



Synthesis, structural characterization and DFT studies of copper(II) complexes with tridentate Schiff bases

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Abstract

Two new synthesized Schiff bases (L_4 and L_5) were derived from the condensation reaction of 2-(methylthiomethyl)anilines and 4-methoxysalicylaldehyde. The complexes of these and four previously reported NOS Schiff bases, $Cu(L_1)_2$ – $Cu(L_6)_2$, were synthesized via the reflux reaction of the various Schiff base ligands with $CuCl_2 \cdot 2H_2O$. The compounds were characterized by means of elemental analysis, FTIR and UV-Vis. The crystal structures of $Cu(L_1)_2$ and $Cu(L_2)_2$ were obtained by X-ray diffraction. The Schiff bases were coordinated to copper ion as monobasic tridentate ligands through the phenolic oxygen, azomethine nitrogen and thioether sulfur. The microanalyses of the coordination complexes were agreeable with bimolar binding of the ligands to the copper metal ion. The crystal structures of the copper complexes confirmed an octahedral geometry around the metal centre and showed they are mononuclear. The magnetic moment values indicated the presence of a lone electron in each copper(II) orbital and confirmed the mononuclearity of the complexes. The electronic spectra of the coordination compounds consist of the intraligand, charge transfer and $d \rightarrow d$ bands. Molecular modeling studies on the complexes ($Cu(L_1)_2$ – $Cu(L_6)_2$) by employing DFT revealed that complex $Cu(L_5)_2$ possessed the smallest optimization energy as well as a small HOMO–LUMO energy gap which may best explain its higher polarizability as well as reactivity in comparison to the other complexes.

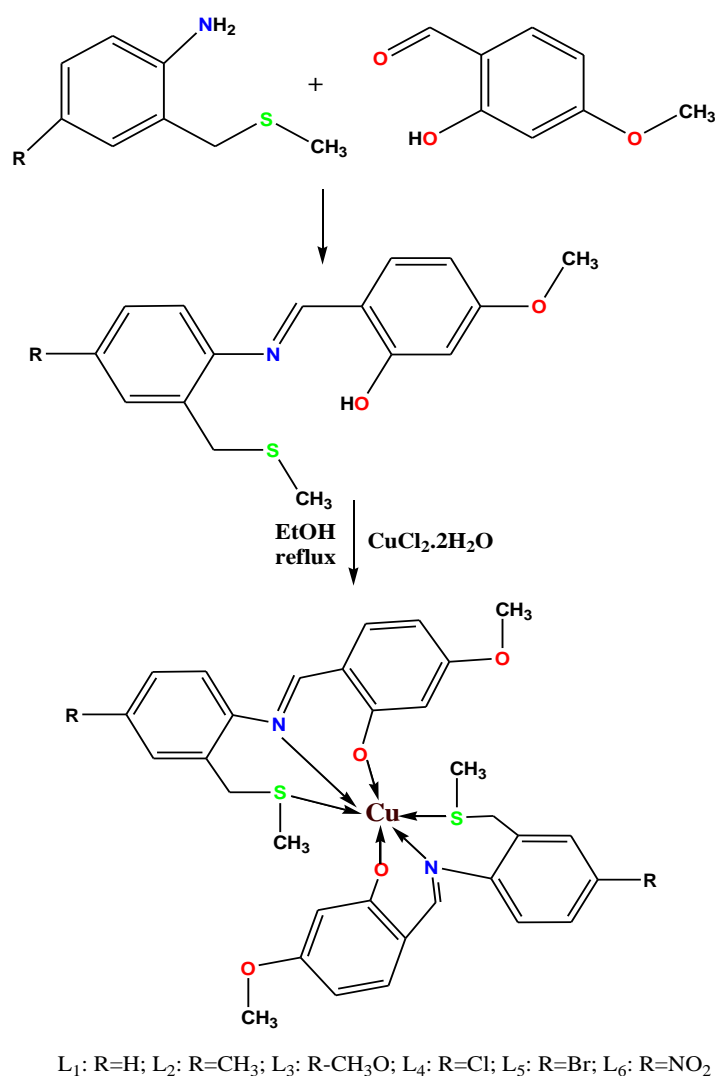
Keywords: NOS Schiff bases, copper(II) complexes, crystal structures, DFT calculations

1. Introduction

Coordination complexes of Schiff bases with various metal ions have been progressively studied for their simple synthesis, crystallographic features, structure-redox relationships, biological activity, fluorescent, enzymatic reactions and catalysis properties [1-9]. Salicylaldehyde Schiff bases have aroused many investigators' interests due to their readiness to chelate as bidentate ligands, through the nitrogen and oxygen atoms, with various transition metal ions [10-12]. Some Schiff bases metal complexes with polymeric structures have demonstrated biological activity [13]. Tridentate Schiff bases with nitrogen, oxygen and sulfur (NOS) donor atoms have shown good coordination with various metal ions, rendering tremendous attraction [14,15]. The borderline nitrogen, hard oxygen and soft sulfur donor atoms present in these ligands enhance their ease of

coordination with many transition metal ions to yield stable complexes. Some Schiff base coordination complexes have exhibited interesting properties and potentials as anti-leukemia agents and membrane sensors [16,17].

