



REGULAR ARTICLE

Structural and spectral characterization of Cu(II) complexes of N(4)-substituted thiosemicarbazones derived from 2-hydroxyacetophenone: Crystal structure of a dinuclear Cu(II) complex

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Abstract. Copper(II) complexes of 2-hydroxyacetophenone-N(4)-cyclohexylthiosemicarbazone (H_2L^1) and 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone (H_2L^2) have been synthesized and characterized by different physicochemical techniques like magnetic studies and electronic, infrared and EPR spectral studies. $[(CuL^1)_2]$ (**1**) is a dinuclear complex having four coordination around copper(II) with distorted square planar geometry. The two individual dinuclear complexes are interconnected through two bifurcated classical hydrogen bond interactions producing a sheet-like structure along b axis. $[(CuL^2)_2] \cdot \frac{1}{2}H_2O$ (**2**) also has a dimeric structure. The thiosemicarbazones bind to the metal as dianionic ONS donor ligand in all the complexes, except in the complexes $[Cu(HL^1)Cl] \cdot 2H_2O$ (**3**), $[Cu(HL^1)Br] \cdot 4H_2O$ (**4**) and $[Cu(HL^1)NO_3] \cdot C_2H_5OH(H_2O)$ (**5**), where the ligand moieties are coordinated as monoanionic (HL) ones. Complexes $[CuL^1-dmbipy]$ (**6**), $[CuL^2-dmbipy] \cdot 3H_2O$ (**7**), $[CuL^2bipy] \cdot H_2O$ (**8**) and $[CuL^2phen] \cdot 2C_2H_5OH$ (**9**) are heterocyclic base adducts.

Keywords. 2-Hydroxyacetophenone; thiosemicarbazone; X-ray crystallography; copper(II) complex; EPR spectrum.

1. Introduction

Thiosemicarbazones form a class of versatile nitrogen and sulfur (NS) donor chelating ligands and are known to exhibit diverse biological activities.¹ The biological activities are dependent upon the chemical nature of the moiety attached to the C=S carbon atom. They can act as tridentate ligands if additional donor atoms are present near the thiosemicarbazone moiety.² Thiosemicarbazones derived from 2-hydroxyacetophenone can act as a dianionic tridentate ligand by deprotonation of both phenol and thiol functions.²

They can also behave as monoanionic tridentate ligands coordinating with a metal centre through the deprotonated phenolic oxygen, thione sulfur and the azomethine nitrogen.² Thiosemicarbazones form complexes with copper(II) exhibiting interesting structures.³

Thiosemicarbazones and their copper complexes are of considerable interest because of their chemical and promising biological properties.^{4,5} They can easily be modified by varying the parent aldehyde or ketone used for the synthesis, particularly with compounds having additional potential coordinating sites or by

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substitutions at the terminal N(4)-position.⁶ The growing interest in copper complexes of thiosemicarbazones containing phenolic group is due to the presence of such moieties in a number of mono- and binuclear copper proteins. In recent years, a number of binuclear and to a lesser extent mononuclear copper complexes containing the phenolate ion have been investigated as models of copper proteins. Copper forms a variety of octahedral, square planar, square pyramidal and trigonal bipyramidal complexes with thiosemicarbazones.^{3,7} Copper forms mononuclear as well as binuclear complexes with thiosemicarbazones. Binuclear copper(II) complexes display interesting pharmacological activity⁸ and emerging interest in catalysis for such complexes.⁹

Metal complexes containing polypyridyl ligands have been found to exhibit anticancer activity.¹⁰ Thiosemicarbazones with substituents at N(4) position exhibit higher bioactivity compared to unsubstituted ones.¹¹ Our aim of the present paper is to investigate the effects of different substituents at the N(4)-position of the thiosemicarbazone to the structural and spectral properties. Here, we describe the synthesis and characterization of monomeric and dimeric Cu(II) complexes with 2-hydroxyacetophenone-N(4)-cyclohexyl/phenyl substituted ONS donor ligands. It also reports the crystal structure of a novel binuclear Cu(II) complex with oxygen bridging and its interesting coordination. This compound $[\text{CuL}^1]_2$ is a rare example of copper(II)-thiosemicarbazone complex with oxygen bridging structure.

2. Experimental

2.1 Materials and physical measurements

$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (Fluka), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (E-Merck), CuBr_2 (Sigma Aldrich), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (S.D.fine-chemicals Ltd), 2,2'-bipyridine (bipy) (Central drug house chemicals), 1,10-phenanthroline (phen) (Ranboxy fine chemicals) and 4,4'-dimethyl-2, 2'-bipyridine (dmbipy) (Sigma Aldrich) were used as received. Carbon, hydrogen and nitrogen content of the thiosemicarbazones and complexes were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a Thermo Nicolet, AVATAR 370 DTGS model FTIR spectrophotometer as KBr pellets at SAIF, Kochi, India. Far IR spectra were recorded in the range $50\text{--}500\text{ cm}^{-1}$ on a NICOLET MAGNA 550 FT-IR spectrometer using polyethylene pellets at SAIF, IIT, Bombay, India. Electronic spectra were recorded on a

Cary 5000 version 1.09 UV-VIS- NIR spectrophotometer using solutions in DMF. Magnetic measurements were made in the polycrystalline state on a vibrating sample magnetometer using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The EPR spectra of polycrystalline samples at 298 K and DMF solution at 77 K were recorded on a Varian E-112 X-band EPR spectrometer with 100- kHz field modulation and g factors were quoted relative to the standard marker TCNE ($g = 2.00277$).

