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Synthesis, Characterization and Quantum Chemical studies of the mixed – ligand complex $[Cu(bipy)_2 S_8](ClO_4)_2$

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ABSTRACT

The mixed-ligand complex of $[Cu(bipy)_2S_8(ClO_4)_2$ was synthesized and characterized by employing elemental analyses, metal analyses, infrared and UV-Vis spectroscopy, room temperature magnetic susceptibility measurements, conductivity measurements and theoretical studies. The elemental and metal analyses show good agreement which support the formulation for the complex. The Cu-S band in the infrared spectrum at 465 cm $^{-1}$, indicate the formation of the complex. The UV-Vis spectra shows different intraligand transitions at 49,505 cm^{-1} , 33,445 cm^{-1}, 32,467 cm^{-1} and the bands at 13,661 cm^{-1} with a shoulder at 11,820 cm^{-1} in the visible region supported the CHN data for the formation of the five-coordinate complex. The magnetic moment value at 1.40 B.M indicates the presence of a strong antiferromagnetic properties of the complex. A 1:2 electrolyte nature of the complex was revealed in the conductivity value of 179 mho cm^2 mol^{-1}. The theoretical calculations predicted a distorted square pyramidal with S_8 in the apical position for the complex with Cu(II)-S bond distance calculated to be 2.874 Å and 2.199 Å for PM3 and DFT methods respectively. The low negative value of S.E (–1.58 kcal/mol) calculated for $[Cu(bipy)_2S_8\ ]^{2+}$ ion suggested that the complex is more likely to exist either in solution or as an amorphous compound.

Introduction

The chemistry of copper chalcogenide compounds is of interest in recent times due to their structural, synthetic and material chemistry [1]. Copper/inorganic-sulphur active-site entities in biological systems have been found in the metalloenzymes which include the Nitrous oxide reductase (N_2OR) which has an active-site $\{(histidine)_7Cu_4S\}$cluster and another in the active site of the aerobic organism carbon monoxide dehydrogenase with a molybdopterin and copper containing Mo-S-Cu^I-$S_{cysteine}$ moiety [1]. Sulfur, with an unusual molecular complexity is the element with the largest number of modifications [2,3]. These allotropes which are more than 20 in number usually exist as S_n ring molecules though not all have been structurally characterized [3,4]. The structurally established modifications are those with n = 6 – 14, 18 and 20 and thermodynamically, only D_{4d} S_8, D_{3d} S_{12} and S_6 in that order have stable ring even though only S_8 is the stable form of elemental sulfur at STP [2,4]. The stability of this form of sulfur may likely be as a result of the cross-ring resonance [2]. From the Literature, the coordination chemistry of sulfur compounds is undermined despite the fact the elemental sulfur has a structural chemistry that is well established. The complexes of the elemental sulfur reported include $[Ag(S_8)]^+$, $[Ag(S_8)]_2^+$, $[\{Rh_2(O_2CCF_3)_4\}_n(S_8)_m]$, $[Re(\mu\text{-}X)_2(CO)_6(S_8)]$ (X = Br, I) [5]. In addition, Cu^I complexes of S_{12} and S_8 have been investigated with the formation of complexes of the type $[Cu(S_{12})(S_8)]^+$, $Cu_2(S_8)_2A^2$ ($A = [Al\{OCH(CF_3)_2\}_4]^-$) [5]. Furthermore, the mixed ligand complex containing the $[Cu(phen)_2S_8]^{2+}$ ion was reported and characterized, the structure of the complex was a five-coordinate geometry [4]. Herein, we report the synthesis, characterization and theoretical studies of the mixed-ligand complexes of $Cu(bipy)_2(ClO_4)_2$ with elemental sulphur.

Experimental

Materials and method

Reagents

2,2'-bipyridine, copper perchlorate hexahydrate, powder elemental sulphur and other reagents were purchased from Aldrich Chemical Co., and were used without further purification. Bis-(2,2'-bipyridine) copper perchlorate, $Cu(bipy)_2(ClO_4)_2$ was synthesized according to the Literature [6].

