0.06	0.09 × 0.08 × 0.07
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	C2/c
a (Å)	7.4355 (3)	26.2578 (7)
b (Å)	7.2952 (3)	7.4334 (2)
c (Å)	26.2729 (11)	16.6237 (5)
α (°)	90	90
β (°)	93.461 (4)	99.089 (3)
γ (°)	90	90
V (Å ³)	1422.52 (10)	3203.95 (16)
Z	4	8
D _{calc} (g·cm ⁻³)	1.554	1.492
λ (MoKα) (Å)	0.71073	0.71073
T (K)	293	293
μ (mm ⁻¹)	1.90	1.62
Index ranges	-6 ≤ h ≤ 10, -9 ≤ k ≤ 8, -34 ≤ l ≤ 32	-36 ≤ h ≤ 36, -10 ≤ k ≤ 10, -22 ≤ l ≤ 22
F(000)	684	1480
θ range (°)	3.64-28.90	3.61-29.73
No. of measured reflections	9763	19919
No. of independent reflections	3299	4128
No. of observed [I > 2σ(I)] reflections	2684	3616
R _{int}	0.035	0.043
R[F ² > 2σ(F ²)]	0.033	0.037
wR(F ²)	0.082	0.104
Goodness-of-fit (Gof) on F ²	1.06	1.06
No. of parameters	167	187
No. of restraints	5	1
Δρ _{max} , Δρ _{min} (e·Å ⁻³)	0.33, -0.34	1.37, -1.07

{Dithiocyanato[N, N-dimethyl-N'-((5-methyl-1H-imidazol-4-yl)methylene)ethane-1, 2-diamine-κ³N, N', N'']copper(II)}: Color: Blue. M.p.: 220-222 °C. Yield: 41.22 %. FT-IR (KBr, ν, cm⁻¹): 2077 (S=C=N), 1634 (C=N), 1442, 1343, 1234, 944, 770, 629. Anal. calcd. for C₁₁H₁₆CuN₅S₂: C, 36.70; H, 4.48; N, 23.35. Found: C, 36.66; H, 4.45; N, 23.15%. UV (λ (nm), Abs): 241.25 (4.9954), 299.5 (4.7678), 677.15 (0.2981). μ_{eff} (μ_B): 1.55. Λ_M (S·cm²·mol⁻¹): 73.

2.3. Crystal structure determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compounds, were grown by slow evaporation of MeOH solution of the complexes. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoKα 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 [24]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F² by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [25]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH₃ groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [26].

3. Results and discussion

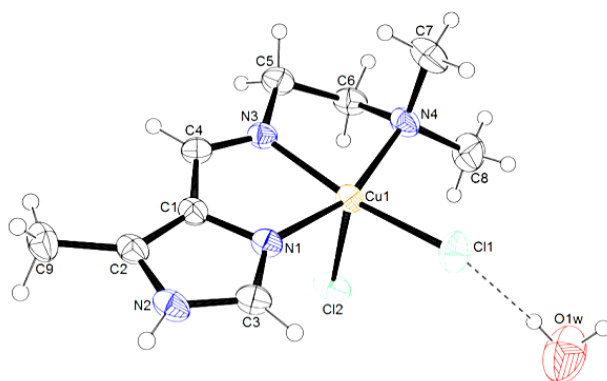
3.1. General studies

The ligand HL was prepared *in situ* by a facile condensation of 5-methyl-1H-imidazole-4-carbaldehyde and N,N-dimethylethane-1,2-diamine in methanol (Scheme 1). The two complexes were obtained by adding to the above solution an equimolecular methanolic solution of CuCl₂ or a mixture of