2.2 Synthesis of the ligands

2-Hydroxyacetophenone-N(4)-cyclohexyl and N(4)-phenyl thiosemicarbazones (H_2L^1 and H_2L^2) were synthesized by the methods reported by us earlier^{12,13} (Scheme S1, Supplementary Information).

2.3 Synthesis of the Cu(II) complexes

2.3a $[(\text{CuL}^1)]_2$ (**1**) and $[(\text{CuL}^2)]_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**): These complexes were synthesized by refluxing an ethanolic solution of the corresponding thiosemicarbazones { H_2L^1 (0.291 g, 1 mmol) for **1** and H_2L^2 (0.285 g, 1 mmol) for **2**} with an aqueous solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.199 g, 1 mmol) for 4 h. The complexes formed were filtered, washed with ethanol and finally with ether and dried over P_4O_{10} *in vacuo*. X-ray quality single crystals of the compound **1** were obtained by slow evaporation of its solution in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ mixture over 2 weeks.

- (**1**): Found (calc) % : C, 51.09 (51.05); H, 5.39 (5.43); N, 11.80 (11.91); μ (B.M.) = 1.15
- (**2**): Found (calc) % : C, 51.46 (51.27); H, 4.00 (3.87); N, 11.73(11.96); μ (B.M.) = 1.39

2.3b $[\text{Cu}(\text{HL}^1)\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**3**), $[\text{Cu}(\text{HL}^1)\text{Br}] \cdot 4\text{H}_2\text{O}$ (**4**) and $[\text{Cu}(\text{HL}^1)\text{NO}_3] \cdot \text{C}_2\text{H}_5\text{OH}(\text{H}_2\text{O})$ (**5**): These complexes were synthesized by refluxing an ethanolic solution of H_2L^1 (1.72 mmol, 0.50 g) with an aqueous solution of corresponding copper salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.50 g, 2.92 mmol), CuBr_2 (0.50 g, 2.24 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (0.50 g, 2 mmol), respectively for 4 h. The complexes formed were filtered, washed with ethanol and finally with ether and dried over P_4O_{10} *in vacuo*.

- (**3**): Found (calc) %: C, 42.03 (42.35); H, 6.00 (5.69); N, 9.37 (9.88); μ (B.M.) = 1.68
- (**4**): Found (calc) %: C, 36.15 (35.61); H, 5.43 (5.58); N, 8.44 (8.31); μ (B.M.) = 1.69
- (**5**): Found (calc) % : C, 42.07 (42.53); H, 5.69 (5.88); N, 11.69 (11.67); μ (B.M.) = 1.69

2.3c $[\text{CuL}^1\text{dmbipy}] \cdot \frac{1}{2}\text{H}_2\text{O}$ (**6**), $[\text{CuL}^2\text{dmbipy}] \cdot 3\text{H}_2\text{O}$ (**7**), $[\text{CuL}^2\text{bipy}] \cdot \text{H}_2\text{O}$ (**8**) and $[\text{CuL}^2\text{phen}] \cdot 2\text{C}_2\text{H}_5\text{OH}$ (**9**). These complexes were synthesized by refluxing an ethanolic solution of H_2L^1 (0.291 g, 1 mmol)/ H_2L^2 (0.285 g, 1 mmol) and heterocyclic bases, 4,4'-dimethyl-2,2'-bipyridine, dmbipy (0.184 g, 1 mmol) (complexes **6** & **7**), 2,2'-bipyridine, bipy (0.156 g, 1 mmol) (complex **8**) and 1,10-phenanthroline, phen (0.198 g, 1 mmol) (complex **9**) with an aqueous solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.199 g, 1 mmol) for 4 h. The complexes formed were filtered, washed with ethanol and finally with ether and dried over P_4O_{10} *in vacuo*.

- (**6**): Found (calc) %: C, 59.23 (59.37); H, 5.88 (5.91); N, 12.95 (12.82); μ (B.M.) = 1.67
- (**7**): Found (calc) %: C, 55.02 (55.42); H, 4.62 (5.34); N, 12.34 (11.97); μ (B.M.) = 1.91
- (**8**): Found (calc) %: C, 57.20 (57.62); H, 4.28 (4.45); N, 13.26 (13.44); μ (B.M.) = 1.77
- (**9**): Found (calc) %: C, 59.83 (60.13); H, 5.07 (5.37); N, 11.90 (11.31); μ (B.M.) = 1.82

The structures of complexes (**1–9**) are presented in Scheme 1.

2.4 X-ray crystallography

A brown block crystal of the compound **1** having approximate dimensions of $0.35 \times 0.30 \times 0.30 \text{ mm}^3$ was sealed in a glass capillary. The crystallographic data and structure refinement parameters for the complex **1** at 293(2) K are given in Table 1.