Investigations of the properties of coordination compounds of tridentate Schiff bases derived from 2-(methylthiomethyl)anilines are not yet reported. Little is known of the spectroscopic properties as well as the theoretical studies of their copper complexes. As an extension of our investigation on the Schiff bases derived from 2-(methylthiomethyl)anilines and 4-methoxysalicylaldehyde [18], we hereby report the synthesis, spectroscopic and theoretical studies of copper(II) complexes of these NOS donor Schiff bases, $\text{Cu}(\text{L}_1)_2$ – $\text{Cu}(\text{L}_6)_2$, Scheme 1. The single crystal structures of the two complexes $\text{Cu}(\text{L}_1)_2$ and $\text{Cu}(\text{L}_2)_2$ obtained were further explored in order to give more insight to the bonding nature in the coordination complexes.



Scheme1 Synthesis of the ligands and copper(II) complexes

2. Experimental

2.1 Materials and methods

All chemicals of reagent grade were commercially available and used without further purification. Elemental analyses (CHNS) were carried out on an Elementar Analysensysteme varioMICRO V1.6.2 GmbH.

^1H , ^{13}C and DEPT135 NMR spectra were obtained in CDCl_3 solvent using TMS as internal standard on Bruker Avance 400 MHz NMR spectrometer. The infrared spectra of the solid samples were determined on PerkinElmer Spectrum 100 ATR-FTIR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$. In the far infrared region $700\text{--}30\text{ cm}^{-1}$, the spectra were obtained from sample mulls held between polyethylene discs on Perkin Elmer Spectrum 400 FTIR/FIR spectrometer. The magnetic susceptibility of the copper compounds was obtained on Sherwood magnetic susceptibility balance and diamagnetic corrections were calculated from Pascal's constants. The electronic spectra of the Schiff bases (250–600 nm) and their coordination compounds (300–900 nm) were obtained in dichloromethane solution on PerkinElmer Lambda 25 UV/VIS Spectrometer. The uncorrected melting points were measured using Gallenkamp melting point apparatus.

The crystallography data for $\text{Cu}(\text{L}_1)_2$ and $\text{Cu}(\text{L}_2)_2$ were collected at 200K on a Bruker KAPPA APEX II diffractometer (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$). The crystals were grown by slow evaporation from chloroform/ethanol mixture and crystallized out in the triclinic P_1 space group. Intensity data were collected on a Bruker APEX II CCD diffractometer with graphite monochromatic Mo $\text{K}\alpha$ radiation using the APEX 2 data collection software [Bruker, 2009]. The structure was solved by direct methods applying SHELXS-2013 and refined by least-squares procedures using SHELXL-2013 [20]. The crystal structure diagrams were drawn with ORTEP-3 for windows [21].

2.2 DFT studies

Density functional theory (DFT) for molecular modeling was employed to understand the electronic properties of the coordination compounds ($\text{Cu}(\text{L}_1)_2$, $\text{Cu}(\text{L}_2)_2$, $\text{Cu}(\text{L}_3)_2$, $\text{Cu}(\text{L}_4)_2$, $\text{Cu}(\text{L}_5)_2$ and $\text{Cu}(\text{L}_6)_2$). B3LYP functional was employed with a 6-311G(d) basis set (calculated at 298K). Full geometry optimizations and vibrational analyses of the coordination compounds were performed using the Gaussian09 software [19]. The orbital energies, orbital energy gap, dipole interaction and partial charge transfer in the compounds were calculated from the optimized structures.

2.3 Synthesis of Schiff bases L_4 and L_5 and coordination compounds $\text{Cu}(\text{L}_1)_2\text{--Cu}(\text{L}_6)_2$

2.3.1 Schiff base L_4

2-[(1Z)-({4-chloro-2-[(methylsulfanyl)methyl]phenyl}imino)methyl]-5 methoxyphenol (L_4) was prepared according to the described procedure [18]. 4-Chloro-2-(methylthiomethyl)aniline (44.5 mg, 0.24 mmol) and 2-hydroxy-4-methoxybenzaldehyde (36.1 mg, 0.24 mmol) were dissolved in a 3:1 mixture of EtOH/DCM (4 mL) and heated to reflux at 50°C for 6 h. The reaction mixture was cooled to room temperature and the solvent was reduced under vacuum, the resulting precipitate was filtered, washed with cold ethanol and air-dried. In order to remove traces of reactants, the solid product was purified by column chromatography on silica gel 60 (0.040–0.063 mm) using hexane/ether (6:1) as eluent; a yellow compound was obtained in 55% yield. Mp $72\text{--}73^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.07$ (s, 3 H, CH_3), 3.75 (s, 2 H, CH_2S), 3.85 (s, 3 H, CH_3OAr), 6.51–7.33 (aromatic protons), 8.46 [s, 1 H, (azomethine $\text{CH}=\text{N}$)], 13.33 (s, 1H, ArOH) ppm.

^{13}C NMR (400 MHz, CDCl_3): $\delta = 15.91$ (SCH_3), 35.23 (CH_2S), 55.89 (OCH_3), 101.07 – 163.79 (aromatic carbons), 162.30 ($\text{CH}=\text{N}$), 163.57 ($\text{C}-\text{OH}$) ppm. IR, ν_{max} (cm^{-1}): 1605, 1591, 1580, 1511, 1441, 1340, 1291, 731; UV, nm (E , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 255 (2500), 304 (11430), 346 (27860). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{ClNO}_2\text{S}$ (321.82): C 59.71, H 5.01, N 4.35, S 9.96; found C 59.72, H 5.18, N 4.35, S 9.63.