Cu(NO₃)₂ and KSCN in 1:2 ratio in methanol. Thiocyanate can act as counter anion or co-ligand. It's a versatile ligand which can act as unidentate or bidentate fashion owing to the presence of a polarizable π system and two atoms donor (S and N). Thiocyanate can be also involved in hydrogen-bond interaction. In the synthesis reaction of complex **2**, nitrate anions of copper(II) nitrate salt are successfully substituted by thiocyanate anion in the reaction with KSCN. This replacement of nitrate anions by thiocyanate is facilitated by the use of the good solubility of methanol solvent for the copper(II) thiocyanate and KSCN and the very poor solubility of KNO₃ in methanol. The compounds yielded are soluble in polar organic solvents such as methanol or acetonitrile. The elemental analyses result are in accordance with the chemical formulae obtained from X-ray diffraction study. Both spectra of the [Cu(HL)Cl₂]-H₂O and [Cu(HL)(SCN)₂] complexes exhibit broad bands in the range 3215-3185 cm⁻¹ which are attributed to N-H stretching [27]. The vibration of the imine function appears in the range 1635-1625 cm⁻¹ while the spectrum of the free Schiff base reveals a band at 1644 cm⁻¹. This shift to low frequencies is indicative of the involvement of the nitrogen atom of the azomethine in the coordination sphere of the Cu(II) atom. Additional broad band is pointed in the spectrum of chloride complex at 3534 cm⁻¹ and attributed to the uncoordinated water molecule [28]. The thiocyanate copper (II) complex shows an intense and sharp band at 2077 cm⁻¹ assignable to the coordinated thiocyanate group [29]. For both spectral bands due to the aromatic ring are pointed in the region 1540-1440 cm⁻¹. The electronic absorption spectral analysis of the two metal complexes exhibit the absorption bands at 241 and 299 nm which are due to π→π* electronic transition in the azomethine chromophore. The thiocyanate complex exhibits also a band at 355 nm which is due to n→π* electronic transition in the thiocyanate chromophore. The bands indicative of the d→d electronic transitions appear at 677 and 653 nm, respectively, for the chloride and the thiocyanate copper complexes. These facts are characteristic of a distorted square-pyramidal environment [30].

Table 2. Selected bond lengths (Å) and bond angles (°) for the crystals (1) and (2).

Complex 1		Complex 2	
Atom-Atom	Bond lengths	Atom-Atom	Bond lengths
Cu1-N3	1.9841 (18)	Cu1-N5	1.954 (2)
Cu1-N1	2.0072 (17)	Cu1-N3	1.9809 (18)
Cu1-N4	2.0596 (19)	Cu1-N1	2.0389 (18)
Cu1-Cl1	2.2452 (6)	Cu1-N4	2.0905 (18)
Cu1-Cl2	2.6245 (6)	Cu1-N6	2.1322 (19)
		S1-C10	1.621 (2)
		S2-C11	1.631 (2)
		N5-C10	1.142 (3)
		N6-C11	1.150 (3)
Atom-Atom-Atom	Bond angles	Atom-Atom-Atom	Bond angles
N3-Cu1-N1	80.24 (7)	N5-Cu1-N3	153.72 (9)
N3-Cu1-N4	81.58 (7)	N5-Cu1-N1	97.51 (8)
N1-Cu1-N4	158.70 (7)	N3-Cu1-N1	80.08 (7)
N3-Cu1-Cl1	164.82 (6)	N5-Cu1-N4	95.89 (9)
N1-Cu1-Cl1	96.01 (5)	N3-Cu1-N4	80.99 (7)
N4-Cu1-Cl1	98.66 (6)	N1-Cu1-N4	159.44 (7)
N3-Cu1-Cl2	92.90 (5)	N5-Cu1-N6	99.67 (9)
N1-Cu1-Cl2	99.29 (5)	N3-Cu1-N6	106.56 (8)
N4-Cu1-Cl2	92.60 (5)	N1-Cu1-N6	99.01 (7)
Cl1-Cu1-Cl2	102.25 (3)	N4-Cu1-N6	94.01 (8)
	79.09 (10)	N5-C10-S1	178.6 (3)
	83.86 (11)	N6-C11-S2	179.07 (19)

**Figure 1.** Crystal structure of the complex 1. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as a small sphere.

The molar conductivity which is $70 \text{ S.cm}^2.\text{mol}^{-1}$ for $[\text{Cu}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$ and $73 \text{ S.cm}^2.\text{mol}^{-1}$ for $[\text{Cu}(\text{HL})(\text{NCS})_2]$ shows that the complexes are 1/1 electrolytes in DMF solution. The values of the magnetic moment at room temperature for the diamagnetic complexes are indicative of the presence of one metal atom per molecule. In fact, the magnetic moment values of $1.75 \mu_B$ and $1.55 \mu_B$ for complexes 1 and 2, respectively, are in accordance with one unpaired electron in d^9 configuration [31].