The X-ray diffraction data for the compound were collected at 293(2) K. Data acquisition and cell refinement were done using the Argus (Nonius, MACH3 software).¹⁴ The Maxus software package (Nonius) was used for data reduction.¹⁴ The structure was solved by direct methods and full-matrix least-squares refinement using SHELXL-2014/7 package.¹⁵ The positions of all the non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELX97 program and all the hydrogen atoms were fixed in ideal positions isotropically. The two cyclohexylamino groups are disordered. The cyclohexyl amino group (N6-C24-C29) is disordered over two sites with relative occupancies of 0.505(6) and 0.495(6) for the A and B components whereas the other group (N3-C9-C14) is disordered over three sites with relative occupancies of 0.536(3), 0.239(3) and 0.225(3) for the A, B and C components respectively. SAME, SIMU, SADI and SUMP instructions were used to restrain the disordered groups. The refinement

converged to a final R value of 0.0554 ($wR_2 = 0.1123$ for 11122 reflections) [$I > 2\sigma(I)$]. The molecular structure of the compound **1** is plotted using the program Diamond Version 3.2k.¹⁶

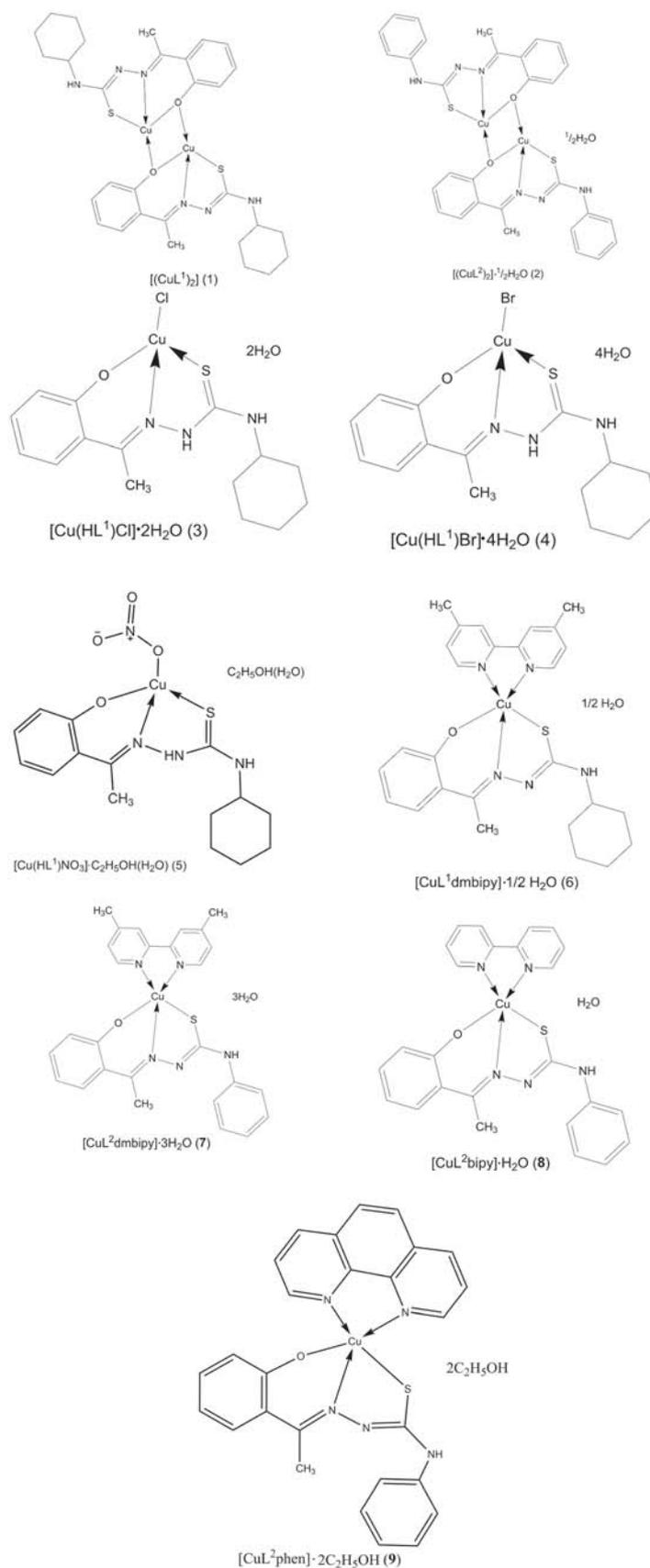
3. Results and Discussion

3.1 Crystal structure of the compound $[(\text{CuL}^1)_2]$ (**1**)

There are some disorders in this compound and are remodeled by using the SHELXL program. Compound **1** got crystallized in triclinic space group $P\bar{1}$. The asymmetric unit of this compound is depicted in Figure 1. There are two binuclear complex molecules in the asymmetric unit. The selected bond lengths and bond angles of the molecule are summarized in Table 2. The two individual dimers are arranged parallel to each other and the consequence arrangements of these molecules a sheet-like structure is formed along b axis (Figure S1, Supplementary Information).

The compound **1** is binuclear with two molecules in the asymmetric unit. The two cyclohexylamino groups of one molecule are disordered with one to two positions and the other three. The coordination geometry around each Cu centre is distorted square planar through Cu–O–Cu bridging. This bridging is through the phenoxy oxygen atoms of the two ligands. The three atoms O(1), N(1) and S(1) of the doubly deprotonated thiosemicarbazone ligand occupy the same plane and lie at 0.339(5), 0.101(5) Å and 0.074(2), respectively and the Cu(1) atom lies 0.084(1) Å out of this plane in the direction of the oxygen atom, O(2), from the other ligand. The basal plane, Cu(1)–O(1)–Cu(2)–O(2) (plane 1), shows a tetragonal distortion with a mean plane deviation of 0.7551 Å, with Cu(1) above the mean plane. Similarly, in the other copper atoms [Cu(2), Cu(3) and Cu(4)].