Synthesis of $[Cu(bipy)_2S_8](ClO_4)_2$

$Cu(bipy)_2(ClO_4)_2$ (920 mg, 1.6 mmole) in a 250 mL beaker, to this 100mL of methanol was added to obtain a suspension which was stirred. Powder sulphur (410 mg, 1.6 mmole) was added and the mixture stirred for 24 hr. The turquoise blue compound obtained after the stirring was filtered by suction, washed with methanol and dried in the dessicator over $CaCl_2$. Every attempt to obtain the single crystals of the compound failed. Yield: 1200 mg (85%). Anal. Calcd for $[Cu(bipy)_2(S_8)](ClO_4)_2$ (%) C, 28.89; H, 1.94; N, 6.74; S, 30.82, Cu, 7.65. Found: C, 27.79; H, 1.80; N, 6.46; S, 31.35; Cu, 7.34. ATRIRν/cm^{-1}: 1068vs, 771s (ClO_4), 1640s, 1605sh, 1445m, 1317, 1251w, 621s, 465w (Cu–S). μ_{eff}: 1.40 B.M. (at 300 K). UV-Vis $(CH_3CN)\lambda_{max}$/cm^{-1}: 49,505, 33,445, 32,467,

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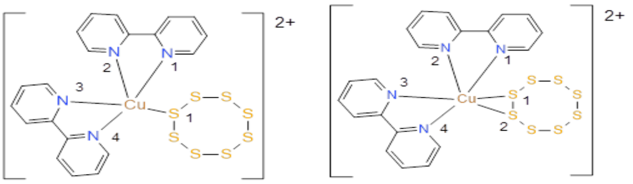
13,661, 11,820 sh. $\Lambda_M(CH_3CN)$: 179 mho cm^2 mol^{-1} (1:2 electrolyte).

Physical Measurements

CHN analyses were carried out by Atlantic Microlab, Atlanta GA. Electronic spectra were recorded on a Genesys 10 UV-Visible Spectrophotometer. Infrared spectra were recorded on a Perkin - Elmer PE 100 spectrometer with an Attenuated Total Reflectance (ATR) window. The room temperature magnetic susceptibility measurements were recorded using Sherwood Scientific magnetic susceptibility balance MSB MK1. The diamagnetic correction evaluated from Pascal's constant. Conductance measurements of *ca.* 10^{-3} M solutions of the complexes in CH_3CN were measured using a Jenway 4310 Conductivity meter. The percentage metal was determined by the employment of complexometric titration using EDTA [7].

Computational details

The $[Cu(bipy)_2S_8]^{2+}$ complex was modeled and optimized using Spartan program (Spartan 10) implemented on an Intel core i3-2350M computer. The complex was modeled based on the possibilities of coordination involving one atom of sulphur (**1**) and/or two atoms of sulphur (**2**) in ligand-metal bonds; hence the two possible complexes (Fig. 1) were modeled to determine their thermodynamic stabilities based on CHN analysis and metal analysis data coupled with the electronic spectra since there were no X-ray crystallographic data available. The two modeled complexes were optimized at both Semi-empirical (PM3) and Density Functional theory (DFT) level based on the preliminary conformational search on all the molecules with MMFF method with Monte Carlo search algorithm [8]. The frequency for the two complexes were performed at single point energy (SPE) calculations using Density Functional theory (DFT) level on the optimized structures. Density functional theory (DFT) calculations were performed with the hybrid B3LYP exchange and correlation functional [9,10] and 6-31G(d) basis set. All calculations were carried out without symmetry restriction.