3.2. Structure description of complex 1

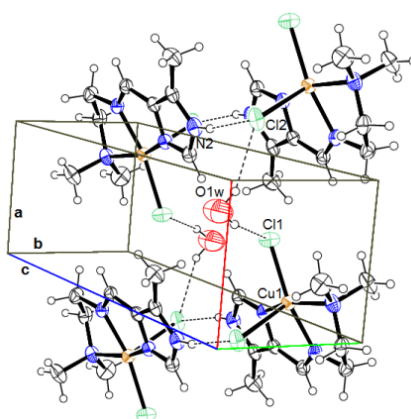
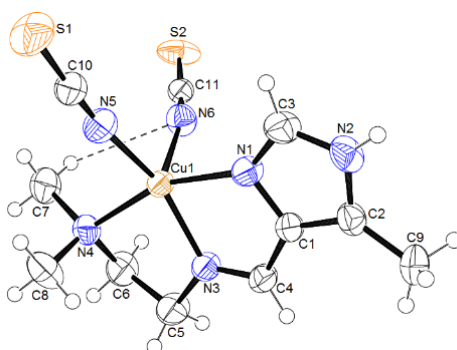
The crystallographic data of compound 1 are listed in Table 1, whereas selected bond lengths and angles of the coordination environment of the metal center are listed in Table 2. Complex $[\text{Cu}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of the structure (Figure 1) of $[\text{Cu}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$ consist of one mononuclear unit where the copper (II) ion is coordinated by three nitrogen atoms from the organic ligand molecule and two different chloride atoms. The CuN_3Cl_2 chromophore is best described as a distorted square pyramidal. Since the distortion value of the coordination polyhedron, $\tau = (\beta - \alpha)/60$, is evaluated by the two largest angles in five-coordination geometry [32], the value of $\tau = 0.102$ which can be compared with the ideal value of 0 for a square-pyramidal environment and 1 for a trigonal-bipyramidal environment, indicates a distorted square-pyramidal geometry around the Cu center with N1, N3, N4, and Cl1 in the plane, the apical position being

occupied by Cl2. The CuCl_2 coordinated with N1, N3 and N4 atoms of the ligand forming two five-membered rings CuN1C1C4N3 and CuN3C5C6N4 . The bond angles between the central Cu-ion and the coordinated sites of the ligand vary between 80 and 82° . The bond angles around the Cu (II) center range from $80.24(7)$ to $98.66(6)^\circ$ in the equatorial positions and from $92.60(5)$ to $102.25(3)^\circ$ for the apical positions. These observations are in agreement with those reported for analogous copper (II) complexes [33]. The bonds lengths Cu-Cl1 is $2.2452(6) \text{ \AA}$ while the distances between the copper atom and the nitrogen atoms of the ligand are slightly different being $1.9841(18)$, $2.0072(17)$ and $2.0596(19) \text{ \AA}$. The distance between the copper and the chloride atom in the apical position which is the longest distance with value of $2.6245(6) \text{ \AA}$ is longer than the Cu-Cl bond lengths in the five-coordinate copper(II) chlorido complexes [34]. This distance is shorter than those found in several complexes. In $\text{Cu}(\text{biaq})_2\text{Cl}_2$ the Cu-Cl distance is $2.650(2) \text{ \AA}$ [35] and varying in the range $[2.658(1)-3.329(2) \text{ \AA}]$ for a series of analogous complexes reported in the literature [36,37]. Hydrogen bonding interaction involving O-H and N-H groups and chloride atom possibly play an important role in the stabilization of the crystal lattice. In fact the O...Cl distances of O-H...Cl hydrogen bonds of $3.293(3)$ and $3.244(3) \text{ \AA}$ and the N...Cl distance value of $3.104(2) \text{ \AA}$, combining with the angles O-H...Cl of $154(4)$ and $155(5)^\circ$ and N-H...Cl of $168(2)^\circ$ which are superior to 150° tend to linearity and are acceptable as good contact [38]. Thus each mononuclear molecule complex is connected to another complex molecule by N-H...Cl hydrogen bonding

