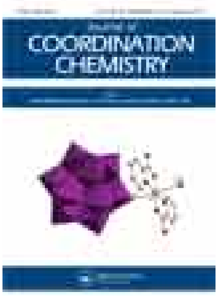

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Synthesis, crystal structures, spectral studies and reactivity of square planar copper(II) complexes containing Schiff base ligand

Poulami Pattanayak [a], Jahar Lal Pratihar [b], Debprasad Patra [c], Chia-Her Lin [d], Paula Brandão [e], Dasarath Mal [e] & Vitor Felix [e]

[a] Department of Chemistry, University of Kalyani, Kalyani, India
[b] Department of Chemistry, Kandi Raj College, Murshidabad, India
[c] Department of Chemistry, East Calcutta Girls' College, Kolkata, India
[d] Department of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan
[e] Department of Chemistry/CICECO, University of Aveiro, Aveiro, Portugal

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Synthesis, crystal structures, spectral studies and reactivity of square planar copper(II) complexes containing Schiff base ligand

POULAMI PATTANAYAK*†, JAHAR LAL PRATIHAR*‡, DEBPRASAD PATRA§, CHIA-HER LIN¶, PAULA BRANDÃO||, DASARATH MAL|| and VITOR FELIX||

†Department of Chemistry, University of Kalyani, Kalyani, India
‡Department of Chemistry, Kandi Raj College, Murshidabad, India
§Department of Chemistry, East Calcutta Girls' College, Kolkata, India
¶Department of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan
||Department of Chemistry/CICECO, University of Aveiro, Aveiro, Portugal

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The reactions of HL^1 [2-((2-(benzylthio)phenylimino)methyl)phenol] and HL^2 [3-((2-(benzylthio) phenylimino)methyl)-2-hydroxy-5-methylbenzaldehyde] separately with $Cu(OAc)_2{\cdot}H_2O$ afforded new Cu(II) complexes $[Cu(L^1)(OAc)]$ (**1**) and $[Cu(L^2)_2]$ (**2**), respectively. These are characterized by microanalytical data and spectroscopic studies. UV–vis spectra of the complexes show intense low-energy transitions ~ 420 nm which are ligand to metal charge transfer (LMCT) transitions. The single-crystal X-ray structures were determined for **1** and **2**. Reactions of $[Cu(L^1)(OAc)]$ (**1**) with N_3^-, SCN^- and NO_2^- show the replacement of weakly coordinated acetate yielding $[Cu(L^1)(N_3)]$, $[Cu(L^1)(SCN)]$ and $[Cu(L^1)(NO_2)]$, respectively. Unequivocal characterization of the substituted products has been done by single-crystal X-ray study of $[Cu(L^1)(N_3)]$. HL^2 and its Cu(II) complex exhibited low-intensity emission bands at ~575 nm upon excitation at 375 nm and at 420 nm, respectively. Redox properties of the complexes were determined electrochemically. Density functional theory (DFT) computations have been carried out to explain the spectroscopic and redox properties of the complexes.

Keywords: Copper(II); Crystal structure; Ligand substitution; Redox; DFT

1. Introduction

Transition metal complexes of Schiff bases derived from salicylaldehyde/substituted salicylaldehydes have received attention for applications in catalysis [1–5], magnetism [6–9], molecular architectures [10–13], materials chemistry and biological activity [14–17].

Metal complexes of (O, N, S) chelating Schiff bases have specific properties, for example, electrochemistry [18–21], photochromism [22], asymmetric catalysis [23,24], oxo-transfer reactions [25–28] and antimicrobial activities [29–32]. Metal complexes of thiosemicarbazones, dithiocarbazic acid and the Schiff base derived from its s-methyl ester show a variety of biological activities against bacteria, fungi and certain type of tumors

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*Corresponding authors. Email: pparka@rediffmail.com (P. Pattanayak); jlpr@rediffmail.com (J.L. Pratihar).

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[15,33–35]. The O,N,S donors, where "O" is phenolato oxygen, "N" is azomethine nitrogen and "S" is thioether sulfur, have not been utilized to explore the chemistry of transition metal ions. The relevance of copper(II) chemistry of O, N, and S donor ligands prompted us to design new tridentate ligands having phenolato, azomethine and thioether donors to copper.

In this article, we describe the preparation, structures, reactivity, spectroscopic and electrochemical properties of copper complexes incorporating bi or tridentate Schiff bases containing nitrogen, oxygen and sulfur donors. The syntheses of HL^1 and HL^2 and their reactions with Cu(II) acetate are described here. Complex **1** underwent ligand substitution with NaN_3, NH_4SCN, and $NaNO_2$. The ligands and metal complexes are characterized by UV–vis, IR and ^1H NMR. Single-crystal X-ray studies on $[Cu(L^1)(OAc)]$, $[Cu(L^2)_2]$ and $[Cu(L^1)(N_3)]$ were done. Photoluminescence of HL^2 and $[Cu(L^2)_2]$ has been investigated. The redox properties and plausible nature of the redox orbitals are described on the basis of single-point DFT calculations.

