

# **Comparative Studies of Some Novel Cu(II) Polymeric Complexes Derived from** Cyanoacetylhydrazine (CAH; L). The Role of Solvents Used on the Structure and Geometry of the Isolated Cu<sup>2+</sup> Complexes

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## Abstract

Novel polymeric Cu<sup>2+</sup> complexes derived from the reaction of cyanoacetylhydrazine (CAH; L) with CuCl<sub>2</sub>·2H<sub>2</sub>O in different solvents were synthesized and characterized. The isolated solid polymeric complexes were investigated using modern conventional physicochemical and spectral (IR, <sup>1</sup>H-NMR, UV-Vis. ESR, Raman), magnetic and thermal studies. The results revealed that CAH behaves in different ways towards the coordination of the Cu<sup>2+</sup> ion. The promotion of solvents to the cyano group was discussed on the basis of the solvent and the Cu<sup>2+</sup> ion used. Magnetic and spectral studies suggest octahedral geometry is proposed for the Cu<sup>2+</sup> complexes. EPR studies indicate the existence of polymeric complexes depending on the results of g-values. The results suggest that the number of copper atoms ranges from three to twelve atoms. The molecular modeling is drawn and some chemical characteristics are calculated such as chemical reactivity and energy components are investigated between the different types of the ligands.

## **Keywords**

Polymeric Cu(II) Complexes, ESR Studies, Cyanoacetylhydrazine, DFT Studies

## **1. Introduction**

The class of organic compounds contains the functional active group (-CONHNH<sub>2</sub>) is known as hydrazides. Great interest in the chemistry of hydrazides is explained by diversity and at times by the originality of their properties. Hydrazides have acquired great importance due to their multifarious biological properties including antibacterial, antifungal, anti-inflammatory and anti-tuberculosis activities [1] [2] [3] [4] [5]. CAH is considered as an intermediate for the synthesis of a variety of heterocyclic compounds. The  $\beta$ -functional nitrile [6] [7] [8] [9] moiety in the compound is a favorable unit for addition followed by cyclization or via cyclo-addition with numerous reagents providing heterocyclic compounds having different ring sizes with one or several heteroatoms that are interesting as pharmaceuticals [10] [11], herbicides [12], antibacterial agents [13], and dyes [14] [15]. Also, hydrazides find wide applications as drugs, chemical preservers for plants, manufacturing polymers, glues and many other purposes [16]. Mostafa et al. [17] reported the reactions of cyanoacetylhydrazine (SCH, L) with some metal ions ( $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $UO_2^{2+}$ ) in EtOH. Three types of complexes with the general formulae,  $[M(L)_2X_2]S$  (M = Co<sup>2+</sup>, Ni<sup>2+</sup> or Cd<sup>2+</sup>; X = Cl<sup>-</sup> or Ac<sup>-</sup>; S = EtOH or (H<sub>2</sub>O),  $[M(L-H)_2]S$  (M = Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>; S  $(H_2O)$  and  $[Hg(L-H)Cl\cdot H_2O]$ , were isolated and characterized. On the other hand, the reaction of Fe<sup>3+</sup> and Cu<sup>2+</sup> chloride or bromide with L in aqueous ethanolic solution is accompanied by the reduction to Fe<sup>2+</sup> and Cu<sup>+</sup>, respectively [17]. The synthesis and characterization of some metal complexes containing salicylaldehyde cyanoacetylhydrazone (SCH), 1-salicyl-hydrazo-3-imino-3-isopropoxy propionic acid hydrazide (SIPPH) and 1-salicylhydrazo-3-imino-3-tertbutoxy propionic acid hydrazide (SIBPH) were reported [18]. The complexes were characterized using elemental analyses, spectral (1H-NMR, IR, visible), conductance and magnetic measurements. IR spectral data suggest that the ligands (SCH, SIPPH and SIBPH) coordinated in tridentate and/or bidentate manners with different modes of bonding toward the metal ions. Moreover, a polymeric structure via an imido group for some Cu<sup>2+</sup> complexes is discussed. Finally, the <sup>1</sup>H-NMR spectra of the ligands and some diamagnetic complexes are discussed. The reactions of salicylaldehyde with a suspension of cyanoacetylhy-drazine and/or malonic acid amido-hydrazide complexes in aqueous EtOH solutions afford novel complexes [19]. The structures of the isolated complexes have been confirmed by conventional physical and chemical measurements. The absence or the weakness of the cyano group in the IR spectra of all complexes, except those of Co<sup>2+</sup> and Ni<sup>2+</sup> complexes, suggests the promotion of H<sub>2</sub>O to the cyano group forming amido group [19]. In this paper, the use of the  $Cu^{2+}$  salts which act as a catalyst in the synthesis of the polymeric complexes helps to a great extent the promotion of the solvents to the cyano group.

The goal of our study is to investigate the role of the solvents on the reaction products of **CAH** in the presence of  $Cu^{2+}$  ions. The isolated polymeric complexes were characterized using different physical, chemical, thermal, spectral and magnetic methods. The results of EPR were studied and the values of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{e}$ ,  $K_{\parallel}$ ,  $K_{\perp}$ ,  $a^2$  and  $B^2$  were calculated. Also, the structures of ligands were elucidated using molecular modeling. Thermal analyses were carried to determine the number of solvents inside or outside the coordination sphere.