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

D-H...A	D-H (Å)	H...A (Å)	D...A (Å°)	D-H...A (°)
[Cu(HL)Cl₂]-H₂O				
O1W-H1WA...Cl1	0.837(18)	2.52(2)	3.293(3)	154(4)
O1W-H1WB...Cl2 ⁱ	0.857(18)	2.45(2)	3.244(3)	155(5)
N2-H2...Cl2 ⁱⁱ	0.831(16)	2.285(17)	3.104(2)	168(2)
C5-H5A...Cl2 ⁱⁱⁱ	0.97	2.86	3.767(2)	155.3
C6-H6A...Cl2	0.97	2.87	3.476(2)	121.3
C7-H7B...O1W ⁱⁱⁱ	0.96	2.64	3.252(4)	121.9
C7-H7C...Cl2 ⁱⁱⁱ	0.96	2.99	3.908(3)	160.4
C8-H8B...Cl2	0.96	2.87	3.548(3)	128.7
C8-H8C...Cl1	0.96	2.93	3.413(3)	112.5
[Cu(HL)(SCN)₂]				
N2-HN2...S2 ^{iv}	0.820(17)	2.629(19)	3.406(2)	159(2)
C7-H7AB...N6	0.96	2.68	3.206(3)	114.7
C9-H9AB...N6 ^v	0.96	2.62	3.463(3)	146.2

* Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+1$; (iii) $x, y+1, z$; (iv) $x, -y+1, z+1/2$; (v) $-x+1/2, -y+3/2, -z+1$.

**Figure 2.** Perspective view of the three dimensional supramolecular network constructed by hydrogen bond interactions for complex 1.**Figure 3.** Crystal structure of the complex 2. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small sphere.

interactions, leading to the formation of a supramolecular chain structure along the c axis. In the N-H...Cl hydrogen bond, the axial chlorine atom of the second molecule complex is the acceptor while the donor is the secondary pyrazolyl nitrogen of the first molecule complex. The uncoordinated water molecule acts via hydrogen bonds O-H...Cl as bridge between the chains leading to the formation of a 3D supramolecular structure. The Chlorine atom in equatorial position in one chain and a chlorine atom in axial position in another chain are the acceptors while the donor is the water molecule: O1w-H1WA...Cl1, O1w-H1WB...Cl2ⁱ (Figure 2, Table 3). The structure is consolidated by weak C-H...Cl, and C-H...Ow (Table 3).

3.3. Structure description of complex 2

The crystallographic data of compound 2 are listed in Table 1, whereas selected bond lengths and angles of the coordination environment of the metal center are listed in Table 2. Complex [Cu(HL)(NCS)₂] crystallizes in the

monoclinic space group $C2/c$. The asymmetric unit contains one neutral mononuclear copper (II) complex. The Cu(II) metal center is coordinated by one organic tridentate ligand and by two thiocyanates. The asymmetric unit is shown in Figure 3. The Cu(II) metal center is five-coordinated with τ parameter [32] value equal to 0.095 which is indicative of a slight distortion from the ideal square-pyramidal geometry. The apical position of the distorted square-pyramid is occupied by a nitrogen atom of a thiocyanate group (Figure 3). The largest bond angles (N1-Cu1-N4 = 159.44(7)° and N5-Cu1-N3 = 153.72(9)°) in the Cu(II) coordination sphere corresponds to the *transoid* angles of the basal plan which is occupied by the N1N3N4 nitrogen atoms of the ligand and the N5 nitrogen atom of a thiocyanate anion. The *cisoid* angles are in the range [80.08(7)-97.51(8)°]. The coordinated nitrogen atoms from the ligand molecule form two five-membered rings (Cu1N1C1C4N3 and Cu1N3C5C6N4) upon coordination to Cu(NCS)₂.

