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Research Article

SPECTROSCOPIC AND THEORETICAL STUDIES OF BRIDGED [CU (PHEN) 2H$_2$O] (CLO$_4$)$_2$ COMPLEXES

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ABSTRACT

[Cu(phen)$_2$H$_2$O](ClO$_4$)$_2$ reacted with bridging ligands; sodium azide, potassium cyanate and potassium thiocyanate. The dimeric compounds obtained were characterized using microanalyses, room temperature magnetic susceptibility measurements, infrared, electronic, and mass spectroscopic methods. The microanalyses data is satisfactory with the formation of dimeric compounds which is supported by the conjoint of infrared, mass spectra (ESI), and electronic spectra of the complexes. The effective magnetic moments of the complexes ($\mu_{eff.}$) observed in the range 2.18-2.53 B.M. is consistent with the dimeric nature of the compounds. The conductivity measurements showed that the azide and cyanate complexes are 1:4 electrolytes. The structures were modeled using PM3 semi-empirical method and the geometry parameters calculated.

Key Words: *Bridging Ligands, Dimeric Compound, Microanalysis, Complexes and Spectroscopic Techniques*

INTRODUCTION

The coordination chemistry of ligands possessing two different atoms capable of coordinating to metal ions has long been a subject of intense interest to both synthetic and theoretical chemists. Ambidentate ligands such as SCN$^-$, SeCN$^-$, CN$^-$, NO$_2^-$, N$_3^-$, C$_2$N$_3$ etc have been reported (Burmeister, 1966; Kabesova *et al*, 1995 and Youngme *et al.*, 2008). Atoms, ions, or molecules which are coordinatively unsaturated i.e, which after forming one bond, still contain at least one unshared pair of electrons and are able to form an additional bond have been investigated. Among such ligands are O^{2-}, O$_2^-$, O$_2^{2-}$, NH$_2^-$, NH^{2-}, SO$_4^{2-}$, etc which have been studied mostly as bridging groups (Kauffman, 1972-1973 and Wing-Wah Yam *et al*, 1998). Phenoxo ligands, pyrazole groups, phospine ligands and acetylides have been employed also as bridges (Wing-Wah Yam *et al*, 1998; Kaden, 1999; Venegas-Yazigi *et al.*, 2010 and Xin Gan *et al.*, 2010). The interest for dinuclear metal complexes arises from the theoretical interest for such compounds, since one can expect that two metal centres especially if paramagnetic kept at a fixed distance not far from each other will interact (Kaden, 1999). On the other hand, these complexes are also interesting because two centres fixed at a certain distance often allow the binding and thus the recognition and or activation of a substrate molecule. This way, they could be used to mimic metalloproteins such as haemocyanin, superoxide dismutase or urease and to study structure reactivity relationships (Kaden, 1999). Phenoxo ligands used as bridged have been employed in the synthesis of many complexes with different transition metals, among which the most frequent ones are those of copper(II). These complexes have been known to show remarkable non-magnetic properties which make them useful in hydrometallurgy, fluorescent sensors, heterogenous catalysis and show catechol oxidases activity (Venegas-Yazigi *et al.*, 2010). In this work, we concentrate on the synthesis, spectroscopic and theoretical studies of the dimeric complexes of [Cu(phen)$_2$H$_2$O](ClO$_4$)$_2$ with bridging ligands such as N$_3^-$, OCN$^-$, and SCN$^-$. Semi-empirical method (PM3) (Kong *et al.*, 2001) was used for the calculations of geometric parameters of the complexes using Spartan 06 program (Spartan 06).

MATERIALS AND METHODS

Reagents Used

$Cu(ClO_4)_2$ $.6H_2O$, 1,10-phenanthroline, sodium azide, potassium thiocyanate, potassium cyanate, methanol, acetonitrile. All reagents are of analytical grade and were used without further purification.