(1) (2)

Fig.1. Schematic structures of the proposed $[Cu(bipy)_2S_8]^{2+}$ complex; (1) = one atom of sulphur involved in coordination and (2) = two atoms of sulphur involved in coordination

Results and Discussion

The mixed-ligand complex $[Cu(bipy)_2S_8]$ $(ClO_4)_2$ was obtained in a good yield of 85% and the CHN analysis and metal analysis data showed good agreement with the calculated values. The infrared spectra of the complex showed the perchlorate peaks at 1068 cm^{-1} and 771cm^{-1} [11], the Cu-N band at 621 cm^{-1} and the absorption band at 465 cm^{-1} was assigned to the ν Cu-S [12,13,14]. The two bands, 621 cm^{-1} and 465 cm^{-1} both support the coordination of the S_8 to the $Cu(bipy)_2(ClO_4)_2$ which is similar to the formation of $Cu(phen)_2S_8(ClO_4)_2$ as reported [4].

In the ultraviolet region of the electronic spectra, the bands at 49,505 cm^{-1}, 33,445 cm^{-1} and 32,467 cm^{-1} were assigned to intra-ligand transition in the 2,2'-bipyridine ligand [12,13,14]. The broad band with a peak at 13,661 cm^{-1} is attributed to the high –energy, high intensity $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$ and shoulder at 11,820 cm^{-1} is assignable to the low energy, low intensity $d_{z^2} \rightarrow d_{x^2-y^2}$ transition of a five -coordinate square pyramidal geometry [11,15]. The conductivity measurement of the complex reveal a 1:2 electrolyte nature of the complex [16, 17]. The low magnetic moment, 1.40 B.M. as compared to the spin –only moment of 1.73B.M. for a copper (II) observed in the complex is an indication of a strong antiferromagnetic interaction present in the complex [18].

Thermodynamic stability and orbital properties

The molecular parameters calculated for the modeled complexes are total energy, the HOMO energy, the LUMO energy, dipole moment, binding energy and stabilization energy as displayed in Table 1. In this work, emphasis was laid on the DFT results, since results from DFT calculations are superior to Semi-empirical [19,20]. Total energies in atomic unit (au), (heat of formation in kJ/mol) for complexes (**1**) and (**2**) are -5816.24 au (1085.74 kJ/mol) and -5816.19au (1148.76 kJ/mol) respectively, from these, it could be inferred that complex (**1**) is thermodynamically more stable by 30.11 kcal/mol and 15.06 kcal/mol for DFT and PM3 respectively than complex (**2**). To further probe the stability as well as evaluate the formation of the complexes (**1**) and (**2**) respectively, the binding energy (B.E) in terms of energy required to bind S_8 molecule to the $[Cu(Bipy)_2]^{2+}$ complex ion and stabilization energy (S.E) from the energy involved in the dissociation processes were determined as shown in the equations (1) and (2) [21,22]:

Binding energy (B.E) $= E[CuX_2L]^{2+} - E[CuX_2]^{2+} - E\ L$ --- (1)

Stabilization energy (S.E) =

$E[CuX_2L]^{2+} - E(Cu^{2+} + 2X + L)$ ---------------------- (2)

where X = 2,2'-bipyridine and L = S_8 molecule and E = energy of each species.

The calculations of the binding energies as well the stabilization energies for the two complex ions were calculated in the ground states. The S.E for complexes (**1**) and (**2**) are -434.21 kcal/mol and -404.24 kcal/mol, whereas the B.E are – 1.58 kcal/mol and +28.53 kcal/mol respectively. The results of the thermodynamic stability and binding energies (B.E) suggested that complex (**1**) is more probable/favorable to exist compared to (**2**). In the same token, the positive value of S.E for complex (**2**) further suggested that interactions between $[CuX_2]^{2+}$ and two S atoms from S_8 are not favorable. The low negative value of S.E (–1.58 kcal/mol) for complex (**1**) indicated that it is more likely to exist either in solution or as an amorphous compound. This corroborated the inability of the complex to form single crystals suitable for X-ray diffraction experiments.