#### 2. Experimental

#### 2.1. Instrumentation and Materials

All chemicals were of AR quality and used without further purification. Elemental analyses (C, H, N) were carried out by Perkin-Elmer CHN 2400 analyzer based on catharometric detection after combustion. Chloride and copper contents were determined by the micronalysis centre, CNRS service central of analysis at Vernaison (France). TGA analysis was performed using Dupont-950 thermogravimetric analyser in KBr discs were recorded on a Mattson 5000 FTIR (Mansoura University) and Perkin-Elmer in the range 20°C - 800°C and recorded on a TGA-50 Shimadzu TGA analyzer at a heating rate of 15°C/min and nitrogen flow rate of 20 ml/min. IR spectra (4000 - 200 cm<sup>-1</sup>) in Perkin-Elmer 883 IF spectrophotometers (France). Electronic spectra were recorded on a Unicam UV-Vis, V-100 and Perkin-Elmer Lambda 9 spectrophotometers. The magnetic measurements were carried out at room temperature (25°C) on a Sherwood magnetic balance. Diamagnetic corrections were calculated using Pascal's constants [20]. <sup>1</sup>H-NMR measurements in  $d_6$ -DMSO at room temperature were carried out on Jeol-90Q Fourier transform (400 MHz) and Bruker AM 250 spectrometers. The results of EPR measurements were obtained using Bruker EPR 200 provided with Hewlett-Packard frequency meter (modulation frequency, 100 KHz; microwave power; 20 mW; field modulation intensity; 3.2 Gpp and gain,  $2.5 \times 10^5$ ).

#### 2.2. Synthesis of Cyanoacetylhydrazine (CAH; L)

CAH (**L**) was synthesized by adding equivalent amounts of hydrazine hydrate (3 ml; 0.1 mol) drop by drop with constant stirring to ethyl cyanoacetate (11 ml, 0.1 mol) in EtOH for 1.5 h at room temperature (25°C). The reaction mixture was cooled in ice bath till a white solid product was obtained. The precipitate was filtered off, recrystallized from absolute ethanol (yield: 89%) and finally dried in a desiccator over  $P_4O_{10}$ . The purity was checked by elemental analyses, TLC and spectra data (IR, <sup>1</sup>H-NMR, Vis-Uv, Raman and TGA). The uncorrected melting point of the product was found to be (108°C - 110°C).

#### 2.3. Synthesis of Cu<sup>2+</sup> Complexes

Twelve novel polymeric  $Cu^{2+}$  complexes were isolated and characterized with the aid of elemental analyses, physical and spectroscopic methods. The different complexes were synthesized by mixing in each reaction equivalent amounts of **L** (0.2 M) in different solvents (H<sub>2</sub>O, MeOH, EtOH, n-proponal, n-butanol and n-pentanol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1 M) in EtOH. The reaction mixtures were refluxed on a hot plate for a time depending on the solvent used. The polymeric complexes formed in the flask were poured in a beaker followed by scratching the reaction mixture in each experiment by a glass rod till solid precipitates were formed as fine powders. The complexes were filtered off and washed several times with the solvent used in the preparation of the complexes followed by washing with diethyl ether. The isolated products were preserved in a vacuum desiccator over  $P_4O_{10}$ . The analyses of the isolated solid complexes together with some physical data are depicted in **Table 1**. The complexes are stable in air and soluble in polar solvents. The numbers of the copper ions in the isolated complexes were estimated from the data of elemental analyses as well as results of EPR and found to be in the range from 3 - 12 atoms. The electronic spectra and the magnetic moments of the Cu(II) complexes are recorded in **Table 2**. The data of the polymeric complexes are summarized as follow:

**Complex (1)** (C<sub>11</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>9</sub>O<sub>6</sub>Cu<sub>3</sub>); yield: 70%; color: dark brown powder; MP > 270°C, M.Wt: 638.9;  $\mu_{eff}$ (1.95 BM) and conductivity (DMSO): 6  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (2)** ( $C_{36}H_{71}Cl_{14}N_{27}O_{18}Cu_{12}$ ); yield: 83%; color: yellowish-green powder; MP > 270°C, M.Wt: 2400.0;  $\mu_{eff}$  (0.91 BM); conductivity (DMSO): 9  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (3)** ( $C_{31}H_{75}Cl_7N_{24}O_{23}Cu_8$ ); yield: 76%; color: brown powder; MP > 270°C; M.Wt. 1908.6;  $\mu_{eff}$  (1.24 BM); conductivity (DMSO): 13  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (4)** (C<sub>19</sub>H<sub>38</sub>Cl<sub>7</sub>N<sub>15</sub>O<sub>8</sub>Cu<sub>4</sub>); yield: 90%; color: kaki-green powder; MP > 270°C; M.Wt: 1107;  $\mu_{eff}$  (1.02 BM); conductivity (DMSO): 13  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

Table 1. Analytical and physical data of the ligands and its Cu<sup>2+</sup> complexes.