The copper atom {Cu(1)} in $[(\text{CuL}^1)_2]$ (**1**) is four coordinated by azomethine nitrogen, N(1), thiolato sulfur, S(1), and by two phenolato oxygen atoms, O(1) and O(2). The other three copper atoms {Cu(2), Cu(3) and Cu(4)} have a similar type of coordination. There are no acetate counterions, indicating loss of both the –OH and ^{-2}NH hydrogens. All the four Cu–O, Cu–S and Cu–N bond distances of $[(\text{CuL}^1)_2]$ are in the same range of other polynuclear Cu(II) thiosemicarbazone complexes.¹⁷ Cu–Cu non-bonding distances are similar in the two dimers with values of Cu(1)–Cu(2)=2.9434(13) and Cu(3)–Cu(4)=2.9401(14). The C–S bond distance [C(8)–S(1)] in compound (**1**) exhibits the value of 1.748(7) Å which is longer than



Scheme 1. Chemical drawings of all the complexes (1–9).

Table 1. Crystal data and structure refinement parameters for $[(\text{CuL}^1)_2]$ (**1**).

Parameters	$[(\text{CuL}^1)_2]$ (1)
Empirical formula	$\text{C}_{60}\text{H}_{76}\text{Cu}_4\text{N}_{12}\text{O}_4\text{S}_4$
Formula weight	1411.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 13.042(3)$ Å $b = 14.182(3)$ Å $c = 18.865(4)$ Å $\alpha = 103.69(3)^\circ$ $\beta = 107.10(3)^\circ$ $\gamma = 96.90(3)^\circ$
Volume	$3172.1(13)$ Å ³
Z	4
Density (calculated)	1.478 Mg/m ³
Absorption coefficient	1.510 mm ⁻¹
F(000)	1464
Crystal size	$0.35 \times 0.30 \times 0.30$ mm ³
θ range for data collection	1.179 to 24.990°
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 0$, $-21 \leq l \leq 22$
Reflections collected	11614
Independent reflections	11172 [R(int) = 0.0464]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11122 / 930 / 955
Goodness-of-fit on F^2	0.979
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0554$, $wR_2 = 0.1123$
R indices (all data)	$R_1 = 0.1947$, $wR_2 = 0.1451$
Largest diff. peak and hole	0.498 and -0.484 e.Å ⁻³

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

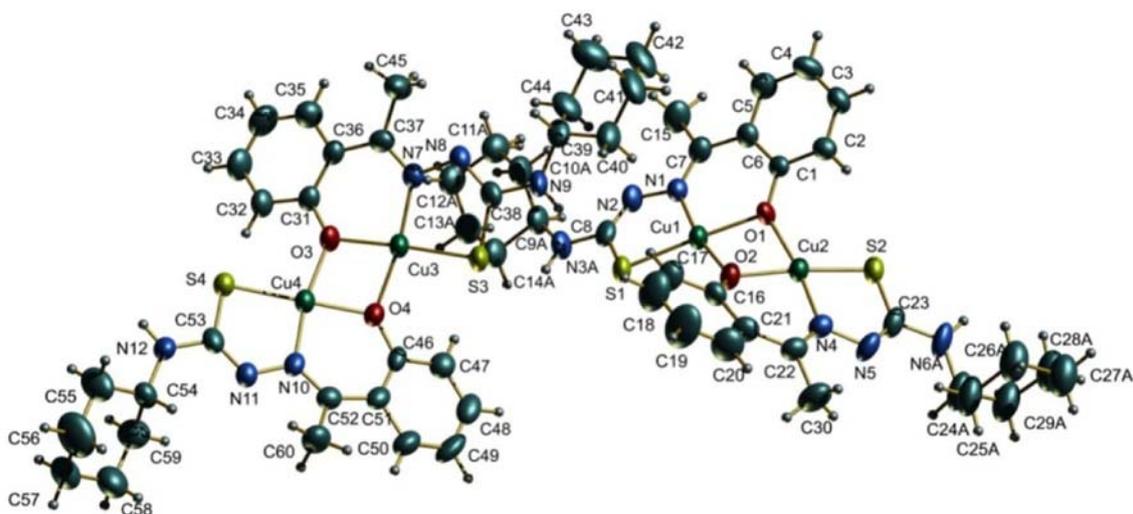
**Figure 1.** Asymmetric unit of $[(\text{CuL}^1)_2]$ (**1**). Only the major disordered parts are shown.

Table 2. Selected bond lengths (Å) and bond angles (°) for the compound **1**.