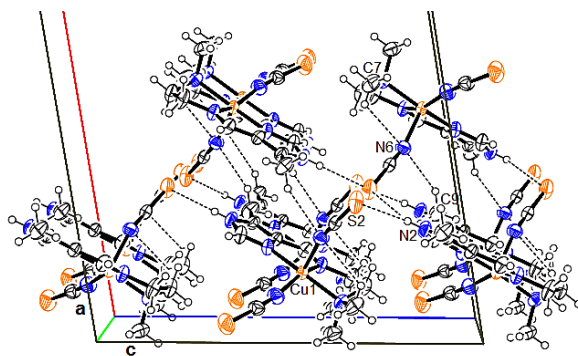


Figure 4. Perspective view of the three dimensional supramolecular network constructed by hydrogen bond interactions (**2**).

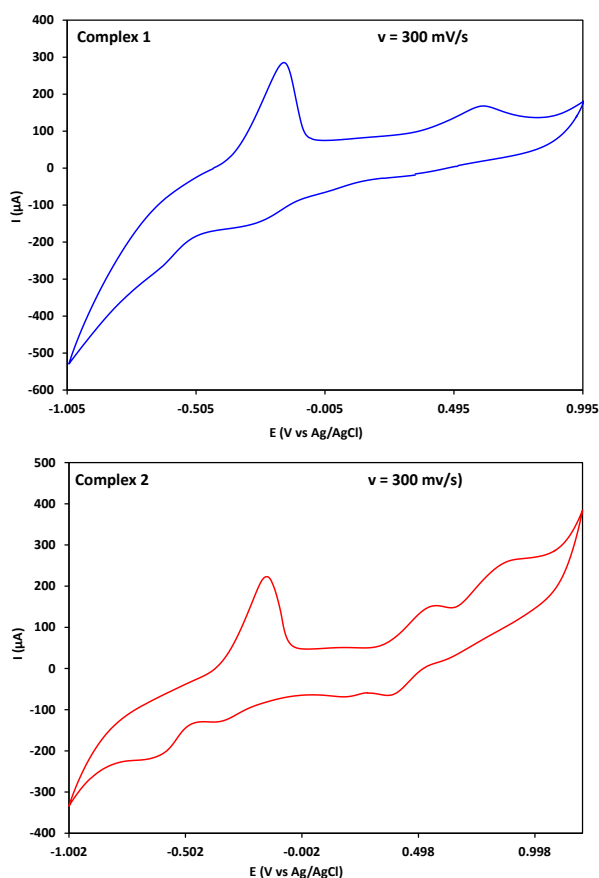


Figure 5. Cyclic voltammograms of the complexes **1** and **2** in acetonitrile containing 0.1 M $[\text{NBu}_4][\text{PF}_6]$ at scan rate = 100 mV/s.

The whole anionic N-donor thiocyanate groups are quasi-linear with angle N-C-S in the range $178.6(3)$ - $179.07(19)^\circ$ and are in accordance with the values reported for similar complexes [39, 40]. These anionic N-donor thiocyanates bind almost linearly to the copper (II) ion with angles Cu-N-CS in the range $166.98(17)$ - $170.4(2)^\circ$. The N...S distances of N-H...S hydrogen bond of $3.406(2)$ Å combining with the angles N-H...S of $159(2)^\circ$, which is superior to 150° , tend to linearity is indicative of a good hydrogen bond contact [38]. The structure is consolidated by extensive intermolecular hydrogen bonds N-H...S and weak C-H...N (Table 3). The molecules are arranged in finite layers parallel to the *bc* plane (Figure 4).