2. Experimental

2.1. *Materials*

The solvents were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedure [36]. Copper acetate monohydrate, benzyl chloride, salicylaldehyde, sodium azide, ammonium thiocyanate, and sodium nitrite were purchased from Emark, India. 2-Aminothiophenol was purchased from Aldrich. 2-(Benzylthio)aniline and 2-hydroxy-5-methylbenzene-1,3-dialdehyde were prepared following reported procedures [37,38].

2.2. *Physical measurements*

Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. UV–vis spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ^1H NMR spectra were obtained on Bruker 400 NMR spectrometers in $CDCl_3$ using TMS as the internal standard. Emission spectra were recorded with a Perkin Elmer LS-55 Luminescence Spectrometer. Electrochemical measurements were made under dinitrogen using a CH instruments model 600D potentiostat. A platinum disk working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.3. *DFT calculations*

Using the X-ray coordinates of $[Cu(L^1)(OAc)]$, $[Cu(L^1)(N_3)]$ and $[Cu(L^2)_2]$, ground state electronic structure calculations have been carried out using DFT [39] methods with the Orca 2.7 program [39]. Becke's hybrid function [40] with the Lee–Yang–Parr correlation function [41] was used throughout the study. LANL2DZ valence and effective core potential functions were used. All energy calculations were performed using the self-consistent field "tight" option of the Orca 2.7 program to ensure sufficiently well converged values for state energies.

2.4. *Synthesis of HL^1 and HL^2*

HL^1 [2-((2-(benzylthio)phenylimino)methyl)phenol] and HL^2 [3-((2-(benzylthio)phenylimino)methyl)-2-hydroxy-5-methylbenzaldehyde] were synthesized following a common procedure. Details of the synthesis for HL^1 are given below.

2-(Benzylthio)aniline (1000 mg, 4.65 mmol) was dissolved in 30 ml ethanol, salicylaldehyde (567 mg, 4.65 mmol) was added to it and the mixture was refluxed for 5 h, filtered, the filtrate collected in a beaker and solvent allowed to evaporate slowly. The yellow crystalline product at the bottom of the beaker was collected, washed with ethanol and dried over $CaCl_2$ in a desiccator. Yield was 80%. Anal. Calcd for $C_{20}H_{17}NOS$ (319.17): C, 75.20; H, 5.37; N, 4.39%. Found: C, 75.37; H, 5.32; N, 4.24. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}cm^{-1}$) = 350 (15,770), 270 (32,760). IR (KBr pellets, cm^{-1}): ν = 3215 (O–H), 1610 (CH=N), 1556 (C–O), 750 (C–S). ^{1}H NMR $CDCl_3$: δ 13.11 (s, 1H), 8.47 (s, 1H), 7.30 (t, 3H), 7.21–7.08 (m, 8H), 7.00 (d, 1H), 6.86 (t, 1H), 4.02 (s, 2H).

HL^2: Yield was 85%. Anal. Calcd for $C_{22}H_{19}NO_2S$ (361.20): C, 73.09; H, 5.30; N, 3.88%. Found: C, 73.21; H, 5.42; N, 4.04. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}cm^{-1}$) = 375 (12,200), 255 (29,700). IR (KBr pellets, cm^{-1}): ν = 3352 (O–H), 1682 (CHO), 1621 (CH=N), 1593 (C–O), 752 (C–S). ^{1}H NMR ($CDCl_3$, ppm) δ: 13.84 (s, 1H), 10.59 (s, 1H), 8.53 (s, 1H), 7.75 (s, 1H), 7.52 (s, 1H), 7.37–7.39 (d, 1H), 7.31–7.33 (d, 2H), 7.19–7.28 (m, 5H), 7.13–7.16 (d, 1H), 4.14 (s, 2H), 2.37 (s, 3H).

2.5. *Synthesis of complexes*

2.5.1. [Cu(L^1)(OAc)](1). To a solution of HL^1 (1000 mg, 3.13 mmol) in 100 mL methanol (625 mg, 3.13 mmol) $Cu(OAc)_2{\cdot}H_2O$ was added. Immediately the color of the solution changed to olive green was stirred for 5 h at room temperature and kept for crystallization. After a few days, dark crystals were obtained. Yield: 90%. Anal. $C_{22}H_{19}NO_3SCu$ (441): Calcd C, 59.87; H, 4.34; N, 3.18. Found: C, 59.67; H, 4.52; N, 3.12%. UV/Vis spectrum (CH_2Cl_2) λ_{max} (ε, $M^{-1}cm^{-1}$) = 425 (10,650), 305 (24,400). IR (KBr pellets, cm^{-1}): ν = 1605 (CH=N), 1389 (OAc), 1529 (C–O), 756 (C–S).