Bond lengths		
Cu(1)–N(1) 1.924(5)	Cu(3)–S(3) 2.2094(19)	N(1)–C(7) 1.301(8)
Cu(1)–O(1) 1.920(4)	Cu(1)–Cu(2) 2.9434(13)	N(1)–N(2) 1.403(7)
Cu(1)–O(2) 1.978(4)	Cu(3)–Cu(4) 2.9401(14)	N(4)–C(22) 1.297(8)
Cu(1)–S(1) 2.2099(18)	Cu(4)–O(4) 1.906(4)	N(4)–N(5) 1.388(7)
Cu(2)–O(2) 1.918(4)	Cu(4)–N(10) 1.939(5)	N(10)–C(52) 1.311(8)
Cu(2)–N(4) 1.939(5)	Cu(4)–O(3) 1.998(4)	N(11)–C(53) 1.297(8)
Cu(2)–O(1) 1.976(4)	Cu(4)–S(4) 2.2122(18)	N(11)–N(10) 1.398(7)
Cu(2)–S(2) 2.1955(19)	S(4)–C(53) 1.744(7)	N(7)–C(37) 1.310(8)
Cu(3)–O(3) 1.914(4)	S(1)–C(8) 1.748(7)	N(7)–N(8) 1.396(7)
Cu(3)–N(7) 1.926(5)	S(2)–C(23) 1.728(7)	
Cu(3)–O(4) 1.965(4)	S(3)–C(38) 1.757(7)	
Bond angles		
N(1)–Cu(1)–O(1) 91.9(2)	N(4)–Cu(2)–O(1) 170.0(2)	N(7)–Cu(3)–S(3) 88.39(17)
N(1)–Cu(1)–O(2) 168.0(2)	O(2)–Cu(2)–S(2) 171.69(15)	O(4)–Cu(3)–S(3) 99.65(13)
O(1)–Cu(1)–O(2) 78.00(17)	N(4)–Cu(2)–S(2) 87.87(18)	O(4)–Cu(4)–N(10) 93.2(2)
N(1)–Cu(1)–S(1) 88.66(16)	O(1)–Cu(2)–S(2) 102.06(13)	O(4)–Cu(4)–O(3) 76.54(18)
O(1)–Cu(1)–S(1) 176.41(15)	O(3)–Cu(3)–N(7) 94.8(2)	N(10)–Cu(4)–O(3) 168.72(19)
O(2)–Cu(1)–S(1) 101.79(13)	O(3)–Cu(3)–O(4) 77.15(18)	O(4)–Cu(4)–S(4) 178.67(15)
O(2)–Cu(2)–N(4) 92.2(2)	N(7)–Cu(3)–O(4) 171.47(19)	N(10)–Cu(4)–S(4) 87.94(16)
O(2)–Cu(2)–O(1) 78.07(17)	O(3)–Cu(3)–S(3) 176.76(14)	O(3)–Cu(4)–S(4) 102.39(13)

the C–S double bond distance [1.688(2) Å] in the uncomplexed ligand and this shows that the ligand is coordinated to the Cu²⁺ core in the deprotonated thiolate form.^{2,7,18} This confirms the enolization and coordination *via* thiolate form.

A comparative analysis of bond distances of compound **1** with the uncoordinated thiosemicarbazone ligand (H₂L¹) shows a slight increase in C=N bond length upon the coordination to the metal [N(1)–C(7) 1.301(8)] and in the N–N bond length [N(1)–N(2) 1.403(7)] as compared to a similar uncoordinated thiosemicarbazone [N(1)–C(7) and N(1)–N(2) are 1.284(2) and 1.392(2), respectively].¹⁷ This provides concrete evidence for the delocalization of electron density of the thiosemicarbazone moiety in the complex.

There are two classical bifurcated hydrogen bonding interactions between S1 with H9 and H12 of the neighboring molecules with H...A distances of 2.77 and 2.69 Å respectively, which play a major role to interconnect the dimers in the asymmetric unit and the consequent dimers build a sheet-like structure along *b* axis (Figure S1). Furthermore, there are three non-classical intramolecular hydrogen bonds [C(2)–H(2)...S(2), C(47)–H(47)...S(3) and C(32)–H(32)...S(4) with H...A distances of 2.85, 2.77 and 2.73 Å, respectively] which reinforce the rigidity of individual molecules (Figure S2, Table S1, Supplementary Information).

Figure 2 shows the contents of the unit cell along *a* axis. In this, two molecules are arranged in an opposite manner. No significant π ... π interactions are present in this compound.

3.2 Infrared spectral studies

The infrared spectral data of the complexes **1–9** are presented in Table S2 (Supplementary Information) with their tentative assignments. On the coordination of azomethine nitrogen, $\nu(\text{C}=\text{N})$ shifts to lower

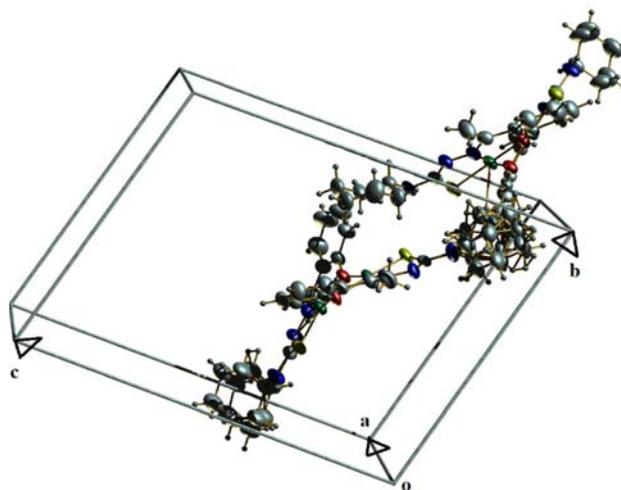


Figure 2. Unit cell packing diagram of compound **1** viewed along *a* axis.