The HOMO, LUMO and HOMO-LUMO band gap energies calculated at DFT (PM3) are -11.73 eV (-13.41 eV), -8.43 eV (-7.68 eV) and 3.30 eV (5.73 eV) for complex (**1**); -11.45 eV (-13.43 eV), -9.65 eV (-7.66 eV) and 1.51 eV (5.77 eV) for complex (**2**). Thermodynamic stability has been found to be related to the HOMO-LUMO energy band gap (ΔEg) of a compound, the lower ΔEg indicates lower thermodynamic stability of the compound. This is also in agreement with the calculated stabilization energy and further supported the synthesis of complex (**1**) (Table 1). The HOMOs revealed that the π-electrons of the system dwell mainly on one unit of sulphur molecule for both complexes (**1**) and (**2**). The LUMO of the complex (**1**) is spread over the two 2,2'-bipyridines while that of complex (**2**) is located partially on sulphur molecule (S_8) and copper ion (Figure 3).

Table 1. Molecular parameters calculated for the complexes at both PM3 and DFT levels.

	Complex (1)		*Complex (2)*	
Parameters	**DFT**	**PM3**	**DFT**	**PM3**
Total Energy (au)	-5816.23771	-	-5816.18974	-
Heat of Formation (kJ/mol)	-	1085.74	-	1148.76
Rel.Energy (kcal/mol)	-	-	30.11	15.06
HOMO (eV)	-11.73	-13.41	-11.16	-13.43
LUMO (eV)	-8.43	-7.68	-9.65	-7.66
Band gap (eV)	3.30	5.73	1.51	5.77
Dipole Moment (Debye)	17.30	6.64	12.71	1.98
B.E (kcal/mol)	-1.58	-	+28.53	-
S.E (kcal/mol)	-434.21	-	-404.24	-
Mullikan charge (e)	-0.671		-0.661	
N1	-0.666		-0.629	
N2	-0.671		-0.658	
N3	-0.666		-0.601	
N4	-0.095		-0.203	
S1	-		0.064	
S2	1.431		1.398	
Cu1				

The dipole moment (D.M) is also an important parameter to be considered in solute-solvent interactions, therefore D.M calculated showed that complex (**1**) should be expected to have more complex-solvent interactions, thus more solvated in aqueous medium than complex (**2**). The average electronic charge on nitrogen atoms involved in the coordination and Cu(II) showed the transfer of charges (electrons) form nitrogen atoms to the Cu(II) ion. The electronic charges on nitrogen atom, sulphur atom, and Cu (II) ion are -0.669 *e*, -0.095 *e* and 1.431 *e* for complex (**1**); and -0.637 *e*, -0.203 *e* and 1.398 *e* for compound (**2**). The vibrational frequencies calculated at DFT level for the Cu-N band were at 295 cm^{-1}, 336 cm^{-1}, 376 cm^{-1} and 661 cm^{-1} for complex (**1**); and 317 cm^{-1}, 650 cm^{-1} and 679 cm^{-1} for complex (**2**). The absorption band ν Cu-S were 100 cm^{-1} and 427 cm^{-1} for complex (**1**) whereas for complex (**2**), they were calculated at 104 cm^{-1}, 184 cm^{-1} and 432 cm^{-1}. Therefore, vibrational frequencies calculated at 661 cm^{-1} and 650 cm^{-1} compares fairly well with the experimentally observed value 621 cm^{-1} for the ν Cu-N band. Likewise, the ν Cu-S absorption band calculated at 427 $cm^{-1}$and 432 cm^{-1} corresponded to 465 cm^{-1} in the experimental value. In addition, ν S-S band were theoretically observed at 243 cm^{-1} and 285 cm^{-1} for complexes (**1**) and (**2**) respectively.

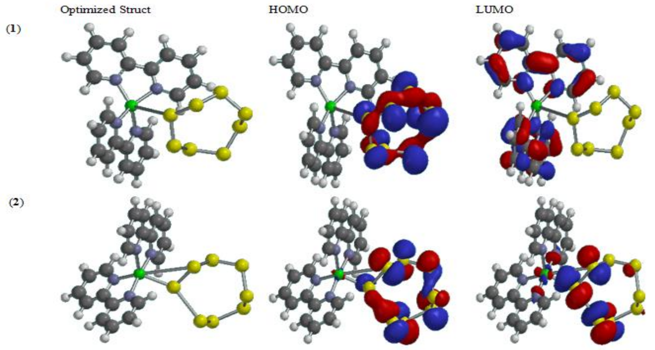


Fig 3. The optimized structures, HOMO and LUMO overlays of the complexes (1) and (2) at DFT level.