2.3.2 Schiff base L_5

2-[(1Z)-[4-bromo-2-[(methylsulfanyl)methyl]phenyl]imino)methyl]-5-methoxyphenol (L_5) was prepared as described for L_4 . 4-Bromo-2-(methylthiomethyl)aniline (118.0 mg, 0.51 mmol) and 2-hydroxy-4-methoxybenzaldehyde (77.3 mg, 0.51 mmol) were used to obtain the yellow L_5 with a yield of 74%. Mp 74–75°C. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.05$ (s, 3 H, CH_3), 3.73 (s, 2 H, CH_2S), 3.83 (s, 3 H, CH_3OAr), 6.49 – 7.46 (aromatic protons), 8.44 [s, 1 H, (azomethine $\text{CH}=\text{N}$)], 13.35 (s, 1 H, ArOH) ppm. ^{13}C NMR (400 MHz, CDCl_3): $\delta = 15.45$ (SCH_3), 34.34 (CH_2S), 55.49 (OCH_3), 101.08 – 163.57 (aromatic carbons), 162.22 ($\text{CH}=\text{N}$), 163.45 ($\text{C}-\text{OH}$) ppm. IR, ν_{max} (cm^{-1}): 1605, 1591, 1580, 1511, 1441, 1340, 1291, 731; UV, nm (E , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 255 (2150), 305 (10140), 347 (24170). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{BrNO}_2\text{S}$ (366.273): C 52.47, H 4.40, N 3.82, S 8.75; found C 52.43, H 4.38, N 3.85, S 8.89.

2.3.3 Synthesis of $\text{Cu}(L_1)_2$

To a solution of Schiff base (60.00 mg, 0.21 mmol) dissolved in equimolar volume of dichloromethane and ethanol (5 mL), 4 drops of triethylamine were added to maintain a basic medium and facilitate proton abstraction for converting the Schiff base to anionic form. The solution was further stirred for 15 min while maintaining the temperature at 30°C. On the addition of ethanol solution $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.80 mg, 0.1 mmol), a grey precipitate was formed and the mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and filtered to collect the solid product. The product was washed with ethanol and air-dried. Single crystals suitable for X-ray diffraction were grown from dichloromethane and ethanol mixture and after a few days, dark grey crystals of $\text{Cu}(L_1)_2$ were seen (71.20 mg, 90%); Mp 178–179°C; IR ν_{max} (cm^{-1}): 1607 $\nu(\text{C}=\text{N})$; 1595, 1581, 1521, 1446 $\nu(\text{C}=\text{C})$; 1310 $\nu(\text{C}-\text{O})$; 1232 $\nu(\text{C}-\text{N})$; 732 $\nu(\text{C}-\text{S}-\text{C})$; 556 $\nu(\text{Cu}-\text{O})$; 452 $\nu(\text{Cu}-\text{N})$; 348 $\nu(\text{Cu}-\text{S})$. UV-Visible spectra (nm): 268, 308, 365, 396, 613(br); Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2\text{Cu}$ (636.28): C, 60.40; H, 5.07; N, 4.40; S, 10.08. Found: C, 59.74; H, 5.25; N, 4.35; S, 9.88.

The other compounds, $\text{Cu}(L_2)_2$ – $\text{Cu}(L_6)_2$, were similarly prepared.

2.3.4 Synthesis of $\text{Cu}(L_2)_2$

L_2 (61.60 mg, 0.21 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.40 mg, 0.1 mmol) were reacted. Single crystals suitable for X-ray diffraction were grown from dichloromethane and ethanol mixture and after a few days, the grey crystals of $\text{Cu}(L_2)_2$ appeared (57.00 mg, 84%); Mp 180–181°C; IR ν_{max} (cm^{-1}): 1615 $\nu(\text{C}=\text{N})$; 1606, 1590, 1564, 1513, 1440 $\nu(\text{C}=\text{C})$; 1318 $\nu(\text{C}-\text{O})$; 1234 $\nu(\text{C}-\text{N})$; 732 $\nu(\text{C}-\text{S}-\text{C})$; 548 $\nu(\text{Cu}-\text{O})$; 449 $\nu(\text{Cu}-\text{N})$; 340 $\nu(\text{Cu}-\text{S})$. UV Visible spectra (nm): 268, 308, 365, 398, 616(br); Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_4\text{S}_2\text{Cu}$ (664.34): C, 61.47; H, 5.46; N, 4.22; S, 9.65. Found: C, 61.16; H, 5.67; N, 4.10; S, 9.67.

2.3.5 Synthesis of $Cu(L_3)_2$

L_3 (45.20 mg, 0.14 mmol) and $CuCl_2 \cdot 2H_2O$ (12.10 mg, 0.07 mmol) were used. The product was brown powder (33.80 mg, 68%); Mp 154-155°C; IR ν_{max} (cm^{-1}): 1612 $\nu(C=N)$; 1598, 1579, 1517, 1447 $\nu(C=C)$; 1312 $\nu(C-O)$; 1233 $\nu(C-N)$; 734 $\nu(C-S-C)$; 546 $\nu(Cu-O)$; 449 $\nu(Cu-N)$; 340 $\nu(Cu-S)$. UV-Visible spectra (nm): 268, 311, 364, 399, 620(br); Anal. Calcd for $C_{34}H_{36}N_2O_6S_2Cu$ (696.34): C, 58.64; H, 5.21; N, 4.02; S, 9.21. Found: C, 57.81; H, 5.14; N, 3.96; S, 9.35.