wavenumbers by 10–20 cm^{-1} , as the band shifts from *ca.* 1608 cm^{-1} in the uncomplexed thiosemicarbazone spectrum to *ca.* 1585 cm^{-1} in the spectra of the complexes.¹⁹ Except in complexes **3**, **4** and **5**, in all other Cu(II) complexes, another strong band is found in the 1525–1545 cm^{-1} region, which may be due to the newly formed $\nu(\text{C}=\text{N})$ bond, resulting from enolization of the thiosemicarbazone ligands. In complexes **3**, **4** and **5**, the thiosemicarbazone is coordinated in the thioketo form. Coordination of azomethine nitrogen is confirmed with the presence of new bands in the range 420–470 cm^{-1} , assignable to $\nu(\text{Cu}-\text{N})$ for these complexes.²⁰ The $\nu(\text{N}-\text{N})$ bands of the thiosemicarbazones were found at 1111 and 1160 cm^{-1} in H_2L^1 and H_2L^2 . The increase in the frequency of this band in the spectra of the complexes is due to the increase in the bond strength, again confirms the coordination *via* the azomethine nitrogen.²⁰

In all the complexes, phenolic oxygen is coordinated to copper by loss of the $-\text{OH}$ proton. The $\nu(\text{OH})$ bands (3308 cm^{-1} for H_2L^1 and 3440 cm^{-1} for H_2L^2) of the free ligands disappear on complex formation which supports coordination through deprotonated phenolate oxygen. The thiosemicarbazone bands at $\sim 1279 \text{ cm}^{-1}$ due to $\nu(\text{C}-\text{O})$ are shifted to $\sim 1236 \text{ cm}^{-1}$ in the complexes, indicating the coordination of O. The IR spectra of the complexes **6**, **7**, **8** and **9** display bands characteristic of coordinated heterocyclic bases.^{2,5,21} Upon complexation, the stretching frequency of $\nu(\text{C}=\text{S})$ band at $\sim 840 \text{ cm}^{-1}$ in the thiosemicarbazones decreases.²² This indicates that the coordination takes place *via* thiolato sulfur atom. In complexes **3–5**, anions like Cl, Br and NO_3 are coordinated to the metal. In chloro complex **3**, the strong band observed at 297 cm^{-1} has been assigned to the terminal $\nu(\text{Cu}-\text{Cl})$ band. The $\nu(\text{Cu}-\text{Br})$ frequency is observed at 256 cm^{-1} , which is consistent with the terminal (Cu–Br) band in the bromo complex **4**.²⁰ In the nitrate complex **5**, the three bands observed at 1503, 1386 and 1079 cm^{-1} indicate the presence of nitrate group. The fact that the nitrate group is terminally bonded and unidentate in nature is understood from the separation of 117 cm^{-1} between the two highest frequency bands just mentioned above.²³ Besides, from the far IR spectrum of the complex, the band observed at 258 cm^{-1} can be assigned to $\nu(\text{Cu}-\text{ONO}_2)$ in consistence with the bands at 253–280 cm^{-1} , reported earlier for Cu– ONO_2 in metal complexes.²⁴ The presence of a new band in the 320–340 cm^{-1} range, assignable to $\nu(\text{Cu}-\text{S})$, is another indication of the involvement of sulfur coordination.

3.3 Electronic spectral and magnetic moment studies

The electronic spectra of the complexes in DMF solution are presented in Table S3 (Supplementary Information) and their representative spectra are presented in Figure S3 (Supplementary Information). Each thiosemicarbazone and its copper(II) complexes have a ring $\pi \rightarrow \pi^*$ band in the range 303–278 nm and an $n \rightarrow \pi^*$ band in the range 357–312 nm. Two ligand to metal charge transfer bands are found in the 435–385 nm range. In accordance with previous studies of copper(II) thiosemicarbazone complexes, the higher energy bands in the range 400–385 nm are assigned to $\text{S} \rightarrow \text{Cu}^{\text{II}}$ transitions.^{24,25} The bands in the 435–416 nm range are assignable to phenoxy $\text{O} \rightarrow \text{Cu}^{\text{II}}$ transitions.^{4,26} Each complex has a $d-d$ band in the range 667–555 nm, which appears as a broadband/shoulder in DMF solution. Due to the broadness of these bands, all possible d-d transitions could not be resolved.

Magnetic moments of the complexes were calculated from magnetic susceptibility measurements applying diamagnetic corrections. Mononuclear Cu(II) complexes exhibit magnetic moments in the range 1.65–1.9 B.M., which are close to the spin-only value.²⁴ The magnetic moments of tetra- and binuclear Cu(II) complexes (**1** and **2**) were found to be 1.15 and 1.39 B.M. This low magnetic moment may be attributed to the presence of a strong antiferromagnetic spin-spin interaction involving oxygen-bridged binuclear structures similar to those proposed for the Cu(II) complexes of analogous tridentate ligands.¹⁷

3.4 EPR spectral studies

The EPR spectra of compounds **1–9** in the polycrystalline state at room temperature show different types of geometrical species. The compounds **1**, **2** and **9** gave isotropic spectra with only one broad signal around $g = 2.074$. The spectra of the compounds **3**, **4**, **5**, **8** and **9** showed typical axial spectra with well-defined g_{\parallel} and g_{\perp} values around 2.157 and 2.052, respectively. The spectrum of compound **6** gave three g values indicating rhombic distortion in its geometry. The closer values of g_1 and g_2 in the compound indicate that the rhombic distortion is very small. The geometric parameter G ²⁷, which is a measure of the exchange interaction between the copper centers in the polycrystalline compound, is calculated using the equation $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ for axial spectra and $G = (g_3 - 2.0023)/(g_{\perp} - 2.0023)$ for

Table 3. EPR spectral assignments for Cu(II) complexes in polycrystalline state at 298 K and DMF solution at 77 K.