No	Chamical formula	() ( ) ()	% Found (Calcd.)										
NO.	Chemical formula	(141. 441)	С	н	Cu	Cl	N	Solvent	Solvent used in synthesis				
1	$C_{11}H_{23}Cl_2N_9O_6Cu_3\\$	638.9	20.7 (21.1)	3.6 (3.1)	29.8 (29.0)	11.1 (11.0)	19.7 (18.6)	5.7 (5.6)	H <sub>2</sub> O				
2	$C_{36}H_{71}Cl_{14}N_{27}O_{18}Cu_{12}$	2400.0	18.0 (17.8)	2.7 (3.0)	31.8 (31.9)	20.7 (20.4)	15.8 (15.6)		МеОН				
3	$C_{31}H_{75}Cl_7N_{24}O_{23}Cu_8\\$	1908.6	19.5 (18.8)	4.0 (3.3)	26.6 (26.4)	12.9 (13.0)	17.2 (17.6)	7.7 (7.7)	H <sub>2</sub> O + MeOH				
4	$C_{19}H_{38}Cl_7N_{15}O_8Cu_4\\$	1107.0	19.8 (20.6)	3.4 (3.5)	24.0 (23.0)	23.0 (22.4)	20.4 (19.0)	6.0 5.8	H <sub>2</sub> O + EtOH				
5	$C_{16.5}H_{29.5}Cl_5N_{13.5}O_{6.5}Cu_4$	952.5	20.3 (20.8)	3.0 (3.1)	26.5 (26.7)	18.6 (18.6)	19.1 (19.9)	8.5 (8.2)	EtOH + H <sub>2</sub> O				
6	$C_{10}H_{22}Cl_3N_6O_{5.5}Cu_3$	611.3	18.6 (19.6)	3.0 (3.6)	31.9 (31.2)	15.5 (17.4)	14,2 (13.8)	12.4 (12.0)	$EtOH + H_2O$				
7	$C_{16.5}H_{29.5}Cl_5N_{135}O_{6.5}Cu_{4.}$	1719.2	19.5 (19.9)	3.1 (3.0)	21.7 (22.0)	22.2 (22.7)	22.O (22.0)	3.4 (3.3)	Propanol + H <sub>2</sub> O				
8	$C_{16}H_{31}Cl_5N_{12}O_6Cu_3$	855.4	22.6 (22.5)	3.3 (3.7)	21.9 (22.3)	21.4 (20.7)	19.1 (19.7)	10.5 (10.8)	EtOH				
9	$C_{11}H_{19}Cl_4N_9O_4Cu_3$	673.8	18.6 (19.6)	2.8 (2.8)	27.9 (28.3)	21.2 (21.1)	19.4 (18.7)	6.4 ( 6.8)	EtOH				
10	$C_{38}H_{66}Cl_{10}N_{30}O_{12}Cu_7\\$	1934.5	23.2 (23.6)	3.3 (3.4)	22.7 (23.0)	18.3 (18.3)	21.9 (21.7)	7.4 (7.7)	Butanol				
11	$C_{28}H_{48}Cl_4N_{18}O_8Cu_5\\$	1224.4	27.4 (27.5)	3.0 (4.0)	25.3 (26.0)	11.5 (11.6)	20.9 (20.6)	14.0 (14.4)	Pentanol				
12	$C_{20.5}H_{35}Cl_7N_{18}O_{6.5}Cu_4$	1140.0	21.1 (21.6)	3.1 (3.1)	22.7 (21.8)	22.6 (21.8)	21.7 (22.1)	3.8 (3.9)	Pentanol				

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Compd.	<i>v</i> (OH)	<i>v</i> (NH <sub>2</sub> )	v(C≡N)	v(C=O); Amide I band	<i>v</i> (NH <sub>2</sub> )	Amide II band	<i>v</i> (N-N)	<i>v</i> (M-O)	<i>v</i> (M-N)	λ(nm) in <i>v</i> (cm <sup>-†</sup> Nujol	<sup>1</sup> ), U <sub>eff</sub> (BM)
$L^1$		3280, 3199	2263	1710, 1680	1619	1530, 1492	998			257.3, 38,865	-1.95
1	3440	3182, 2997	2264	1660, 1634	1586	1519, 1435	975	440	350	800, 12,500	1.95
2	3400	3320, 3185	2260	1720, 1670	1589	1401	940	400	335	740, 13,514	0.91
3		3445, 2993	2264	1760, 1640	1585	1440, 1360	980	440	388	800, 12,500	1.24
4	3400	3180, 3100	2264	1710, 1640	1582	1440, 1400	975	439	385	780, 12,821	1.02
5		3180, 3210		1700, 1650	1585	1445, 1395	976	425	390	780, 12,821	1.14
6		3415, 3346	2270	1740, 1600	1540	1406, 1300	940	400	360	830, 12,408	0.78
7	3480	3220, 3170, 2980		1636	1618	1575, 1540	955	400	345	760, 13,158	0.75
8	3350	2968, 2930, 2800	2260	1720	1590	1529, 1402	940	440	399	750, 13,333	0.85
9	3440	3280, 3231, 3180		1638	1620	1572, 1440	940	433	400	760, 13,158	0.86, 0.89
10	3426	3200, 2987	2263	1700, 1660	1590	1531, 1430	980	440	400	780, 12,821	0.78
11	3420	3260, 3200	2260	1700	1621	1540, 1416	953	450	389	740, 13,514	0.84
12	3426	3200	2263, 2170	1700, 1660	1590	1537, 1430	940	440	400	730, 13,699	0.88

Table 2. The most important IR, electronic spectral bands and the values of  $U_{eff}$ .