Syntheses of The Complexes

$[Cu(phen)_2 H_2O](ClO_4)_2$ was prepared according to a literature procedure (Murphy *et al.*, 1997).

$[Cu(phen)_2 H_2O](ClO_4)_2$ with sodium azide (A)

13 mg (0.2 mmole) sodium azide was added to 256 mg (0.4 mmole) $[Cu(phen)_2 OH_2](ClO_4)_2$ dissolved in 100 ml acetonitrile with constant stirring. The lemon-green coloured solution obtained immediately was stirred for 24 hrs. It was filtered by gravity after stirring and the filtrate kept on the bench for crystallization to take place. The green crystals obtained after 6 days was filtered by suction, washed with acetonitrile and dried in air. Yield: 175 mg (72%), $C_{48}H_{34}N_{11}O_{13}Cl_3Cu_2$ (M.M: 1205.93) Anal. Obs (Cal): C, 47.77(47.76); H, 2.72(2.84); N, 12.53(12.78). FTIR: ν/cm^{-1}: 2033 (N_3); 623s, 1094vs (ClO_4). UV-Vis: cm^{-1}14,311; 24,439; 34,463; 37,439; 45,439. Λ_M/mho cm^2mol^{-1}: 502.66 (1:4 electrolyte). $\mu_{eff} =$ 2.28 B.M. ESI-MS (CH_3CN) m/z: 301.99 (52 %$\{Cu_2(phen)_4N_3\}^{3+}$), 523.95(50% $\{Cu_2(phen)_4(ClO_4)_2\}^{2+}$) and 211.51(70% $\{Cu_2(phen)_4\}^{2+}$).

$[Cu(phen)_2H_2O](ClO_4)_2$ with potassium cyanate (B)

8.1 mg(0.1 mmole) potassium cyanate was added to 128 mg(0.2 mmole) $[Cu(phen)_2 OH_2](ClO_4)_2$ suspended in 50 ml methanol and the mixture stirred for 24hrs. A turquoise blue precipitate obtained after 24 hrs was filtered by suction and dried in vacuum. Yield: 82 mg (62%).$C_{49}H_{32}N_9O_{13}Cl_3Cu_2$ (M.M: 1187.90): Anal. Obs(Cal). C: 49.49(49.50); H; 2.72(2.60); N, 10.61(10.09). FTIR: ν/cm^{-1}: 2183 (C-N); 1520 (C-O); 623s, 1092vs (ClO_4). UV-Vis: cm^{-1}: 14,400; 30,889; 34,412; 37,494; 45,055. Λ_M/mho cm^2mol^{-1}: 534.39 (1:4 electrolyte). $\mu_{eff} =$ 2.18 B.M. ESI-MS (CH_3CN) m/z: 523.67(29% $\{Cu_2(phen)_4(ClO_4)_2\}^{2+}$) and 211.40 (70% $\{Cu_2(phen)_4\}^{2+}$)

$[Cu(phen)_2H_2O](ClO_4)_2$ with potassium thiocyanate (C)

256 mg (0.4 mmole) $[Cu(phen)_2OH_2](ClO_4)_2$ in 100 ml methanol was stirred, and 19.4 mg(0.2 mmole) potassium thiocyanate was added. The lemon-green cloudy solution obtained was stirred for 24 hrs, after which it was filtered by gravity. The volume of the filterate obtained was reduced to half the initial volume before it was kept on the bench for crystallization to take place. The green crystals obtained after 6 days was filtered by suction, washed with methanol and dried in air. Yield: 179 mg (67%). $C_{49}H_{32}N_9O_{12}Cl_3SCu_2$ (M.M: 1203.90): Anal. Obs (Cal.) C,49.57(48.84); H, 2.66(2.68); N, 10.75(10.47). FTIR: ν/cm^{-1}: 851 (C-S); 2083 (C-N); 623s, 1090vs (ClO_4). UV-Vis: cm^{-1}: 11,391; 14,104; 24,773; 34,369; 37,473; 45,259. $\mu_{eff} =$ 2.53 B.M.