2.5.2. [Cu(L^2)$_2$](2). To a solution of HL^2 (361 mg, 1 mmol) in 25 mL methanol (200 mg, 1 mmol) $Cu(OAc)_2{\cdot}H_2O$ was added. Immediately the color of the solution changed to green, was stirred for 4 h at room temperature and kept for crystallization. After a few days, dark crystals were obtained. Yield: 75%. Anal. Calcd for $C_{44}H_{36}N_2O_4S_2Cu$ (784.44): C, 67.31; H, 4.62; N, 3.57. Found: C, 67.16; H, 4.73; N, 3.61%. UV–vis λ_{max} (dichloromethane, nm) ε /M^{-1}, cm^{-1}): 420 (19,270), 250 (68,150). IR (KBr pellets, cm^{-1}): ν = 1668 (CHO), 1617 (CH=N), 1537 (C–O), 746 (C–S).

2.5.3. Syntheses of [Cu(L^1)(N$_3$)] (3), [Cu(L^1)(NCS)] (**4**) and [Cu(L^1)(NO$_2$)] (**5**). [Cu(L^1)(N$_3$)], [Cu(L^1)(NCS)] and [Cu(L^1)(NO$_2$)] were prepared by adding methanol solution (10 mL) of sodium azide (30 mg, 0.45 mmol), ammonium thiocyanate (35 mg, 0.45 mmol) or sodium nitrite (31 mg, 0.45 mmol), respectively, to methanol solution (10 mL) of [Cu(L^1)(OAc)] (200 mg, 0.45 mmol); the mixture was stirred for 3 h. In all cases, dark green crystals were obtained after a few days.

Complex **3** (Yield was 90%). Anal. Calcd for $C_{20}H_{16}N_4OSCu$ (423.99): C, 56.61; H, 3.80; N, 13.21%. Found: C, 56.37; H, 3.71; N, 13.38. UV–vis λ_{max} (dichloromethane, nm) ε/M^{-1}, cm^{-1}): 425 (10,230), 315 (22,050). IR (KBr pellets, cm^{-1}): ν = 1607 (CH=N), 2037 (N_3), 1531 (C–O), 759 (C–S).

Complex **4** (Yield was 90%). Anal. Calcd for $C_{21}H_{16}N_2OS_2Cu$ (439.84): C, 57.30; H, 3.67; N, 6.37%. Found: C, 57.44; H, 3.78; N, 6.14. UV–vis λ_{max} (dichloromethane, nm) ε /M^{-1}, cm^{-1}): 435 (9600), 315 (23,500). IR (KBr pellets, cm^{-1}): ν = 1603 (CH=N), 2087 (NCS), 1533 (C–O), 754 (C–S).

Complex **5** (Yield was 90%). Anal. Calcd for $C_{20}H_{16}N_2O_3SCu$ (427.97): C, 56.08; H, 3.77; N, 6.54%. Found: C, 56.23; H, 3.65; N, 6.31. UV–vis λ_{max} (dichloromethane, nm) ε /M^{-1}, cm^{-1}): 415 (7540), 300 (17,300). IR (KBr pellets, cm^{-1}): ν = 1605 (CH=N), 1271 (NO_2), 1531 (C–O), 754 (C–S).

2.6. *Crystallography*

Single crystals of [Cu(L^1)(OAc)], [Cu(L^2)$_2$] and [Cu(L^1)(N_3)] were grown by slow evaporation of methanol solution at 298 K. Data were collected by ω-scan on a Bruker Smart CCD diffractometer with Mo-K$_\alpha$ radiation monochromated by graphite crystal. Structure solution was done by direct methods with SHELXS–97 [42,43]. Full matrix least square refinements on F^2 were performed using SHELXL–97 [42,43]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma$ (I). All hydrogens were included at calculated positions. Data collection parameters and relevant crystal data are collected in table 1.

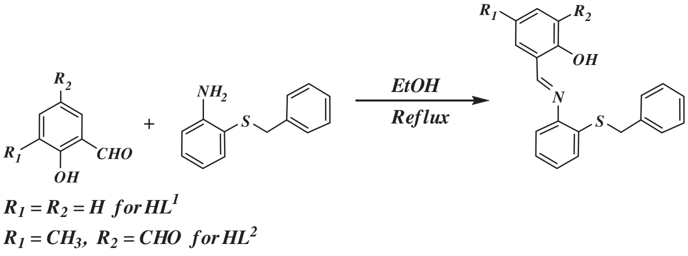
3. Results and discussion

3.1. *Synthesis*

HL^1 and HL^2 are synthesized by condensation of 2-(benzylthio)aniline and salicylaldehyde and 2-hydroxy-5-methylbenzene-1,3-dialdehyde in dry ethanol (scheme 1), respectively.

Table 1. Crystallographic data for **1**, **2** and **3**.