Geometries of the Cu(II) complex (1)

In the absence of available X-ray crystallographic data, the use of quantum chemical methods in determining the equilibrium geometries of complexes becomes a veritable tools, although the accuracy is dependent of the computational methods used. Semi-empirical (PM3) and DFT methods have been found to predict geometries of the metal-complex with reasonable accuracy [23-28]. The experimental and theoretical observations as discussed earlier have established the synthesis of complex (**1**), therefore some selected equilibrium geometries for the complex (**1**) calculated at PM3 and B3LYP/6-31G* levels were displayed in Table 3. The structure of complex (**1**) predicted by both PM3 and DFT was a distorted square pyramidal with S_8 ligand in the apical position; such geometry has been predicted for similar complex, $[Cu(phen)_2S_8]^{2+}$ [4]. The average Cu-N bond distance calculated at PM3 and DFT was 1.978 Å and 1.902Å for the complex (**1**) respectively. Also, the Cu(II)-S bond distance calculated at PM3 and DFT was 2.874 Å and 2.199 Å respectively for the complex. The Cu(II)-S bond distance calculated at B3LYP/6-31G(d,p) level was comparable to the Cu-S bond distance (2.86Å) obtained at higher DFT level (Mo62X/6-311G(2d,p)) of calculations [4]. Although, this was shorter than Cu(II)-S bonds observed for oxidized plastocyanins [29,30]. This indicates that the geometry predicted at B3LYP/6-31G(d,p) for the complex (**1**) ion is reasonable. The Cu-N and Cu-S bond distances calculated at DFT/6-31G* were longer than that of semi-empirical method, however it has been reported that geometrical parameters from DFT calculations for transition metal complexes are more accurate than that of PM3 method [46].

The bite angles N1-Cu-N2 (N1-Cu-N4) and N2-Cu-N3 (N2-Cu-N4) calculated to be 83.05° (151.95°) and 146.457° (105.27°) at DFT level respectively. These angles were predicted to be 88.42° (174.12°) and 115.70° (94.80°) at PM3 respectively. The N1-Cu-S (N2-Cu-S) and N3-Cu-S (N4-Cu-S) bite angles were calculated to be 70.68° (99.20°) and 114.25° (81.48°) respectively at DFT. The PM3 calculation showed these angles at 122.22° (90.65°) and 121.63° (83.47°) respectively.

Table 2. Selected bond distances (Å) and bond angles (º) for the complex (1).

Geometry	DFT	PM3
Cu – N1	1.974	1.877
Cu – N2	1.981	1.925
Cu – N3	1.983	1.881
Cu – N4	1.973	1.925
Cu – S	2.872	2.199
N1, Cu, N2	83.05	88.42
N1, Cu, N3	104.92	94.88
N1,Cu, N4	151.95	174.12
N2, Cu, N3	146.45	115.70
N2, Cu, N4	105.27	94.80
N3, Cu, N4	83.09	88.17
N1 ,Cu, S	70.68	122.52
N2, Cu, S	99.20	90.65
N3 ,Cu, S	114.25	121.63
N4, Cu, S	81.48	83.47

Conclusion

The synthesis of $[Cu(bipy)_2 S_8](ClO_4)_2$ was successfully synthesized and characterized. The CHN and metal analysis supported the formulation of the complex. The quantum chemical calculations revealed that the complex was a distorted square pyramidal with S_8 in the apical position as predicted by both PM3 and DFT.

The electronic transitions in the complex corroborated the geometry prediction by the theoretical calculations with the employment of both PM3 and DFT. The calculated thermodynamic stability and binding stabilization energy also affirmed the formation of the complex.

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