Physical Measurements

Microanalyses were performed by a Perkin-Elmer 2400II CHNS analyzer. Room temperature magnetic moments were measured by a magnetic susceptibility balance procured from Sherwood Scientific, UK. The diamagnetic corrections were evaluated using Pascal's constants. UV/VIS spectra were recorded on a Perkin-Elmer Lambda 950 spectrophotometer, FTIR spectra(KBr) on a Shimadzu FTIR-8400S spectrometer and ESI mass spectra on a waters Qtof Micro YA263 spectrometer. Molar conductances were measured by a syntronics (India) conductivity meter (model 306) in acetonitrile.

Theoretical Calculations

Semi-empirical method (PM3) (Kong *et al.*, 2001) was used for the calculations of geometric parameters of the complexes using Spartan 06 program (Spartan 06) implemented on an Intel Pentium M 2.0 GHz Computer, since PM3 has been successfully used either only or with other theoretical methods for structural analysis of Cu (II) complexes (Johnson *et al*, 2000; Bernabè *et al*, 2001; Seguel *et al.*, 2005; Adeoye *et al*, 2010 and Seguel *et al*, 2010). The molecular occupied orbitals (HOMO) and molecular unoccupied orbitals (LUMO) of the complex ions were also displaced in order to know the effect of bridging ligands on the molecular properties as it affects electronic transitions.

RESULTS AND DISCUSSION

The formation of the dimeric complexes proceeded generally in appreciable yields as shown in the following equations:

$2Cu(phen)_2OH_2(ClO_4)_2 + NaN_3 \rightarrow 2[Cu(phen)_2]OH_2(ClO_4)_3N_3$ …..(1)
$2Cu(phen)_2OH_2(ClO_4)_2 + KOCN \rightarrow 2[Cu(phen)_2](ClO_4)_3OCN$ ……(2)
$2Cu(phen)_2OH_2(ClO_4)_2 + KSCN \rightarrow 2[Cu(phen)_2](ClO_4)_3SCN$ ……(3)

The dimeric complexes were obtained as lemon-green and torquiose blue. The complexes were very soluble in acetonitrile and dimethylformamide but not soluble in dichloromethane.

Infrared Spectra

The major vibrations used successfully to infer the formation of the dimeric compounds are the N_3^- and the ClO_4^- stretching frequencies for the azide complex, the C - N and C-O stretching frequencies for the cyanate complex with the ClO_4^- stretching frequency and C - S and C - N bands in addition to the ClO_4^- stretching frequency for the thiocyanate complex. The $\nu_{asym}(N_3)$ absorption band is found usually between 2038 - 2042 cm^{-1} (Youngme *et al*, 2008); in the prepared azide complex this was observed at 2033 cm^{-1} which is within the range of similar complexes prepared. The presence of the ClO_4^- stretching band at 623 cm^{-1} and 1094 cm^{-1} also revealed that the perchlorate ion is involved. The C-N and C-O absorption bands were observed at 2183 $cm^{-1}$and 1520 cm^{-1} respectively (Schoenherr, 1986) while the ClO_4^- ion was observed at 623 cm^{-1} and 1092 cm^{-1} for the complex. The thiocyanate complex shows the C-N stretching frequency at 2083 cm^{-1} which is within the literature value between 2000 - 2280cm^{-1} (Burmeister, 1966; Silverstein *et al*, 2005) and the C-S absorption band at 851 cm^{-1} which is in agreement with literature value of 697 cm^{-1} - 855 cm^{-1} (Burmeister, 1966) . The perclorate absorption band was at 623 cm^{-1} and 1090 cm^{-1} for the synthesized compound. The presence of these observed structural bands in each of the complexes confirmed the formation of the desired complexes.