Chemical formula	$C_{22}H_{19}CuNO_3S$	$C_{44}H_{36}CuN_2O_4S_2$	$C_{20}H_{16}CuN_4OS$
Formula weight	441.00	784.44	423.99
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1 (No. 2)	*C2/c* (No. 15)	*P*-1 (No. 2)
a/Å	10.1015(5)	22.4537(7)	9.5322(4)
b/Å	12.1951(6)	13.3246(4)	12.3638(5)
c/Å	15.5937(7)	14.4452(4)	15.6199(7)
α/°	81.199(3)	90	77.509(2)
β/°	80.102(3)	121.819(10)	80.512(2)
γ/°	89.735(3)	90	89.289(2)
λ/Å	0.71073	0.71073	0.71073
V/Å^3	1869.63(16)	3672.32(19)	1772.19(13)
F(000)	908	1628	868
Z	4	4	4
T/K	296	150	150
D/mg/m^{-3}	1.567	1.419	1.589
μ/mm^{-1}	1.304	0.756	1.368
*R*1 (all data)	0.0863	0.0405	0.0390
w*R*$_2$[*I* > 2(*I*)]	0.2430	0.1263	0.1101
GOF	1.02	0.97	1.00



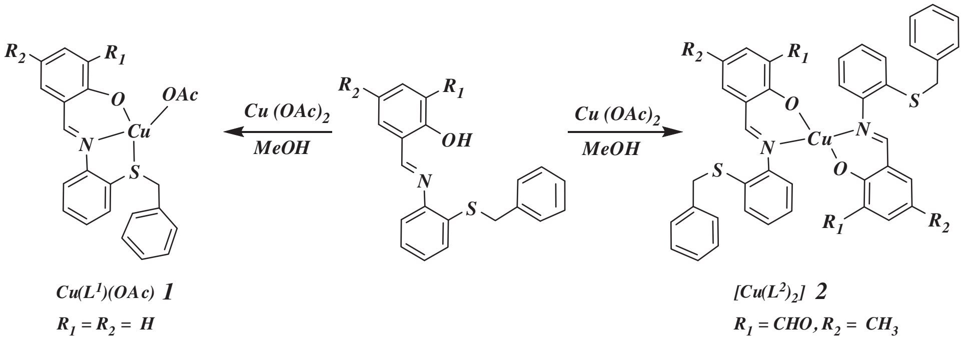
Scheme 1. Synthesis of HL^1 and HL^2.

Reaction between HL and $Cu(OAc)_2 \cdot H_2O$ in MeOH gave the tridentate (O,N,S) and bidentate (O, N) bis chelate complexes of composition $[Cu(L^1)(OAc)]$ (**1**) and $[Cu(L^2)_2]$ (**2**) (scheme 2). We tried to obtain (O, N, S) coordination of HL^2 by changing the metal/ligand ratio, but we always obtained bidentate (O, N) coordination. The subtle change in binding mode of HL^2 may be due to presence of –CHO and $–CH_3$ in 3 and 5 positions, respectively, of the phenyl ring of aldehydic component of aldimine. The compounds are neutral and their composition is supported by microanalytical data. The structures of $[Cu(L^1)(OAc)]$ and $[Cu(L^2)_2]$ have been established by single-crystal X-ray diffraction study.

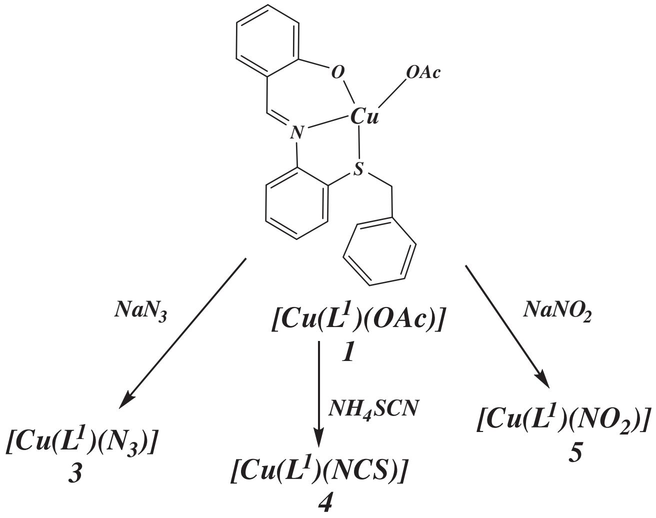
Reactions of $[Cu(L^1)(OAc)]$ (**1**) with sodium azide, ammonium thiocyanate and sodium nitrite gives $[Cu(L^1)(N_3)]$ (**3**), $[Cu(L^1)(NCS)]$ (**4**) and $[Cu(L^1)(NO_2)]$ (**5**), respectively (scheme 3). Formation of **3–5** from **1** clearly indicates that the weakly coordinated acetate can be replaced easily by stronger coordinating N_3^-, SCN^- and NO_2^-. Single-crystal X-ray study of $[Cu(L^1)(N_3)]$ has been done for the unequivocal characterization.