4. Electrochemistry

The electrochemical behaviors of the two complexes **1** and **2** have been studied in acetonitrile solution. Figure 5 and 6

show respectively the cyclic voltammograms of complexes **1** and **2** in CH_3CN solution in the potential ranges of -1.0 to 1.25 V. For both complexes **1** and **2**, the electrochemically irreversible oxidation peak observed at -0.17 V is due to the oxidation of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{III}}$ center. This value is in agreement with those observed in the related Cu(II) Schiff base complexes [41]. The irreversibility of the redox processes can be attributed to the stability of the oxidized species in CH_3CN solvent. The kinetic studies of this peak at different scanning speeds show that the phenomena are governed by diffusion. The presence of others pics owing to their surfaces does not seem to be related to electrochemical phenomena involving the studied complexes (Figure 6). Additional reduction pic is observed for both complexes at -0.6 V which intensity decreases when the scan rate increases. The disappearing of this reduction pic when the scan rate increases is indicative of the presence of a chemical reaction.

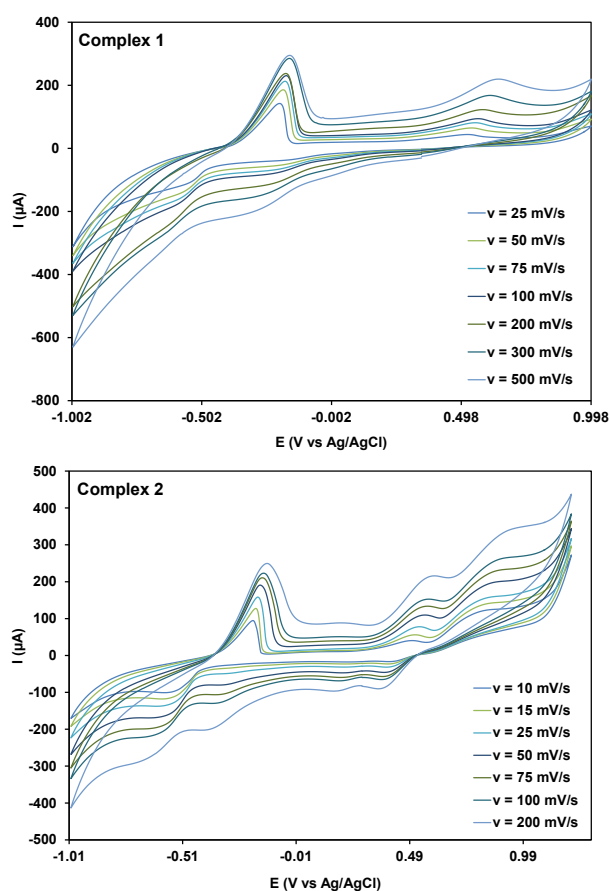


Figure 6. Cyclic voltammograms with different scan rates of the complexes 1 and 2 in acetonitrile containing 0.1 M $[\text{NBu}_4][\text{PF}_6]$.

5. Conclusion

The HL organic ligand with pyrazolyl ring showed similar mode coordination in the Cu(II) complexes **1** and **2** which are prepared and characterized by elemental analysis, magnetic moment, molar conductivity, IR, UV-Vis. The structures of the mononuclear copper (II) complexes were determined by single-crystal X-ray diffraction showing similar kinds of coordination geometry for copper in both complexes. The complexes are non-ionic electrolyte in DMF solutions. In both structures the organic molecule HL acts as tridentate ligand through pyrazole nitrogen atom, azomethine N atoms and an amino nitrogen atom. Considering the magnetic moment, infrared spectra and the electronic spectrum data for Cu(II) complexes, square pyramidal planar geometries are proposed for the two Cu(II) complexes as observed in X-ray diffraction studies. The structure of complex **1** is consolidated by extensive intermolecular hydrogen bonds between chloride ligands and the water molecules (Cl1/Cl2 and OW1) and by weak C-H...Cl, and C-H...Ow (Figure 2) which produce a three-dimensional network in the solid. In complex **2** intermolecular hydrogen bonds N-H...S and weak C-H...N form a three dimensional network (Figure 4).

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Supporting information

CCDC-1908999 and 1909000 contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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