Electronic Spectra and Mass Spectra

The UV-Vis spectra complexes at the visible region show the high-energy, high- intensity peaks at 14,311 cm^{-1} for the azide complex, 14,400 cm^{-1} for the cyanate and 14,101 cm^{-1} for the thiocyanate compound with a low-energy, low- intensity shoulder at 11,391 cm^{-1} for only the thiocyanate complex. The order of one-electron ground-state configurations is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} = d_{yz}$ and the transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ for the low-energy shoulder for the thiocyanate complex and the $d_{xz} = d_{yz} \rightarrow d_{x^2-y^2}$ for the high-energy peak (Seguel *et al*, 2010). From the literature, five-coordinate transition metal complexes without constraints of chelating ligands occur in the trigonal bipyramidal geometry, while ligand-ligand repulsion also favour these arrangements (Douglas *et al*, 2007). The information gathered from the UV-Vis spectra of the complexes in the visible region indicate that the complexes have square pyramidal geometries due to the chelating ligand constraints and the reduction in ligand-ligand repulsion since the 1,10-phenanthroline ligand will repel equally. The fragmentation patterns of the complexes show the peaks at m/z = 301.99, 523.95 and 211.51 respectively for $\{Cu_2(phen)_4N_3\}^{3+}$, $\{Cu_2(phen)_4(ClO_4)_2\}^{2+}$and $\{Cu_2(phen)_4\}^{2+}$. The peaks at m/z = 523.67 and 211.40 stand for stand for $\{Cu_2(phen)_4(ClO_4)_2\}^{2+}$and $\{Cu_2(phen)_4\}^{2+}$ respectively in the cyanate complex. The measured molecular weights of these fragmentation patterns were consistent with expected values.

Conductivity Measurement

The conductance of the solutions of the complexes in acetonitrile, CH_3CN (10^{-3} mol L^{-1}) are shown in Table 1. The molar conductances of the azide and cyanate bridging complexes are 502.66 Ω^{-1} cm^2 mol^{-1} and 534.39 Ω^{-1} cm^2 mol^{-1} respectively indicating the electrolytic nature of the complexes (A.S.El-Tabi *et al* 2011). The dimeric complexes are 1:4 electrolytes and appear to have the ionic structures $\{[M_2(phen)_4](ClO_4)_3L\}$ on the basis of the conductivity.

Magnetic Measurement

The magnetic moments of the complexes are 2.28B.M, 2.18B.M and 2.53B.M respectively for the azide, cyanate and thiocyanate complexes. The magnetic moment of these dinuclear complexes at room temperature are distinctly lower than what is expected for two independent paramagnetic Cu ions, which is indicative for an antiferromagnetic coupling (Kaden, 1999).

Computational Studies

Optimized geometries

The complexes were modeled based on the data obtained from infrared spectra, UV-Vis spectra, mass spectra and elemental analysis of the complexes. The modeled structures consist of binuclear, five coordinated Cu(II) complexed with four units of 1,10-phenanthrolines, two units on each metal ion. The metal ions are linked together by bridging ligands (N_3, SCN and OCN), thus giving five coordination around each metal ion as shown in Figures 1 and 2.

Table1. Geometry parameters for the modeled complexes calculated using PM3 method.