3.2. *Characterizations*

3.2.1. UV–vis spectra. HL^1, HL^2 and **1–5** are soluble in common organic solvents with yellow and light green color, respectively. UV–vis spectra of the ligand and complexes were recorded in dichloromethane. High-energy transitions at 320 nm are associated with ligand centered $\pi-\pi^*$ transitions [21]. A low-energy absorption near 425 nm has been assigned to LMCT transition, consistent with DFT results (see below). UV–vis spectra of **3–5** were very similar with **1**. UV–vis spectra of all the compounds are deposited as ESI (figures S1–S7) and data are collected in the experimental section.



Scheme 2. Synthesis of **1** and **2**.



Scheme 3. Synthesis of **3**–**5**.

3.2.2. Infrared spectra. The free Schiff bases HL^1 and HL^2 show strong bands at 1621 and 1610 cm^{-1}, characteristic of the azomethine ν(C=N) [20]. The ν(C=N) shifts to lower frequency in all the complexes 1617–1603 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen. Phenolic C–O at 1282 and 1261 cm^{-1} [20] in HL^1 and HL^2 shifts to higher frequency, 1382–1394 cm^{-1}, indicating coordination through the phenolic oxygen. In IR spectra of **3** a strong band at 2055 cm^{-1} indicates the presence of coordinated azide [44]. Similarly, bands at 2077 and 1271 cm^{-1} in **4** and **5** indicate the presence of the N-coordinated thiocyanate and O-coordinated nitrite [44], but no acetate band near 1100 cm^{-1} was observed. The ν(C–S) near 750 cm^{-1} indicates coordination of the thio-benzyl group. IR spectral data of HL^1 and HL^2 and their corresponding complexes are given in the experimental section and the spectra are deposited as ESI (figures S8–S14).

3.2.3. ^{1}H NMR spectra. Free Schiff bases HL^1 and HL^2 have been characterized by ^{1}H NMR spectra and the data are given in the experimental section (figures S15 and S16). In HL^1 and HL^2, the phenolic –OH appears as a broad singlet at 13.11 and 13.84 ppm, respectively [20]. The broadness is due to hydrogen bonding between phenolic –OH and azomethine (–CH=N–) hydrogen. The azomethine protons in HL^1 and HL^2 are sharp singlets at 8.47 and 8.53 ppm, respectively [20]. A sharp singlet at 4.02 and 4.14 ppm for HL^1 and HL^2, respectively, is assigned for benzyl protons of the ligands. All the aromatic protons are 7.75–6.86 ppm. The –CHO and –CH$_3$ signals in HL^2 are at 10.59 and 2.37 ppm, respectively.

3.2.4. X-ray crystal structure. *[Cu(L^1)(OAc)] and [Cu(L^1)(N$_3$)]*. Suitable crystals of [Cu (L^1)(OAc)] and [Cu(L^1)(N$_3$)] were grown by slow evaporation of mother liquor. The X-ray structures of [Cu(L^1)(OAc)] and [Cu(L^1)(N$_3$)] were determined and the perspective view

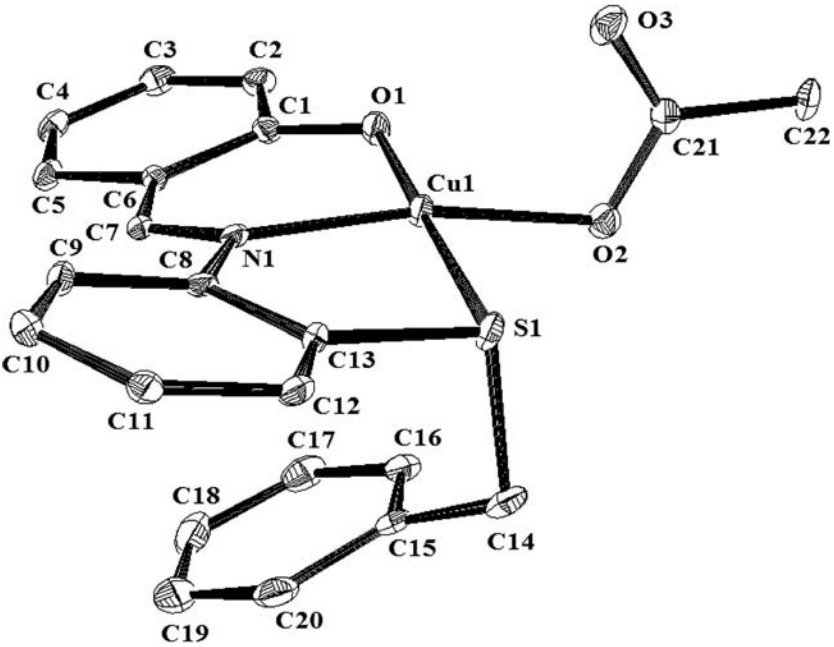


Figure 1. ORTEP plot of **1** with atom-numbering scheme. Hydrogens are omitted for clarity.