**Complex (5)** ( $C_{16.5}H_{29.5}Cl_5N_{13.5}O_{6.5}Cu_4$ ); yield: 69%; color: brown powder; MP > 270°C; M.Wt: 952.5;  $\mu_{eff}$  (1.14 BM); conductivity (DMSO): 13  $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ .

**Complex (6)** ( $C_{10}H_{22}Cl_3N_6O_{5.5}Cu_3$ ); yield: 69%; color: brown powder; MP > 270°C; M.Wt: 611.3;  $\mu_{eff}$  (0.78 BM); conductivity (DMSO): 8  $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ .

**Complex (7)** ( $C_{16.5}H_{29.5}Cl_5N_{13.5}O_{6.5}Cu_4$ ); yield: 77%; color: yellowish-green powder; MP 155°C; M.Wt: 1719.2;  $\mu_{eff}$  (0.75 BM); conductivity (DMSO): 7  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>. **Complex (8)** ( $C_{16}H_{31}Cl_5N_{12}O_6Cu_3$ ); yield: 77%; color: dirty-green powder; MP >

270°C; M.Wt: 855.4;  $\mu_{eff}$  (0.85 BM); conductivity (DMSO): 6 Ω<sup>-1</sup>·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (9)** (C<sub>11</sub>H<sub>19</sub>Cl<sub>4</sub>N<sub>9</sub>O<sub>4</sub>Cu<sub>3</sub>); yield: 90%; color: military-green powder; MP > 270°C; M.Wt: 673.8;  $\mu_{eff}$  (0.85 BM); conductivity (DMSO): 4  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (10)** ( $C_{38}H_{66}Cl_{10}N_{30}O_{12}Cu_7$ ): yield: 85%; color: kaki-green powder; MP > 270°C; M.Wt: 1934.5;  $\mu_{eff}$  (0.75 BM); conductivity (DMSO): 9  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (11)** ( $C_{28}H_{48}Cl_4N_{18}O_8Cu_5$ ); yield: 79%; color: brownish-green powder; MP: 200°C; M.Wt: 1224.4;  $\mu_{eff}$  (0.84 BM); conductivity (DMSO): 10  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

**Complex (12)** ( $C_{20.5}H_{35}Cl_7N_{18}O_{6.5}Cu_4$ ); yield: 85%; color: grayish-green powder; MP: 103°C; M.Wt: 1140.0;  $\mu_{eff}$  (0.85 BM); conductivity (DMSO): 10  $\Omega^{-1}$ ·cm<sup>2</sup>·mol<sup>-1</sup>.

### 3. Results and Discussion

The data of some physical properties and elemental analysis of the isolated  $Cu^{2+}$  complexes are summarized in **Table 1**. The structures of the compounds are established by elemental analyses, spectral, magnetic studies and confirmed by weight loss determination. The values of molar conductivity of all complexes lie in the 4 - 13 ohm<sup>-1</sup>·cm<sup>2</sup>·mol<sup>-1</sup> range indicating the non-electrolytic nature of the  $Cu^{2+}$  complexes [21]. Also, it suggests the polymeric nature as well as the strong covalent bonding between the ligand and the copper(II) ion. Unfortunately, the

isolation of single crystal for any one of the isolated solid complexes to confirm the exact coordination sites and the geometry around the Cu<sup>2+</sup> ions is very difficult due to the polymeric nature of these complexes.