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Bond distance (Å)	***N_3 (X=N)***	***SCN (X=S)***	***OCN (X=O)***
Cu1-N1	1.924	1.929	1.927
Cu1-N1	1.916	1.918	1.909
Cu1-N3	1.902	1.903	1.894
Cu1-N4	1.910	1.915	1.905
Cu2-N5	1.903	1.934	1.917
Cu2-N6	1.913	1.895	1.908
Cu2-N7	1.925	1.900	1.916
Cu2-N8	1.903	1.900	1.916
Cu1-N9	1.881	1.875	1.875
Cu2-X	1.914	2.238	1.991
		Bond Angles (°)	
N1-Cu1-N2	95.19	94.99	95.24
N1-Cu1-N3	96.61	96.46	95.55
N1-Cu1-N4	123.02	121.44	123.41
N2-Cu1-N3	91.78	91.57	92.41
N2-Cu1-N4	141.31	143.21	140.90
N3-Cu1-N4	89.77	89.36	89.69
N1-Cu1-N9	87.06	88.26	86.90
N2-Cu1-N9	88.58	89.05	90.98
N3-Cu1-N9	176.26	175.17	175.62
N4-Cu1-N9	87.62	87.28	85.93
N5-Cu2-N6	89.89	92.66	91.59
N5-Cu2-N7	95.54	100.48	99.61
N5-Cu2-N8	94.34	107.84	96.76
N6-Cu2-N7	125.44	163.48	124.05
N6-Cu2-N8	137.49	94.69	136.67
N7-Cu2-N8	96.25	90.79	96.37
N5-Cu2-X	171.97	106.89	177.32
N6-Cu2-X	83.42	83.73	86.63
N7-Cu2-X	84.82	82.90	83.21
N8-Cu2-X	93.59	145.25	83.05
		Dihedral Angle (°)	
Cu1-N9-N-X	-178.61	-178.86	176.71
N9-N-X-Cu2	2.08	-7.32	-3.79

The geometric parameters calculated at PM3 level of semi-empirical method are listed in Table1. The calculated results show that all the three complexes experienced greater distortion around the Cu^{2+} ion;

this brings about disparities in the value of similar bonds around the two Cu ions. For instance, Cu1-N1(Cu2-N5) are 1.924Å (1.903Å), 1.929Å (1.934Å) and 1.927Å (1.917Å) for bridged N_3, SCN and OCN complexes respectively. This is also reflected in the bond angles around metal ions. The bond angles N2-Cu1-N3 (N6-Cu2-N7) are 91.78 (125.44), 91.78 (163.48) and 92.41 (124.05) for N_3, SCN and OCN bridged complexes respectively. The torsion angles Cu1-N9-N-X (N9-N-X-Cu2) are -178.61 (2.08), -178.86 (-7.32) and 176.71 (-3.79) for N_3, SCN and OCN bridged complexes respectively. Therefore, the bridging ligands have profound effect on the geometries even when comparing the three complexes; hence this is reflected in the electronic properties and electronic interactions of the complexes.