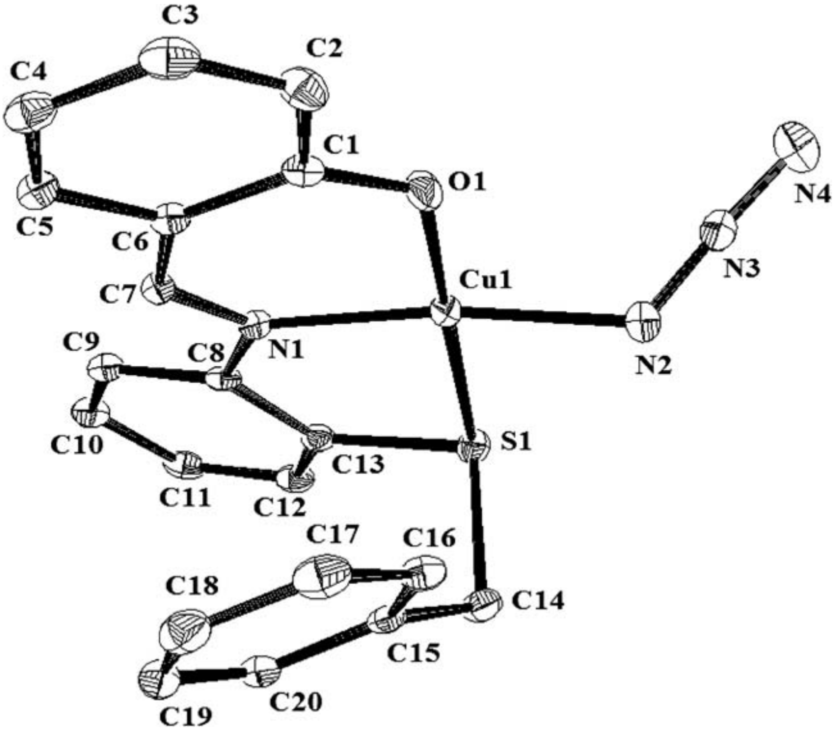


Figure 2. ORTEP plot of **3** with atom-numbering scheme. Hydrogens are omitted for clarity.

of the molecules along with the atom numbering scheme are shown in figures 1 and 2 and selected bond distances and angles are collected in tables 2 and 4. The asymmetric unit contains two molecules, both molecules have the same structural parameters for [Cu(L^1)(OAc)] and [Cu(L^1)(N$_3$)], respectively. So structure analysis of one molecule is considered in each case. The geometry about copper(II) is distorted square planar where uni-negative L^1 binds tridentate (O, N, S). An acetate (for **1**) and azide (for **3**) satisfies the four coordination. The three donors are deprotonated phenolic oxygen, imine nitrogen and sulfur. The Cu1–S1, Cu1–N1, Cu1–O1, Cu1–O2 and C7–N1 lengths (2.3142(15), 1.952 (5), 1.904(4), 1.955(4) and 1.305(7) Å, respectively) for **1** and the Cu1–S1, Cu1–N1, Cu1–O1, Cu1–N2 and C7–N1 lengths (2.3229(7), 1.961(2), 1.898(2), 1.962(2) and 1.306 (3), respectively) for **3** are within the normal range [45–48]. The geometries about Cu(II) are planar (mean deviation 0.075 Å for **1** and 0.062 Å for **3**).

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Distances			
Cu1–S1	2.3142(15)	Cu1–N1	1.952(5)
Cu1–O1	1.904(4)	C8–C13	1.389(7)
Cu1–O2	1.955(4)	S1–C13	1.764(5)
C6–C7	1.422(7)	S1–C14	1.842(6)
O1–C1	1.310(7)	O2–C21	1.290(7)
O3–C21	1.250(7)	N1–C8	1.426(7)
N1–C7	1.305(7)	C14–C15	1.510(8)
Angles			
S1–Cu1–O1	177.42(13)	O1–Cu1–O2	91.30(17)
S1–Cu1–O2	86.77(13)	Cu1–N1–C7	122.2(4)
S1–Cu1–N1	86.77(13)	Cu1–N1–C8	118.3(3)
O1–Cu1–N1	94.88(17)	C7–N1–C8	119.1(5)
O2–Cu1–N1	169.33(18)	N1–C7–C6	126.6(5)
Cu1–S1–C13	95.76(17)	Cu1–S1–C14	98.34(18)
N1–C8–C13	117.4(4)	C13–S1–C14	103.8(3)
Cu1–O1–C1	125.6(4)	Cu1–O2–C21	106.9(4)