2.3.6 Synthesis of $Cu(L_4)_2$

L_4 (22.60 mg, 0.07 mmol) and $CuCl_2 \cdot 2H_2O$ (6.00 mg, 0.03 mmol) were reacted. The product was grey powder (18.50 mg, 75%); Mp 186-187°C; IR ν_{max} (cm^{-1}): 1607 $\nu(C=N)$; 1595, 1584, 1518, 1439 $\nu(C=C)$; 1316 $\nu(C-O)$; 1238 $\nu(C-N)$; 733 $\nu(C-S-C)$; 554 $\nu(Cu-O)$; 437 $\nu(Cu-N)$; 338 $\nu(Cu-S)$. UV-Visible spectra (nm): 267, 308, 366, 398, 603(br); Anal. Calcd for $C_{32}H_{30}Cl_2N_2O_4S_2Cu$ (705.17): C, 54.50; H, 4.29; N, 3.97; S, 9.09. Found: C, 53.58; H, 3.56; N, 3.99; S, 9.08.

2.3.7 Synthesis of $Cu(L_5)_2$

L_5 (49.30 mg, 0.14 mmol) and $CuCl_2 \cdot 2H_2O$ (10.90 mg, 0.07 mmol) were reacted. The product was grey powder (44.40 mg, 87%); Mp 184-185°C; IR ν_{max} (cm^{-1}): 1604 $\nu(C=N)$; 1595, 1578, 1519, 1438 $\nu(C=C)$; 1315 $\nu(C-O)$; 1237 $\nu(C-N)$; 734 $\nu(C-S-C)$; 544 $\nu(Cu-O)$; 458 $\nu(Cu-N)$; 350 $\nu(Cu-S)$. UV-Visible spectra (nm): 265, 313, 358, 398, 594(br); Anal. Calcd for $C_{32}H_{30}Br_2N_2O_4S_2Cu$ (794.08): C, 48.40; H, 3.81; N, 3.53; S, 8.08. Found: C, 48.19; H, 3.85; N, 3.49; S, 7.94.

2.3.8 Synthesis of $Cu(L_6)_2$

L_6 (21.50 mg, 0.07 mmol) and $CuCl_2 \cdot 2H_2O$ (5.50 mg, 0.03 mmol). The product was green powder (18.00 mg, 77%); Mp 210-211°C; IR ν_{max} (cm^{-1}): 1611 $\nu(C=N)$; 1602, 1579, 1512, 1442 $\nu(C=C)$; 1314 $\nu(C-O)$; 1240 $\nu(C-N)$; 737 $\nu(C-S-C)$; 550 $\nu(Cu-O)$; 446 $\nu(Cu-N)$; 344 $\nu(Cu-S)$. UV-Visible spectra (nm): 265, 310, 377, 403, 585; Anal. Calcd for $C_{32}H_{30}N_4O_8S_2Cu$ (726.28): C, 52.92; H, 4.16; N, 7.71; S, 8.83. Found: C, 53.05; H, 4.60; N, 7.72; S, 8.46.

3. Results and discussion

The preparation and characterization of the Schiff bases L_1 , L_2 , L_3 and L_6 were previously reported [18]. Ligands L_4 and L_5 were prepared using similar procedure (Scheme 1). They are soluble in common organic solvents such as acetone, chloroform, dichloromethane, DMSO, DMF but insoluble in water, methanol or ethanol. The copper(II) complexes were derived when the reaction medium was made alkaline (pH 9) by the addition of a few drops of triethylamine. The microanalysis data of their CHNS content, which were in excellent agreement with the predicted values, indicated 2:1 ligand to metal combination in the compounds. The electrolytic nature of the metal compounds was not determined due to their solubility in only common organic solvents such as dichloromethane, chloroform and acetone.

3.1 NMR data for Schiff bases L_4 and L_5

The Supplementary material contains the ^1H and ^{13}C NMR spectra for the ligands. The proton NMR data for Schiff bases L_4 and L_5 showed the peaks due to the methyl, methylene and methoxy protons at high field region, all appearing as singlets at 2.05–3.85 ppm. The multiple peaks for the aromatic protons were seen in the range 6.49–7.46 ppm and the singlet peaks of the azomethine and phenolic protons appeared at 8.44–8.46 ppm and 13.33–13.35 ppm respectively. The resonance signals for the ^{13}C NMR of the Schiff bases consisted of the peaks of the saturated carbon atoms in the high field region around 15.45–55.89 ppm. Those of the aromatic rings absorbed between 101.07 and 163.79 ppm and the peaks at 162.22–162.30 ppm were assigned to the imine carbon atoms.

3.2 Crystallographic data for $\text{Cu}(L_1)_2$ and $\text{Cu}(L_1)_2$

The crystallographic data with the inter-atomic distances, bond angles and dihedrals are provided in the Supplementary material (Tables 1 and 2). Two molecules of the tridentate ligand are coordinated to the copper(II) through their nitrogen, sulfur and oxygen donors (Fig. 1). The deprotonated phenolic oxygen presented each Schiff base as anionic ligand and upon chelation to the copper(II), resulted to neutral copper compounds. The basal plane of the crystal structures contains the nitrogen and oxygen donors bonded to the central copper ion trans-wise.

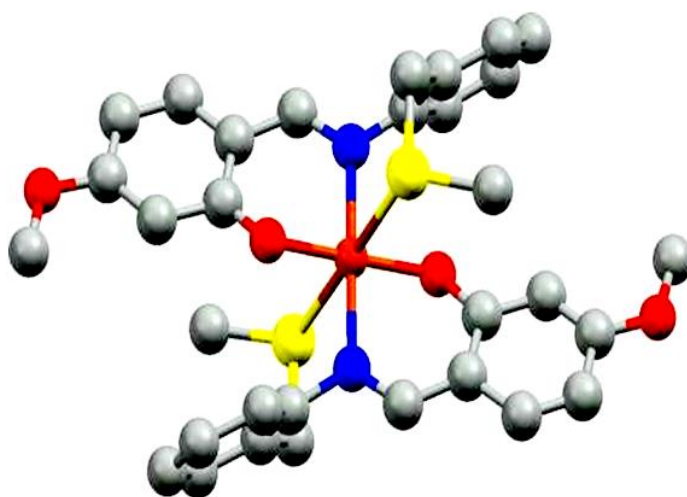


Fig. 1 Crystal structure of complex 1.