#### 3.1. IR, <sup>1</sup>H-NMR, Raman, Electronic and Mass Spectra of L (CAH)

The IR spectra of CAH (L) in KBr and/or Nujol mull are cognate and show three bands at 3280sh, 3199s and 3056s cm<sup>-1</sup> assigned to  $\nu_{2}$ (NH<sub>2</sub>),  $\nu_{3}$ (NH<sub>2</sub>) and  $v_a(NH_2)$  vibrations, respectively. Also, the bands located at 2263s, 1710sh and 1680sh cm<sup>-1</sup> are assigned to  $\nu$ (C=N)s,  $\nu$ (C=O)sh (free) and  $\nu$ (C=O)s (hydrogen-bonded) vibrations, respectively. Moreover, the two bands at 1530m and 1492s are attributed to amide II vibrations. The observation of the carbonyl band as a shoulder together with the existence of the NH<sub>2</sub> at lower wavelength suggests that the carbonyl group is partially hydrogen-bonded to the amino group as shown in Figure 1. Also, the <sup>1</sup>H-NMR spectrum of L in d<sub>6</sub>-DMSO shows three signals at 10.06, 9.53 and 9.1 ppm assigned to  $NH_2$  and NH groups which obscured on adding  $D_2O$ . Both the methyl and ethyl proton signals are observed as triplet signals in the ranges 1.76 - 1.96 and 3.66 - 3.76 ppm, respectively. The calculated value of the mass spectrum of L equals 141 which is quite agrees with the experimental value of M + 1 (142). The electronic spectrum of L in DMSO shows two bands at 220 nm  $(45,455 \text{ cm}^{-1})$  and 262 nm  $(38,170 \text{ cm}^{-1})$  attributed to  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the C=O and C=N groups, respectively. The Raman spectrum of CAH shows active bands at 3341m, 2926m, 2260s 1670w and 1010 cm<sup>-1</sup> assigned to  $\nu(NH_2)$ ,  $\nu(CH)$ ,  $\nu(C=N)$  and  $\nu(N-N)$  vibrations, respectively. These foundations are taken as strong evidences for our assumptions and the existence of the ligand (CAH) as shown in Figure 1.

A comparison of the IR spectra of **CAH** and its  $Cu^{2+}$  complexes (**Table 2**) shows that the ligand behaves in a neutral bidentate fashion *via* the (C=O) and NH<sub>2</sub> groups.

The mode of chelation is confirmed by the following remarks:

1) The measurably shifts of both the (C=O) and (NH<sub>2</sub>) groups to lower wavenumbers in all complexes indicating that these groups are participating in coordination of the  $Cu^{2+}$  ion.

2) The vibrations of the amide II bands are also shifted to lower wavenumbers suggesting the participation of both groups in coordination.

3) New bands are observed in the range 400 - 440 and 350 - 400 cm<sup>-1</sup> are assigned to (M-O) and (M-N), respectively [13].

4) The spectra of the complexes show broad medium band in the region 3440 - 3426 cm<sup>-1</sup>, attributable to the existence of solvent inside and/or outside the coordination sphere [14].



Figure 1. Hydrogen bond exists in CAH (L<sup>1</sup>).

5) The observation of two bands at 1710s and 1680sh together with the presence of weak broad bands in the 2800 - 2920  $\text{cm}^{-1}$  suggests the existence of strong hydrogen bonding.

All these foundations suggest that the ligand is existed as a mixture of the keto (A) and enol (B) forms as shown in **Figure 1**.

The obscure and/or the weakness of the cyano group  $(C \equiv N)$  in some  $Cu^{2+}$  complexes is taken as strong evidence for the promotion of the solvent as shown in **Scheme 1**. The mechanism of promotion was proposed and confirmed in our previous works [18] [19].

#### 3.2. Molecular Modeling

#### **Global Reactivity Descriptors**

Quantum chemical calculations are concerned with the determination of energies of both HOMO ( $\pi$ -donor) and LUMO ( $\pi$ -acceptor) parameters. HOMO orbital acts as an electron donor while LUMO orbital acts as an electron acceptor. These molecular orbitals are also called the frontier molecular orbitals (FMOs).



Scheme 1. Promotion of solvents to the cyano group.

1) The negative values of both  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  and their neighboring orbitals (**Table 3**) indicate that the molecules are stable [22].

2) The FMOs theory predicts the essential sites participate in coordination (electrophilic attack). An initial assumption proposes that the reaction occurred with maximum overlap between the HOMO on one molecule and the LUMO on the other. The overlap between HOMO and the LUMO is essential factor in any reactions. The goal obtained from the calculations is to get the largest values of molecular orbital coefficients. Accordingly the orbitals of the ligands under investigation have the largest value of molecular orbital.

3) Gutmann's variation rules indicate that the strength of bonds increase as the adjacent bonds become weaker as found by Linert *et al.* [23].

4) The energy gap ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ) expresses the stability index which helps to characterize the chemical reactivity and kinetic stability of the molecule [24]. The gap ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ) is patented to develop a theoretical model to explain the structure and verify the barriers in different systems, which affect the biological activity of the molecule. Small gap within the molecule means that the molecule is polarized and acts as soft molecule. It is well known that the soft molecules are more reactive than hard ones since they easily donate electrons to an acceptor. The energy gap is small in the compound indicate that the charge-transfer easily occurs in it influencing the biological activity of the molecule. Energy gap with low values is also attributed to the groups that enter into conjugation [24].

5) Low energy values of HOMO indicate that the donating electron ability of the molecules is the weaker. Contrarily, the higher HOMO energy suggests that the molecule is a good electron donor. LUMO energy presents the ability of a molecule receiving electron [25]. The results are depicted in **Figures 2-7**.

DFT concept illustrates neatly the chemical reactivity and the site selectivity of the molecular systems. Both the energies of  $(E_{\text{HOMO}} + E_{\text{LUMO}})$  and band gap  $(E_{\text{HOMO}} - E_{\text{LUMO}})$  illustrate preemptory the charge-transfer interplay within the molecule, electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global softness (S) and global electrophilicity index ( $\omega$ ) [26] [27] [28] are listed in Table 4.

$$\chi = -1/2 \left( E_{\rm LUMO} + E_{\rm HOMO} \right) \tag{1}$$

Table 3. Some of energetic properties of the ligands and calculated by DMOL<sup>3</sup> using DFT-method.