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Distances			
Cu1–O1	1.905(2)	Cu1–N1	2.004(2)
S1–C15	1.775(3)	S1–C16	1.829(4)
O1–C1	1.305(3)	O2–C8	1.215(4)
N1–C9	1.295(4)	N1–C10	1.437(4)
C16–C17	1.506(4)	C2–C8	1.468(4)
C4–C7	1.512(5)	C6–C9	1.438(5)
Angles			
O1–Cu1–N1	89.38(9)	N1–Cu1–N1#	180.00
O1–Cu1–O1#	180.00	O1#–Cu1–N1#	89.38(9)
O1–Cu1–N1#	90.62(9)	C15–S1–C16	101.50(15)
O1#–Cu1–N1	90.62(9)	Cu1–O1–C1	123.46(16)
Cu1–N1–C9	121.5(2)	Cu1–N1–C10	120.22(17)
S1–C16–C17	109.9(3)	N1–C9–C6	125.5(2)

[Cu(L^2)$_2$]. Suitable crystals of [Cu(L^2)$_2$], for X-ray studies, were grown upon slow evaporation of methanol solution. A perspective view of the molecular structure is shown in figure 3. Selected bond distances and angles are collected in table 3. Each deprotonated ligand binds bidentate (O, N) with each ligand symmetry equivalent to the other held *trans*. The perfectly square planar CuN_2O_2 coordination (mean deviation 0.00 Å) is consistent with Cu(II) and uninegative ligand. Cu1–N1, Cu1–O1 and C9–N1 lengths (2.004(2), 1.905(2) and 1.295(4) Å, respectively) are within the normal range [45–48]. The fragment containing C9, N1, C6, C1, C2, C3, C4, C5 and O1 is satisfactorily planar (mean deviation 0.063 Å) and the dihedral angle with the CuN_2O_2 plane is 21.6°. Therefore the metallocycle has an envelope conformation (figure 4) due to steric crowding around copper [49]. The metal–ligand bonding in six-membered analogous boat-shaped chelate ring

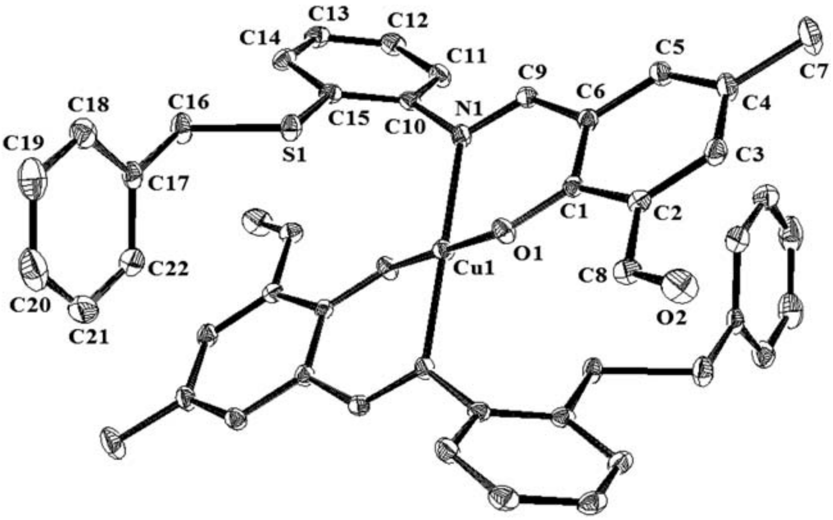


Figure 3. ORTEP plot of **2** with atom-numbering scheme. Hydrogens are omitted for clarity.

Table 4. Selected bond distances (Å) and angles (°) for **3**.

Distances			
Cu1–S1	2.3229(7)	Cu1–N2	1.962(2)
Cu1–O1	1.898(2)	S1–C14	1.850(3)
Cu1–N1	1.961(2)	S1–C13	1.769(3)
C6–C7	1.421(4)	O1–C1	1.312(3)
N1–C8	1.431(3)	N1–C7	1.306(3)
N2–N3	1.198(3)	N3–N4	1.157(3)
Angles			
S1–Cu1–O1	178.22(6)	O1–Cu1–N1	94.62(8)
S1–Cu1–N1	86.35(6)	O1–Cu1–N2	91.47(10)
S1–Cu1–N2	87.44(8)	N1–Cu1–N2	172.37(10)
O1–C1–C6	124.0(2)	N2–N3–N4	176.4(3)
Cu1–S1–C14	98.12(9)	Cu1–S1–C13	96.32(9)
C13–S1–C14	103.63(12)	Cu1–O1–C1	125.63(17)
Cu1–N1–C7	122.56(17)	S1–C14–C15	112.5(2)
Cu1–N2–N3	123.9(2)		

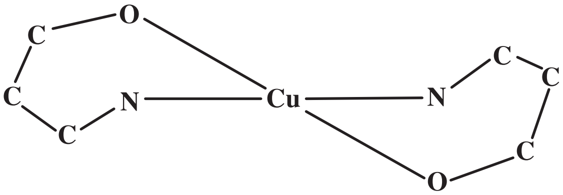


Figure 4. Envelope-shaped structure of **2**.

should be appropriately described by σ and π interactions [50], but for less puckered systems (in this case) the π interactions are unlikely to be significant [51].