The distances of Cu–O in $\text{Cu}(L_1)_2$ and $\text{Cu}(L_2)_2$ are shorter at 1.892–1.941 Å than those of Cu–N at 1.975–2.002 Å. The smaller Cu–O lengths is probably due to the contribution of the more electronegative oxide ion to the bond. The sulfur atoms are axially connected to the central metal, giving rise to an octahedral arrangement around the metal ion. The two Cu–S distances in $\text{Cu}(L_1)_2$ (2.956 Å, 2.960 Å) and $\text{Cu}(L_2)_2$ (2.973 Å, 2.793 Å) are equal, though longer than axial Cu–S distances reported in other Schiff base metal complexes [22,23]. Longer bond distances usually observed in Cu–L, (where L is Cl^- , Br^- , I^- or S) arise as a result of the large size of the donor atom and may not imply weaker binding [24]. The bond distances between the phenolic oxygen and the aromatic carbons (C102–O101, C202–O201) between 1.288 and 1.310 Å showed marked

decrease from the C–O distances in the Schiff bases (1.348–1.353 Å), due to coordination through the oxygen [18]. The distances of the azomethine C=N (1.275–1.322 Å), C–N (1.362–1.475 Å) and C–S (1.774–1.859 Å) are indicative of conjugation with the aromatic rings as well as the involvement of nitrogen and sulfur atoms in metal chelation [18]. The phenyl C=C distances, 1.320–1.472 Å, are within the expected range for carbon atoms in resonance. The covalent C–O distances in the structures are shorter (1.348–1.453 Å) than those of Cu–O (1.892–1.941 Å) probably as a result of the covalent nature of the bonding in the former case (Fig. 2).

The in-plane angles (O101–Cu1–N201, O201–Cu1–N201, O101–Cu1–N101, O201–Cu1–N101, N201–Cu1–N101) around the copper centers in Cu(L₁)₂ and Cu(L₂)₂ are close to 90° and 180° as expected in metal centers with octahedral geometries. It could be noted the greatest deviation from linearity was seen in O101–Cu1–O201 for Cu(L₂)₂ at 177.5°. The bond angles around the copper(II) and involving sulfur atoms also showed deviations from orthogonality and linearity, being in the range 82.0–97.5° and 177.7°. The coordination sphere around the copper(II) centers could be better described as tetragonally distorted octahedral. The aromatic planar angles between 115.9° and 124.8° are as usually observed in sp²-hybridized atoms. The arrangement around the nitrogen atoms is planar as the lone electrons pairs were coordinated to the copper ion, the bond angles are in the range 115.8–123.6°. The angles of the phenolic oxygen and the methoxy oxygen are closer to 120° than 105°, as would have been expected for sp³-hybridized atoms with two lone pairs. This could be due to their nearly planar configuration as they are bonded with neighbouring copper ion and carbon atoms, in conjugation with the aromatic pi system. The linkage of the sulfur atom to the copper ion and the methylene carbon, in C115–S101–Cu1 and C215–S201–Cu1, is almost orthogonal (92.8–94.3°) while the bonding of the sulfur atom to the copper ion and the methyl carbon is nearly planar (118.2–119.7°). The thioether sulfur angle is around 100.0° in both compounds.

The dihedral angles (C101–C108–N101–C109, C201–C208–N201–C209) connecting the two adjacent benzene rings of the ligand molecules are 171.9° and 173.5° (Cu(L₁)₂) and 168.6° and 174.1° (Cu(L₂)₂). This showed the two rings are aligned parallel to each other in the structures.

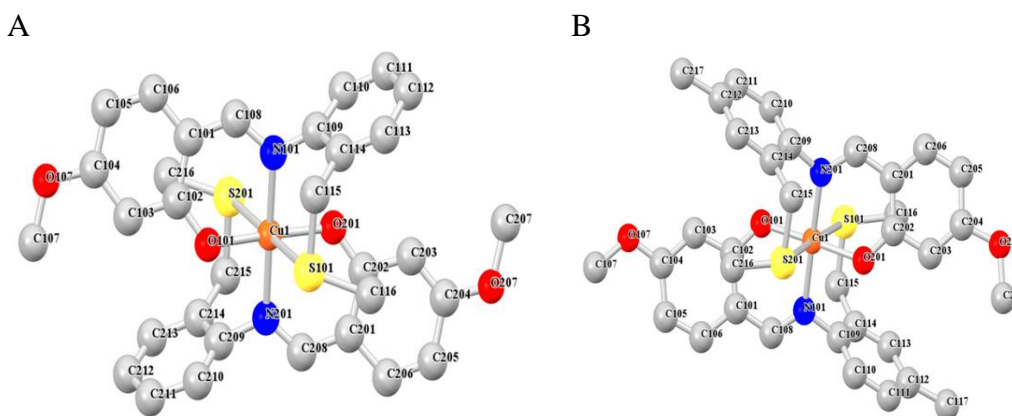


Fig. 2 Atom labelling for (CuL₁)₂ (A) and (CuL₂)₂ (B). Hydrogen atoms are omitted for clarity