No.	Compound	$\begin{array}{c} \text{HOMO}  \text{LUMO}  \begin{array}{c} E_{\text{HOMO}} - E_{\text{LOMO}} \\ \text{(eV)}  \text{(eV)}  \text{(eV)} \end{array}$		Binding energy (Kcal/mol)	Total energy (Kcal/mol)	Kinetic energy (Kcal/mol)	
1	L; CAH (C3H5N3O)	-5.575	-0.449	-5.126	-1233.73	$-2.24 \times 10^{5}$	-2106.03
2	L <sup>1</sup> ; (C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> )	-5.538	-0.321	-5.217	-1500.15	$-2.72 \times 10^{5}$	-2267.83
3	L <sup>2</sup> ; (C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> )	-4.802	0.405	-4.397	-1748.98	$2.96  imes 10^5$	-1910.25
4	L <sup>3</sup> ; (C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> )	-5.36	-0.242	-5.118	-2063.23	$-3.21 \times 10^{5}$	-3174.85
5	L <sup>4</sup> ; (C <sub>6</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> )	-5.597	-0.243	-5.354	-2358.60	$-3.46 \times 10^{5}$	-3538.18
6	L <sup>5</sup> ; (C7H16N3O2)	-5.630	-0.293	-5.337	-2655.31	$-3.70 \times 10^{5}$	-3879.51
7	L <sup>6</sup> ; (C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> )	-5.832	-0.529	-5.303	-2949.04	$-3.95 \times 10^{5}$	-4468.66



Figure 2. (a, b, c, d) Molecular modeling of (a) L<sup>1</sup>, (b) electron density, (c) HOMO, and (d) LUMO.



Figure 3. (a, b, c, d) Molecular modeling of (a) L<sup>2</sup>, (b) electron density, (c) HOMO, and (d) LUMO.





Figure 4. (a, b, c, d) Molecular modeling of (a)  $L^3$ , (b) electron density, (c) HOMO, and (d) LUMO.



Figure 5. (a, b, c, d) Molecular modeling of (a) L<sup>4</sup>, (b) electron density, (c) HOMO, and (d) LUMO.



Figure 6. (a, b, c, d) Molecular modeling of (a)  $L^5$ , (b) electron density, (c) HOMO, and (d) LUMO.



**Figure 7.** (a, b, c, d) Molecular modeling of (a) **L**<sup>6</sup>, (b) electron density, (c) HOMO, and (d) LUMO.

**Table 4.** Calculated  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy band gap ( $E_{\text{H}} - E_{\text{L}}$ ), chemical potential ( $\mu$ ), electro-negativity ( $\chi$ ), global hardness ( $\eta$ ), global softness (S) and global electrophilicity index ( $\omega$ ) for ligands.

Compound	Compound $egin{array}{cccc} & & & & & & & & & & & & & & & & & $		$(E_{\rm H}-E_{\rm L})$ eV	χ eV	μ eV	η eV	<i>S</i> eV <sup>-1</sup>	Ω eV	Σ eV
L; CAH (C3H5N3O)	-5.575	-0.449	-5.126	3.01	-3.01	2.56	1.28	1.76	0.39
L <sup>1</sup> ; (C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> )	-5.538	-0.321	-5.217	2.93	-2.93	2.61	1.31	1.64	0.38
L <sup>2</sup> ; (C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> )	-4.802	0.405	-4.397	2.6	-2.6	2.2	1.1	1.53	0.45
L <sup>3</sup> ; (C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> )	-5.36	-0.242	-5.118	2.8	-2.8	2.56	1.28	1.53	0.39
L <sup>4</sup> ; (C <sub>6</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> )	-5.597	- 0.243	-5.354	2.92	-2.92	2.67	1.34	1.59	0.37
L <sup>5</sup> ; (C <sub>7</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> )	-5.630	-0.293	-5.337	2.96	-2.96	2.67	1.34	1.64	0.37
L <sup>6</sup> ; (C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> )	-5.832	-0.529	-5.303	3.18	-3.18	2.65	1.32	1.9	0.38

1

H = HOMO, L = LUMO.

$$\mu = -\chi = 1/2 \left( E_{\text{LUMO}} + E_{\text{HOMO}} \right) \tag{2}$$

$$\gamma = 1/2 \left( E_{\rm LUMO} - E_{\rm HOMO} \right) \tag{3}$$

$$=1/2\eta \tag{4}$$

$$\omega = \mu^2 / 2\eta \tag{5}$$

The inverse value of the global hardness is designed as the softness ( $\sigma$ ) as follow:

S

$$\sigma = 1/\eta \tag{6}$$

The electrophilicity index  $(\omega)$  is considered as important quantum chemical descriptors. Also, this value used to estimate the stabilization energy when the system acquires an additional electronic charge from the environment. The molecular stability and reactivity of the compounds depends mainly on the values of

 $\eta$  and  $\sigma$ . The ligand acts as a Lewis base while the metal ion acts as a Lewis acid during complex formation.