3.2.5. Fluorescence spectra. Fluorescent properties of HL^2 and its complex with Cu(II) in dichloromethane exhibit low-intensity emission bands at ∼575 nm upon excitation at 375 nm for HL^2 and at 420 nm for its complex (figures S17 and S18). The usual quenching effect of Cu(II) in the emission of ligand was not noticed. The reason behind this is currently under investigation.

3.2.6. Electrochemistry. Electrochemical behavior of $[Cu(L^1)(OAc)]$ and $[Cu(L^2)_2]$ was investigated in dichloromethane/acetonitrile mixed solvent (0.1 M TBAP) by cyclic voltammetry with a scan rate of 50 mV s^{-1} (figures S19 and S20). The cyclic voltammogram of $[Cu(L^1)(OAc)]$ displayed one cathodic peak and one anodic peak at −0.5 V and 0.75 V,

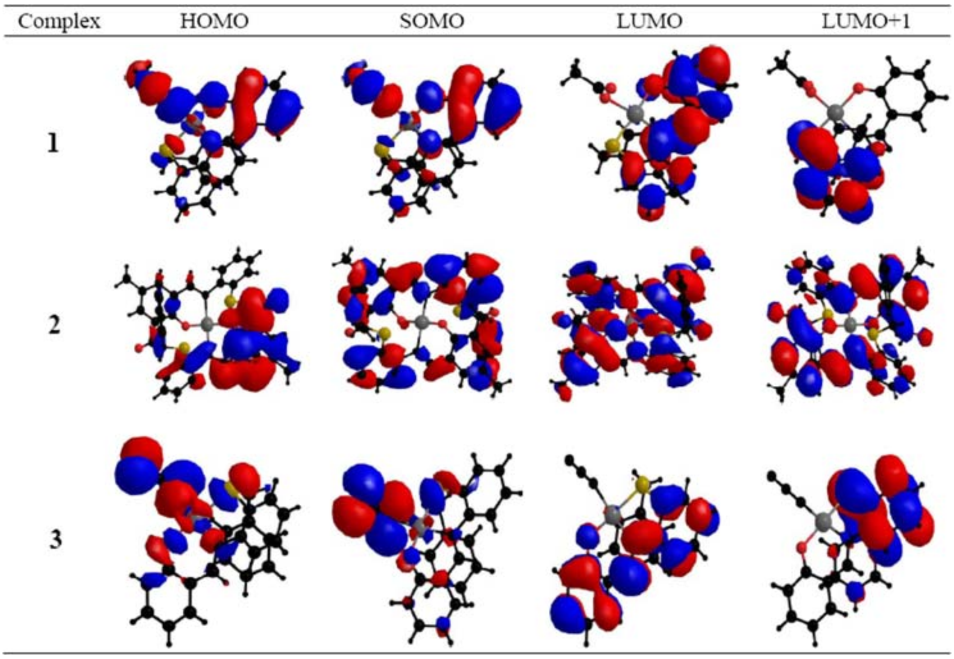


Figure 5. Surface plots of HOMO, SOMO, LUMO and LUMO + 1 of Cu(L)(OAc) (**1**), $Cu(L)_2$ (**2**) and Cu(L) (N_3) (**3**).

while [Cu(L^2)$_2$] exhibited only one anodic peak at 0.63 V. According to DFT results the composition of HOMO, SOMO, LUMO and LUMO + 1 (figure 5) of **1–3** are ligand centered, indicating irreversible oxidation and reduction of ligand.

4. Conclusion

Copper complexes containing (ONS and ON) donors and their activities have been reported [18–32,52–55] but O,N, and S donor ligands, where "O" is phenolato oxygen, "N" is azomethine nitrogen and "S" is thioether sulfur, have not been reported. Newly synthesized HL^1 and HL^2 afforded [Cu(L^1)(OAc)] and [Cu(L^2)$_2$], respectively, upon reaction with Cu(OAc)$_2$, where HL^1 binds tridentate (O,N,S) and HL^2 bidentate (O,N). The subtle change in binding mode of HL^2 may be due to the presence of –CHO and –CH_3 in 3 and 5 positions, respectively, of the phenyl ring of aldehydic component of aldimine. Acetate substitution in **1** upon reaction with NaN_3, NH_4SCN and $NaNO_2$ established weak coordination of the acetate to Cu(II). Single-point DFT calculation shows that the redox properties of the complexes are ligand centered.

Supplementary material

Figures S1–S14 show the UV/Vis and IR spectra and figures S15–S20 the ^{1}H NMR spectra, emission and cyclic voltammogram of the ligands and complexes. CCDC-806267, 872080 and 872081 contains the supplementary crystallographic data for [Cu(L^1)(OAc)], [Cu(L^2)$_2$] and [Cu(L^1)(N_3)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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