3.3 Infra red spectra

The intense bands due to the carbonyl $\nu\text{C}=\text{O}$ ($1670\text{--}1730\text{ cm}^{-1}$) and the amine νNH_2 ($3300\text{--}3500\text{ cm}^{-1}$) of the reactants were not observed in the infrared spectra of the Schiff bases L_4 and L_5 while the characteristic azomethine $\text{C}=\text{N}$ band was seen at 1608 and 1603 cm^{-1} respectively. In the copper compounds, bands of medium intensities in the ranges $1605\text{--}1615$ and $1232\text{--}1240\text{ cm}^{-1}$ were assigned as $\nu\text{C}=\text{N}$ and $\nu\text{C}\text{--}\text{N}$ respectively. The frequencies of $\nu\text{C}=\text{N}$ are lowered by $5\text{--}10\text{ cm}^{-1}$ and those of $\nu\text{C}\text{--}\text{N}$ decreased by $40\text{--}50\text{ cm}^{-1}$ as a result of coordination of azomethine nitrogen to the metal centre [25,18]. The removal of the phenolic proton and the coordination mode of the Schiff bases as monoanionic ligands were shown in the infrared spectra. The strong bands due to $\nu\text{C}\text{--}\text{O}$ seen at $1328\text{--}1342\text{ cm}^{-1}$ in the ligands were lowered to $1310\text{--}1318\text{ cm}^{-1}$ in the spectra of the coordination compounds and showed the Schiff bases were bonded to the copper ion through the deprotonated phenolic oxygen [18,26]. The in-plane skeletal vibrations of the phenyl rings were found in the ranges $1595\text{--}1606$, $1578\text{--}1584$, $1512\text{--}1521$ and $1438\text{--}1447\text{ cm}^{-1}$. $\text{Cu}(\text{L}_6)_2$ with the nitro substituent showed the strong absorptions due to $\text{N}\text{--}\text{O}$ asymmetric and symmetric stretches at 1513 and 1315 cm^{-1} . Low intensity bands around $732\text{--}737\text{ cm}^{-1}$ were assigned as $\text{C}\text{--}\text{S}\text{--}\text{C}$ vibrations in these compounds. In the far infrared region of the copper compounds, bands in the ranges $437\text{--}458\text{ cm}^{-1}$ and $546\text{--}556\text{ cm}^{-1}$ are assigned as $\nu\text{Cu}\text{--}\text{N}$ and $\nu\text{Cu}\text{--}\text{O}$ respectively. The low intensity bands at $338\text{--}350\text{ cm}^{-1}$ were designated as $\text{Cu}\text{--}\text{S}$ vibrations. These bands support the coordination of the Schiff bases to the copper centre through the azomethine nitrogen [27,28], phenolic oxygen and thioether sulfur [29].

3.4 Magnetic susceptibility and Electronic spectra

The magnetic susceptibility measurements of the copper coordination compounds were taken at room temperature. The effective values were derived between 1.80 and $1.83\mu_{\text{BM}}$ and these are close to $1.73\mu_{\text{BM}}$ expected for spin only susceptibility readings. The electronic spectra of the Schiff bases and the copper(II) compounds were recorded in DCM and the corresponding absorption maxima are presented in Figure 2. The Schiff bases showed absorptions at 255 nm and 305 nm due to aromatic $\pi\text{--}\pi^*$ transitions in the ligands and the band around 346 nm is assigned to $\text{n--}\pi^*$ transition of the nitrogen lone pairs to the aromatic ring. The three bands were observed to be bathochromically shifted upon coordination of the Schiff bases to the copper as a result of extensive conjugation of π electrons in the compounds. They are observed around $265\text{--}268\text{ nm}$, $308\text{--}313\text{ nm}$ and $358\text{--}377\text{ nm}$ (Fig. 3). In the spectra of the copper compounds, the band of high intensity tailing into the visible region, around 400 nm , has been attributed to ligand to metal ($\text{S}\text{--}\text{Cu}$) charge transfer transition [4,30,31]. Similar transitions were reported in Schiff bases comprising of NOS donor set [32]. The $d\text{--}d$ band of low intensity in the region $585\text{--}613\text{ nm}$ is assigned to ${}^2\text{E}_g\text{--}{}^2\text{T}_{2g}$ transition. It has a large bandwidth, which is suggestive of a square-based geometry around copper(II) in a weak tetragonal field [33]. This is consistent with the observed crystal structures of $\text{Cu}(\text{L}_1)_2$ and $\text{Cu}(\text{L}_2)_2$ where the elongated $\text{Cu}\text{--}\text{S}$ apical bonds give rise to a distorted octahedral geometry for the copper ion.