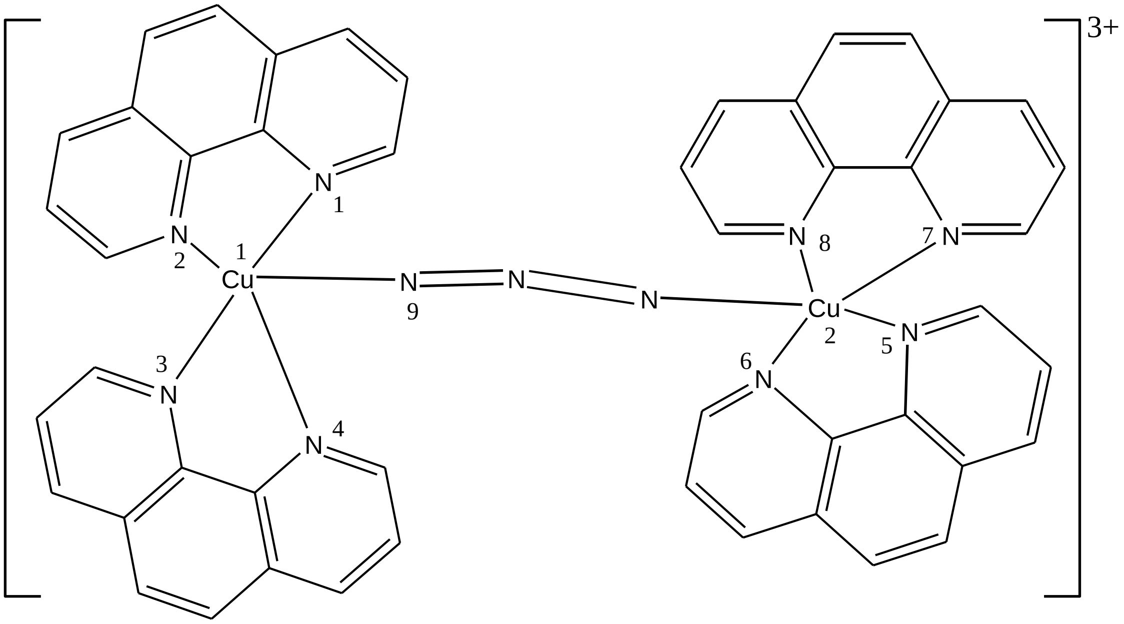

Figure 1: Schematic Structure of Complex (A) With Numbering of Atoms

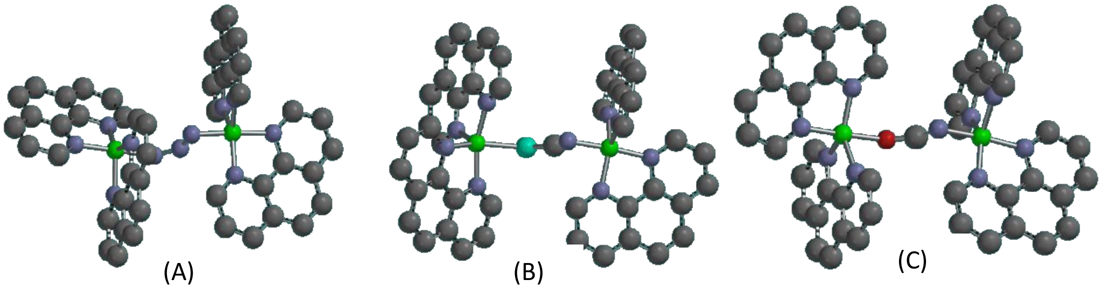

Figure 2: Optimized Structures of the Modeled Complexes of A, B and C

The frontier molecular orbitals were computed at the PM3 level of semi-empirical for three modeled complexes and are shown in Figure 3. The HOMO orbitals are mainly localized on one of the 1, 10-phenanthroline ligands on Cu1 side while LUMO is principally delocalized on bridging ligands (i.e. N_3, SCN and OCN). The HOMO-LUMO band gap of the complexes suggested that they may all have good stability and high chemical hardness (Table 2). According to molecular orbital theory, HOMO and LUMO are two important factors influencing the bioactivity; therefore π-π interactions among these molecular orbitals could play important roles in bioactivity of these complexes.The Mulliken atomic charges for Copper atoms, nitrogen atoms and bridging ligands are displayed in Table 2. All nitrogen atoms of 1,10-phenanthroline fragments on the complexes have positive values from 0.509 - 0.699 except

N9 part of bridging ligand that bonded to Cu1 atom; thus providing effective electrostatic interaction of these nitrogen atoms with copper atoms having negative charges of ≈ -0.850. Also, X carries negative charges (X = N and C) but positive when it is sulphur (Table 2). The charges on two copper atoms and that of bridging ligand atoms support the reduction in electrostatic repulsion in the complexes as earlier suggested. The dipole moments of the complexes are 1.455, 2.016 and 7.736 (Debye) for the complexes with N_3, SCN and OCN bridging ligands respectively. The high dipole moment observed in OCN bridging complex is due high electronegative value of oxygen atom.