Compound	Polycrystalline state (298 K)	DMF solution (77 K)					
		g_{\parallel}	g_{\perp}	g_{av}	A_{\parallel}^a	A_{\perp}^a	A_{av}^a
[(CuL ¹) ₂] (1)	2.080 (g_{iso})	2.177	2.050	2.092	189	20	76
[Cu(HL ¹)Cl]·2H ₂ O (3)	2.173/2.053 ($g_{\parallel} / g_{\perp}$)	2.183	2.049	2.093	193	19	77
[Cu(HL ¹)Br]·4H ₂ O (4)	2.162/2.058 ($g_{\parallel} / g_{\perp}$)	2.207	2.046	2.099	186	23	77
[Cu(HL ¹)NO ₃]·C ₂ H ₅ OH(H ₂ O) (5)	2.199/2.061 ($g_{\parallel} / g_{\perp}$)	2.204	2.055	2.104	196	15	75
[CuL ¹ dmbipy]· ¹ / ₂ H ₂ O (6)	2.194/2.117/2.045 ($g_3/g_2/g_1$)	2.189	2.058	2.101	185	18	74
[(CuL ²) ₂]· ¹ / ₂ H ₂ O (2)	2.064 (g_{iso})	2.174	2.052	2.092	188	20	76
[CuL ² dmbipy]·3H ₂ O (7)	2.079 (g_{iso})	2.186	2.050	2.095	186	20	75
[CuL ² bipy]·H ₂ O (8)	2.186/2.060 ($g_{\parallel} / g_{\perp}$)	2.240	2.064	2.104	183	–	–
[CuL ² phen]·2C ₂ H ₅ OH (9)	2.066/2.030 ($g_{\parallel} / g_{\perp}$)	2.170	2.092	2.118	190	–	–

^aExpressed in units of cm⁻¹ multiplied by a factor of 10⁻⁴

Table 4. EPR bonding parameters for compounds 1–9.

Compound	G (298 K)	R	DMF solution (77 K)					
			α^2	β^2	γ^2	K_{\parallel}	K_{\perp}	f^a
[(CuL ¹) ₄] (1)	–	–	0.75	0.89	0.66	0.67	0.50	115.2
[Cu(HL ¹)Cl]·2H ₂ O (3)	3.26	–	0.76	0.86	0.88	0.66	0.67	112.8
[Cu(HL ¹)Br]·4H ₂ O (4)	2.84	–	0.77	0.94	0.72	0.73	0.68	118.5
[Cu(HL ¹)NO ₃]·C ₂ H ₅ OH (H ₂ O) (5)	3.26	–	0.80	0.91	1.09	0.73	0.75	118.3
[CuL ¹ dmbipy]· ¹ / ₂ H ₂ O (6)	2.39	0.935	0.75	0.88	0.96	0.66	0.72	118.0
[(CuL ²) ₂]· ¹ / ₂ H ₂ O (2)	–	–	0.75	0.88	0.81	0.66	0.72	115.5
[CuL ² dmbipy]·3H ₂ O (7)	–	–	0.75	0.88	0.76	0.66	0.67	117.6
[CuL ² bipy]·H ₂ O (8)	3.10	–	0.75	0.90	0.82	0.68	0.74	119.8
[CuL ² phen]·2C ₂ H ₅ OH (9)	2.20	–	0.77	0.87	1.11	0.67	0.97	114.2

^a Expressed in units of (cm)

rhombic spectra, where $g_{\perp} = (g_1 + g_2)/2$. If $G > 4.0$, the exchange interaction is negligible and if it is less than 4.0, considerable exchange interaction is indicated.²⁷ The G values of around 2.84 for the compounds **3**, **4**, **5**, **8** and **9** (for axial spectra) and for the compound **6** (rhombic spectrum) in polycrystalline state at 298 K, indicate considerable exchange interactions in the complexes. In all the copper(II) complexes, $g_{\parallel} > g_{\perp} > 2.0023$ are consistent with a $d_{x^2-y^2}$ ground state. The parameter R { $R = (g_2 - g_1)/(g_3 - g_2)$ for rhombic systems} value of 0.53 ($R < 1$) calculated for the compound **6** indicates a $d_{x^2-y^2}$ ground state of the copper(II) ion.²⁸

The EPR spectra of all the compounds in DMF solution at 77 K are axial and the hyperfine lines in the parallel region corresponding to the electron spin – nuclear spin interaction (^{63,65}Cu, $I = 3/2$). The fourth copper hyperfine line is overlapped with the high field component (g_{\perp}). In all these compounds, $g_{\parallel} > g_{\perp} > 2$ corresponding to the presence of an unpaired electron

in the $d_{x^2-y^2}$ orbital.^{28,29} Spectra in DMF solution at 77 K are simulated to their best fits using EasySpin³⁰ and EPR parameters are presented in Tables 3 and 4. EPR spectra (experimental and simulated) of the complexes **6** and **7** in DMF solution at 77 K are presented in Figure 3.