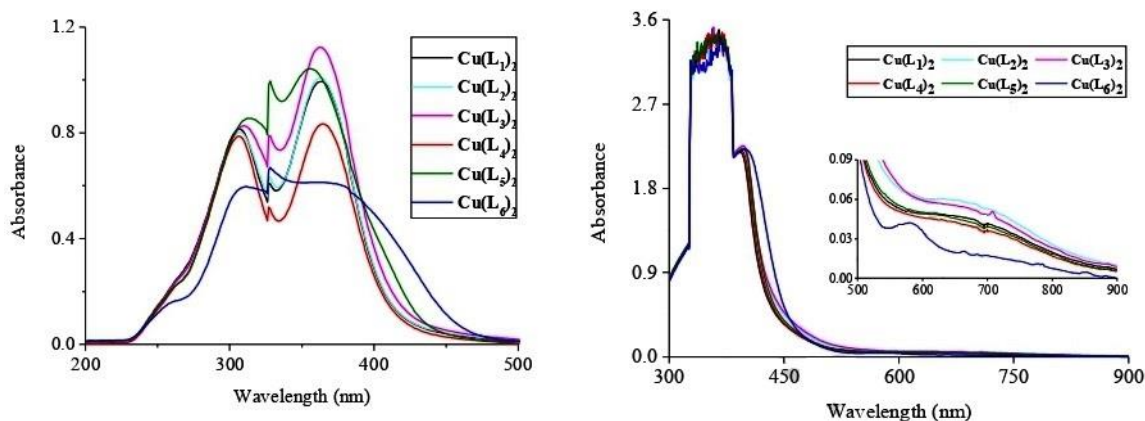


Fig. 3 UV-Visible spectra of copper(II) compounds

3.5 Theoretical studies: Electronic properties

Optimized structures presented close atomic bond distance parameters as compared to the crystal structures (Figure1). The optimization energies of the complexes ($\text{Cu}(\text{L}_1)_2$, $\text{Cu}(\text{L}_2)_2$, $\text{Cu}(\text{L}_3)_2$, $\text{Cu}(\text{L}_4)_2$, $\text{Cu}(\text{L}_5)_2$ and $\text{Cu}(\text{L}_6)_2$) are presented in Table 1. Complexes with high energy have higher compactness, hence, making it difficult for incoming molecules to reorganize around the complex, while complexes with smaller energies have lower compactness, therefore allowing facile association with incoming molecules.

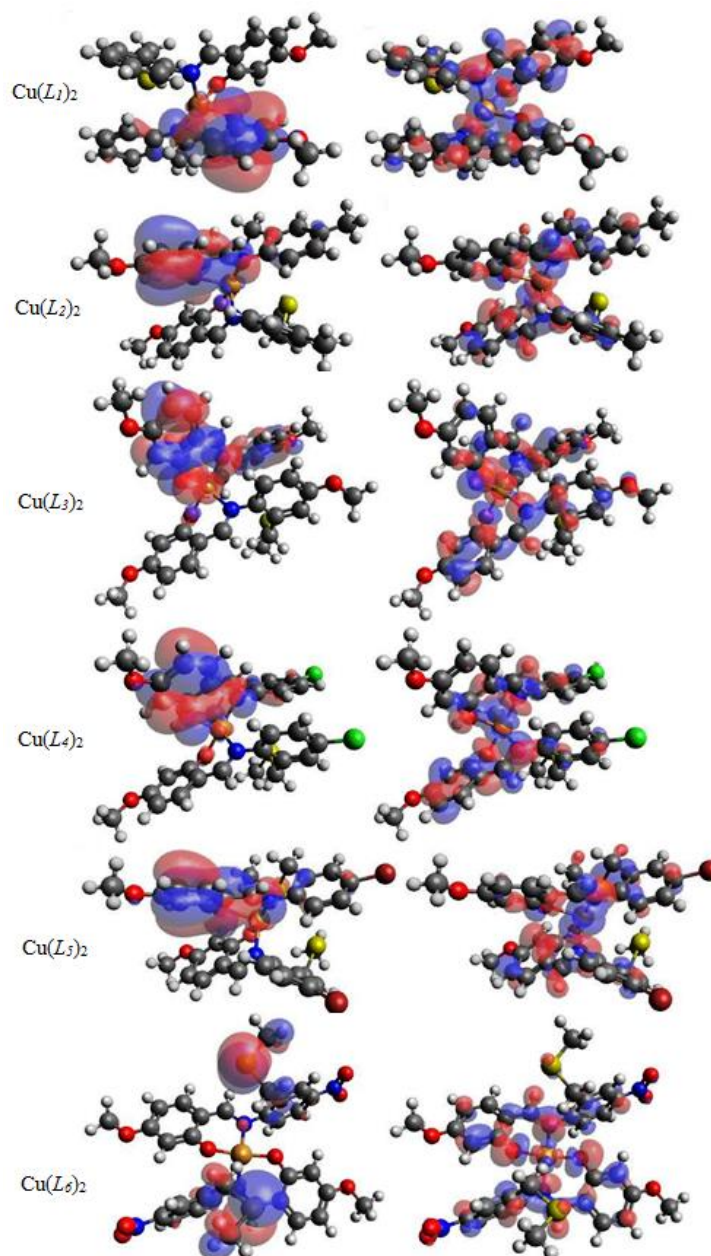
3.5.1 HOMO-LUMO analysis

The molecular orbital plays an important role in the electric and optical properties of the complexes as it helps describe the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) positions. The HOMO represents the ability to donate an electron, and LUMO as an electron acceptor [34,35]. The plots of the HOMO and LUMO orbitals for all complexes modelled in gas phase are shown in Figures 3. The HOMO position of the complexes is localized mostly around the ligand atoms (nitrogen (N), oxygen (O) and sulfur (S)), while the LUMO is distributed within the complex (metal centre and ligand). The HOMO, LUMO and their energy gaps of the various complexes are provided in Table 1. The change in the HOMO and LUMO centers within the various complexes indicated an electron density transfer within the complexes. $\text{Cu}(\text{L}_4)_2$ and $\text{Cu}(\text{L}_5)_2$ offered the lowest optimization energies and also the least HOMO–LUMO gap, which indicates high polarizability (soft molecule) [35]. Hence the reactivity of $\text{Cu}(\text{L}_4)_2$ and $\text{Cu}(\text{L}_5)_2$ with respect to the other complexes would be higher. Substituents such as $-\text{Cl}$, $-\text{Br}$, $-\text{NO}_2$ increased the HOMO energy values as electrons are withdrawn from the metal center, Cu and donor atoms (N, O and S). The electron donating substituents such as $-\text{OCH}_3$, $-\text{CH}_3$ decreased the HOMO energies.