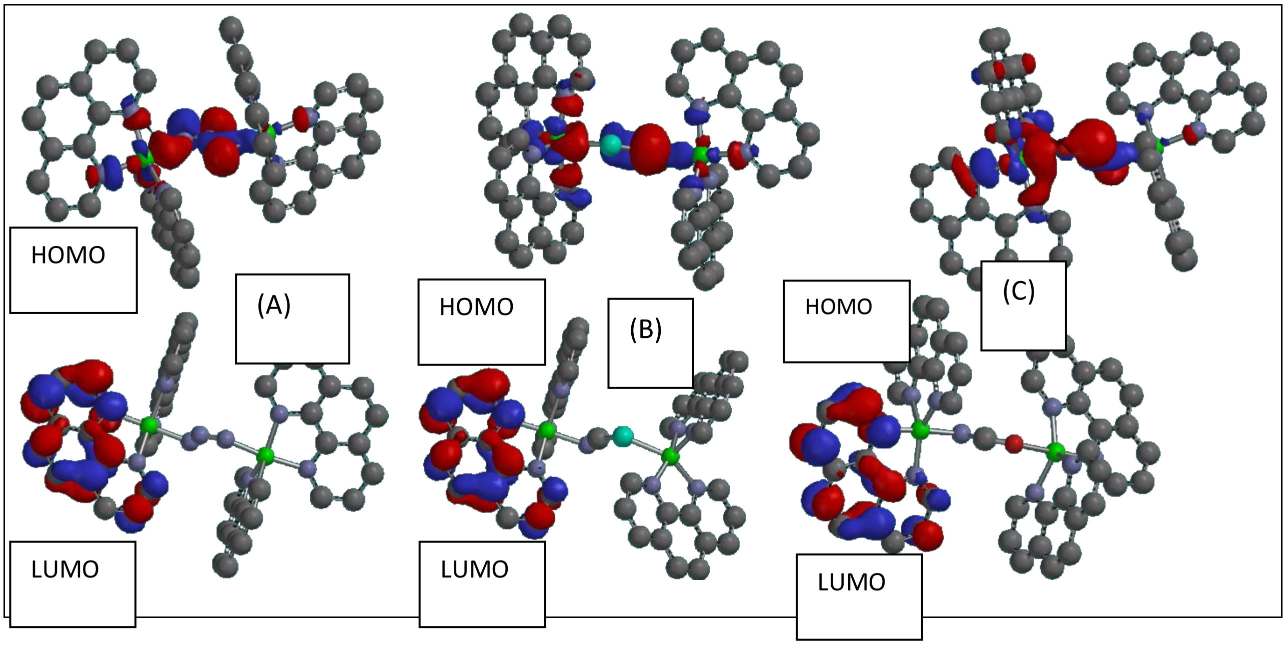

Figure 3: Frontier Molecular Orbitals: HOMO and LUMO of Complexes A, B and C

Table 2: HOMO (eV), LUMO (eV), Dipole Moment (Debye) and Mulliken Charges of Some Selected Atoms

	N_3	*SCN*	*OCN*
HOMO (H)	-14.660	-13.570	-14.479
LUMO (L)	-8.2879	-8.1881	-8.6276
Δ(H-L)	6.3721	5.3819	5.8514
D.M	1.4547	2.0163	7.7363
		Mulliken Charges	
Cu1	-0.808	-0.802	-0.846
Cu2	-0.841	-0893	-0.856
X	-0.215	0.100	-0.016
N1	0.559	0.528	0.543
N2	0.556	0.554	0.574
N3	0.590	0.597	0.625
N4	0.675	0.651	0.691
N5	0.585	0.509	0.533
N6	0.699	0.650	0.635
N7	0.547	0.653	0.545
N8	0.598	0.551	0.562
N9	-0.350	-0.009	-0.159

Conclusion

The dimeric copper (II) complexes of 1-10-phenanthrolines with N_3, SCN and OCN as bridging ligands were synthesized. The microanalysis revealed the formation of the dimeric compounds which is supported by the conjoint of infrared, UV-VIS spectra and theoretical studies of the complexes. The fragmentation patterns observed in these complexes were consistent with the formation of the dimers while the conductivity measurements confirm that the azide and cyanate complexes are 1:4 electrolytes. The calculated results show that all the three complexes experienced greater distortion around the Cu^{2+} ion.

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