The empirical factor $f = g_{\parallel}/A_{\parallel}$ (cm⁻¹) is an index of tetragonal distortion, is calculated and found that it falls in the range 108–119 cm. This shows a medium distortion from the geometry.³¹

4. Conclusions

In this research work, new Cu(II) complexes of two N(4)-substituted thiosemicarbazones were synthesized and characterized by spectral and analytical techniques. The complexes **1** and **2** were readily formed by refluxing their respective ligands and Cu(OAc)₂·H₂O in 1:1 ratio. The complexes **3**, **4** and **5** were prepared

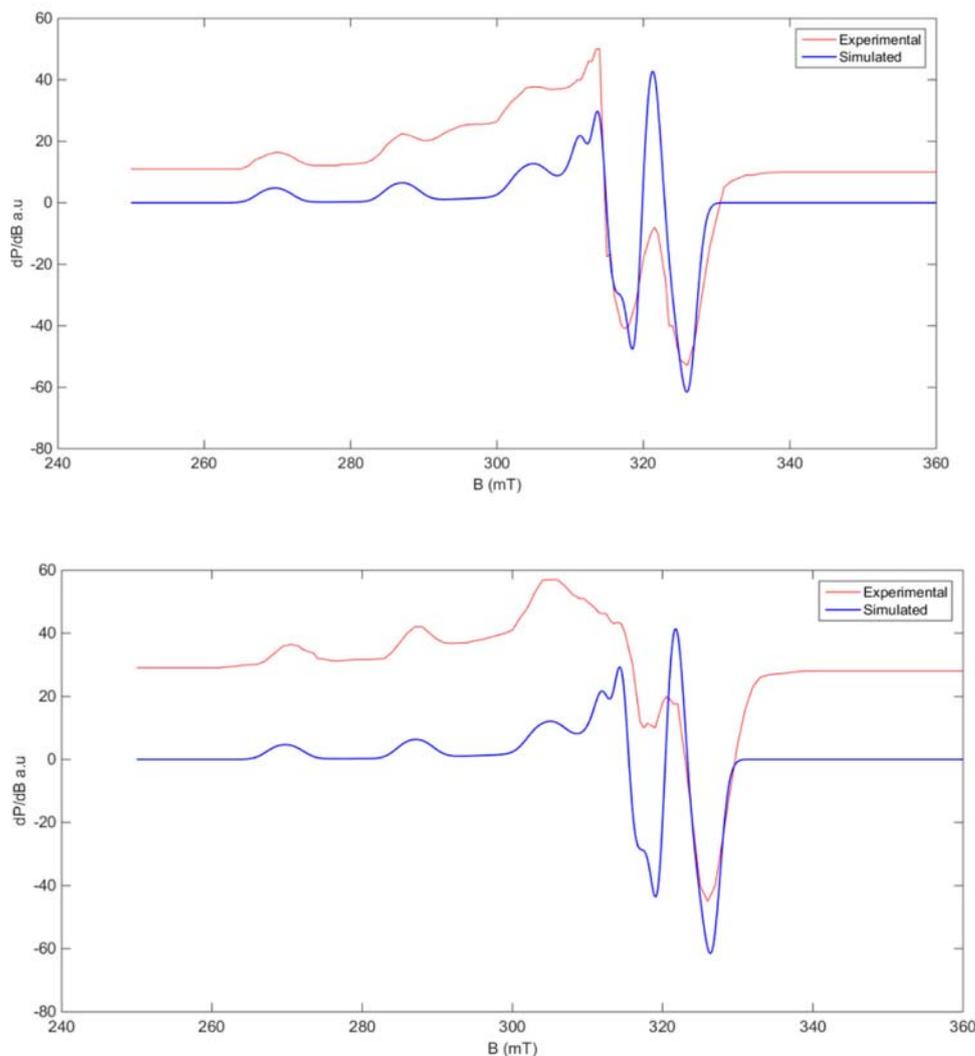


Figure 3. Experimental (red) and simulated (blue) best fit EPR spectra of the complexes $[\text{CuL}^1\text{dmbipy}] \cdot \frac{1}{2} \text{H}_2\text{O}$ (**6**) and $[\text{CuL}^2\text{dmbipy}] \cdot 3\text{H}_2\text{O}$ (**7**) in DMF at 77 K.

by refluxing the ligand H_2L^1 with $\text{CuX}_2 \cdot n\text{H}_2\text{O}$ [$\text{X} = \text{Cl}$, Br and NO_3 respectively] by taking equal amount of copper(II) salts. The complexes **6**, **7**, **8** and **9** were prepared by using their respective ligands, polypyridyl bases like dmbipy, bipy or phen and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 1:1:1 molar ratio. After double deprotonation, thiosemicarbazones coordinate as tridentate ligands in the thiolate form (L^{2-}) in all the complexes, except in complexes **3**, **4** and **5**. In complexes **3**, **4** and **5**, the ligands were coordinated as monoanionic (HL^-) forms. The partial elemental analyses and spectral studies of the complexes are in agreement with the general formula $[(\text{ML})_2]$ (for complexes **1** and **2**), complexes **3**, **4** and **5** have $[\text{M}(\text{HL})\text{X}]$ and complexes **6**, **7**, **8** and **9** have $[\text{MLB}]$. $[(\text{CuL}^1)_2]$ (**1**) is a dinuclear complex having four coordination around copper(II) with a distorted square planar geometry. Two individual dimers are present in one asymmetric unit and are

arranged parallel to each other and these molecules form a sheet-like structure.

Supplementary Information (SI)

CCDC 292101 contains the supplementary crystallographic data for $[(\text{CuL}^1)_2]$. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Figures S1–S3 and Tables S1–S3 are available at www.ias.ac.in/chemsci.

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