Table 1 Calculated electronic parameters of the complexes **1-6**.

Complexes	E_H (eV)	E_L (eV)	E_G (eV)	Dipolemoment (Debye)	Optimization Energy(kJ mol^{-1})
Cu(L1)2	-8.193	-6.941	1.252	2.204	-10.733×10^6
Cu(L2)2	-8.101	-6.835	1.266	2.050	-10.942×10^6
Cu(L3)2	-7.967	-6.677	1.290	3.644	-11.337×10^6
Cu(L4)2	-8.336	-7.094	1.242	6.775	-13.150×10^6
Cu(L5)2	-8.318	-7.071	1.247	8.658	-24.258×10^6
Cu(L6)2	-8.830	-7.403	1.427	4.337	-11.810×10^6

E_H = energy of HOMO, E_L = energy of LUMO, $E_G = E_L - E_H$

Fig. 3 The HOMO and LUMO position of complexes **1-6**.

3.5.2 Dipole interactions and Electrostatic charge transfer

The strength of a dipole interaction depends on the size of each dipole, dipole energies and on their relative orientation. The extent of charge separation within a metal complex is characterized by its dipole moment (Table 1), which also explains the nature of polarity. Polarity prompted by dipole moment brings about a number of physical properties such as solubility (wettability) and surface tension [36]. The compound Cu(L₅)₂ presented the highest dipole moment, probably as a result of its large size and this suggests that it can show better wettability properties from a neighboring polar molecule. Changes in partial charge within atoms of ligand and the various complexes were observed (Table 2).

Three classes of natural bond orbitals (NBOs) were observed and these include, (i) Lewis-type (σ and π bonding or lone pair) orbitals, (ii) valence non-Lewis (acceptors formally unfilled) orbitals and (iii) Rydberg NBOs, which originate from orbitals outside the atomic valence shell. Charge transfer occurs through boundary orbitals and usually proceeds in the direction from HOMO to LUMO [34]. Partial charge within atoms significant decrease in the partial charge of Cu was observed with TOP-NO₂ while the partial charge of sulfur in ligand (0.056) increased upon formation of complex [37-39].

Table 2 Summary of natural charge of the relevant atoms /ions.

Compounds	Cu	N(1)	N(2)	O(1)	O(2)	O(3)	O(4)	S(1)	S(2)
Cu(L ₁) ₂	1.165	-0.658	-0.536	-0.828	-0.736	-0.522	-0.515	0.187	0.174
Cu(L ₂) ₂	1.172	-0.657	-0.533	-0.827	-0.740	-0.522	-0.516	0.187	0.173
Cu(L ₃) ₂	1.162	-0.561	-0.424	-0.804	-0.781	-0.529	-0.523	0.273	0.188
Cu(L ₄) ₂	1.175	-0.668	-0.543	-0.828	-0.739	-0.521	-0.514	0.192	0.176
Cu(L ₅) ₂	1.381	-0.643	-0.583	-0.763	-0.721	-0.502	-0.500	0.319	0.177
Cu(L ₆) ₂	1.395	-0.619	-0.519	-0.723	-0.723	-0.494	-0.494	0.206	0.206

3.5.3 NBO study on complexes (Cu(L₁)₂-Cu(L₆)₂)

Natural Bond Orbitals (NBOs) are an orthonormal set of localized “maximum occupancy” orbitals whose leading N/2 members (or N members in the open-shell case) give the most accurate possible Lewis-like description of the total N-electron density [40-42]. NBO analysis was performed on (Cu(L₁)₂-Cu(L₆)₂) at the DFT/6-311G(d) level in order to elucidate the intra molecular re-hybridization and delocalization of electron density within the complexes. The analysis examines all possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs, hence estimating their energetic importance by 2nd- order perturbation theory. Three classes of NBOs observed include, (i) Lewis-type (σ and π bonding or lone pair) orbital's, (ii) valence non-Lewis (acceptors formally unfilled) orbital's and (iii) Rydberg NBOs, which originate from orbitals outside the atomic valence shell.

The NBO calculated hybridization for (Cu(L₁)₂-Cu(L₆)₂) shows that all of complexes have sp^x hybridization, where x ranges from approximately 1 to 5 (Supplementary material, Table 3). The result shows

the hyper conjugation of electrons between ligand atoms. The lone pair located on the oxygen (methoxy), chlorine and bromine atoms on complexes Cu(L₃)₂, Cu(L₄)₂ and Cu(L₅)₂ respectively show significantly delocalized hybrid orbitals, most observed at the C-OCH₃, C-Cl and C-Br bonds.

Conclusion

The copper(II) coordination compounds of Schiff bases derived from 2-(methylthiomethyl)anilines and 4-methoxysalicylaldehyde were prepared and characterized on the basis of their elemental analysis and spectroscopic data. The copper complexes are characterized by N₂O₂S₂ coordination mode in the octahedral geometry, with long axial Cu–S bonds arising in the tetragonal distortion within the molecules. The elongated axial Cu–S distances and the distortions in the molecules around the sulfur atoms are probably due to the strain imposed on the copper(II) ion by the bulky mixed-donor tridentate ligands. The single crystal structures of two of the complexes were discussed. The compounds are monomeric and mononuclear with no copper-to-copper interaction as suspected from the magnetic susceptibility measurements. Computational studies revealed that the HOMO positions of the complexes are localized mostly around the ligand nitrogen, oxygen and sulphur atoms while the LUMO is distributed within the complex (metal centre). Further electronic study confirmed the higher polarizability and reactivity of Cu(L₅)₂ compared to other complexes.

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