The three-dimensional plots of frontier orbital energies using the DFT method for  $L^2-L^7$  are shown in Figures S1-S6.

#### 3.3. EPR Spectral Studies of the Isolated Cu<sup>II</sup> Complexes

The results of the EPR spectra of the polymeric Cu<sup>2+</sup> complexes in DMSO at low temperature (127°C - 160°C) are depicted in **Table 5**. The trend  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) observed for the Cu<sup>2+</sup> complexes suggests that the unpaired electron is localized in the  $d_{x_2-y_2}$  (<sup>2</sup> $B_{1g}$ ) orbital [29] [30]. It is well known that the axial symmetry parameter (*G*) is defined as:

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$$

If G > 4 the exchange interaction is negligible between Cu(II) ions, whereas G < 4 means a significant Cu-Cu interaction and tone straightly with measured magnetic moment [31]. The *G* values for all complexes are larger than 4 (4.0 - 6.0) suggesting the absence of any copper-copper interaction. Orbital reduction factors ( $K_{\parallel}$  and  $K_{\perp}$ ) which are a measure of covalence were determined using the following two expressions:

$${}^{2}K_{\parallel} = \frac{\left(g_{\parallel} - 2.0023\right)}{8\lambda o} \times \Delta E$$
$${}^{2}K_{\perp} = \frac{\left(g_{\perp} - 2.0023\right)}{2\lambda o} \times \Delta E$$

The value of  $\lambda o$  (spin-orbital coupling constant) for  $d^9$ -system equals -828 cm<sup>-1</sup>. Hathaway [31] pointed out that that in case of pure  $\sigma$ -bonding,  $K_{\parallel} = K_{\perp} =$ 

Table 5. EPR X-band data of the Cu<sup>II</sup> complexes in DMSO at low temperature.

Complex	<i>Тетр.</i> ( <i>К</i> )	<b>g</b> ⊥	<i>8</i> 11	gav.	G	$A_{\parallel}  imes 10^{-4}$ cm <sup>-1</sup>	K⊥	K <sub>ll</sub>	Η	$g_{\parallel}/A_{\parallel}$	a²	B²	$\gamma^2$
$C_{11}H_{23}Cl_2N_9O_6Cu_3$ (1)	149	2.07	2.33	2.16	4.71	195	0.59	0.81	2303	100	0.94	0.86	0.63
$C_{36}H_{71}Cl_{14}N_{27}O_{18}Cu_{12}$ (2)	132	2.07	2.32	2.15	4.57	200	0.55	0.65	3160	116	0.94	0.69	0.59
C31H75Cl7N24O23Cu8 (3)	127	2.08	2.44	2.20	5.50	190	0.59	0.83	3200	136	0.90	0.92	0.66
C19H38Cl7N15O8Cu4 (4)	160	2.06	2.29	2.14	4.83	190	0.45	0.56	3245	121	0.88	0.64	0.51
C16.5H29.5Cl5N13.5O6.5Cu4 (5)	155	2.07	2.33	2.16	4.71	185	0.52	0.64	3190	126	0.91	0.70	0.57
C10H22Cl3N6O5.5Cu3 (6)	155	2.08	2.44	2.20	5.50	170	0.57	0.63	3150	144	0.98	0.64	0.58
C16.5H29.5Cl5N135O6.5Cu4 (7)	135	2.06	2.36	2.16	6.00	180	0.46	0.67	3106	131	0.92	0.73	0.50
C <sub>16</sub> H <sub>31</sub> Cl <sub>5</sub> N <sub>12</sub> O <sub>6</sub> Cu <sub>3</sub> (8)	127	2.07	2.31	2.15	4.43	195	0.55	0.61	3160	119	0.92	0.66	0.60
C <sub>11</sub> H <sub>19</sub> Cl <sub>4</sub> N <sub>9</sub> O <sub>4</sub> Cu <sub>3</sub> (9)	127	2.07	2.31	2.15	4.43	160	0.54	0.61	3240	144	0.82	0.74	0.66
C38H66Cl10N30O12Cu7 (10)	139	2.11	2.43	2.22	4.00	170	0.83	0.83	3210	143	0.99	0.78	0.84
C <sub>28</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>18</sub> O <sub>8</sub> Cu <sub>5</sub> (11)	137	2.06	2.30	2.14	5.00	180	0.47	0.61	3175	128	0.87	0.70	0.54
C <sub>20.5</sub> H <sub>35</sub> Cl <sub>7</sub> N <sub>18</sub> O <sub>6.5</sub> Cu <sub>4</sub> (12)	140	2.07	2.39	2.18	5.57	190	0.56	0.80	3106	121	0.89	0.90	0.63

0.77 and for in-plane  $\pi$ -bonding  $K_{\parallel} < K_{\perp}$ , while for out-of-plane  $\pi$ -bonding  $K_{\perp} < K_{\perp}$  $K_{\parallel}$  the following simplified expressions were used to calculate  $K_{\parallel}$  and  $K_{\perp}$ . In all cases of Cu(II) complexes under investigation the observed  $K_{\parallel} > K_{\perp}$  indicating that the presence of out-of-plane  $\pi$ -bonding as depicted in **Table 5**. The value of  $K_{\parallel} = K_{\perp} = 0.83$  in case of the Cu<sup>2+</sup> complex (10) suggesting the existence of pure  $\sigma$ -bonding. For all the complexes the evaluated values of  $\alpha^2$ ,  $\beta^2$  and  $\gamma^2$  are consistent with both in plane  $\sigma$ -bonding and in plane  $\pi$ -bonding as shown in **Table 5**. Moreover, all the above values  $(\alpha^2, \beta^2 \text{ and } \gamma^2)$  are less than 1 suggesting 100% ionic nature of the bonds [32]. The bonding parameters for the Cu(II) complexes are found to be  $\alpha^2$  in the 0.82 - 0.99,  $\beta^2$  in the 0.64 - 0.92 and  $\gamma^2$  in the 0.5 - 0.84 ranges. The extent of departing of these parameters from unity measures the range of delocalization of metal electrons due to M-L bonding and hence  $a^2$ measures  $\sigma$ -bonding within the complexes [33],  $\beta$  measures out of (xy) plane  $\pi$ -bonding while  $\gamma^2$  shows in plane  $\pi$ -bonding contribution. No doubt that the deviation from unity in  $\beta^2$  and  $\gamma^2$  values suggests the presence of considerable out of plane and in plane  $\pi$ -bonding contribution in M-L  $\pi$ -bonding. Accordingly, the EPR studies of the copper complexes have provided supportive evidence to the optical and magnetic results.

#### 3.4. Electronic Spectra and Magnetic Behavior

The electronic spectra of the Cu(II) complexes were displayed in Nujol mull and/or DMSO. The electronic spectra show a broad band lie in the 13,551 -17,860 cm<sup>-1</sup> range suggesting d-d transition  $({}^{2}E_{2g} \rightarrow {}^{2}T_{2g})$  in octahedral geometry around the Cu<sup>2+</sup> ion [34] [35]. Also, the values of the corrected subnormal magnetic moment of the complexes (2-12) fall in the 0.75 - 1.24 BM are taken as strong evidence for the existence of polymeric nature [36] [37] and strong Cu-Cu interaction. The value of magnetic moment of complex (2, C<sub>11</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>9</sub>O<sub>6</sub>Cu<sub>3</sub>) was found to be 1.95 BM. The high value of magnetic moment of complex (2) in comparison to the previous complexes (3-12) in spite of the polymeric nature of this complex, which contains three copper atoms, is due to the absence of any Cu-Cu interaction within this complex either in the *xy* or directions. The data of electronic spectra and magnetic moments are shown in Table 2.

#### 3.5. TGA Studies

The amounts of the coordinated solvents and/or the hydrated solvents have been determined in the range  $25^{\circ}$ C -  $200^{\circ}$ C. The experimental weight loss values are in good agreement with the calculated values. The TGA curves of the Cu<sup>2+</sup> complexes exhibit two different types of weight loss, in the above range, indicating the presence of two types of solvents. The Former in the  $50^{\circ}$ C -  $120^{\circ}$ C range suggesting the presence of hydrated solvents while the latter in the range  $125^{\circ}$ C -  $200^{\circ}$ C illustrating the presence of coordinated solvents.

## 4. Conclusion

The new polymeric Cu2+ complexes derived from cyanoacetylhydrazine in dif-

ferent solvents were characterized by spectral, magnetic and thermal analyses. The different ligands obtained by the promotion of different solvents to the cyano groups were suggested according to the spectral studies. The ligands obtained coordinate in a bidentate manner via the carbonyl and the NH<sub>2</sub> groups forming five-membered rings around the copper(II) ion. The results of spectral together with the values of magnetic moments suggest distorted-octahedral geometry around the Cu<sup>2+</sup> ion. The Spin-Hamiltonian parameters obtained from the EPR spectra of the complexes in DMSO at low temperature were used to calculate the bonding parameters. DFT calculations illustrate the chemical reactivity and the site selectivity of the molecular systems. Both the energies of ( $E_{HOMO} + E_{LUMO}$ ) and band gap ( $E_{HOMO} - E_{LUMO}$ ) illustrate preemptory the charge-transfer interplay within the molecule, electronegativity, chemical potential, global hardness, global softness and global electrophilicity index are listed.

## **Conflicts of Interest**

The article is original and unpublished and is not being considered for publication elsewhere. The author declares that he has no conflict of interests that could influence this work.

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## **Supplementary**



**Figure S1.** Three-dimensional plots of frontier orbital energies using the DFT method for **L**<sup>2</sup>.







**Figure S3.** Three-dimensional plots of frontier orbital energies using the DFT method for L<sup>4</sup>.







**Figure S5.** Three-dimensional plots of frontier orbital energies using the DFT method for L<sup>6</sup>.



