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Spectral and structural studies of mono- and binuclear copper(II) complexes of salicylaldehyde N(4)-substituted thiosemicarbazones

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Abstract

Three copper(II) complexes of salicylaldehyde N(4)-phenyl thiosemicarbazone (H_2L^1) and two copper(II) complexes of N(4)-cyclohexyl thiosemicarbazone (H_2L^2) have been synthesized and characterized by different physicochemical techniques like magnetic studies and electronic, infrared and EPR spectral studies. The complexes $[(CuL^1)_2]\cdot\frac{1}{2}H_2O$ (**1**) and $[(CuL^2)_2]$ (**4**) having dimeric structure. The thiosemicarbazones bind to the metal as dianionic ONS donor ligand in all the complexes, except in the complex $[Cu(HL^1)_2]\cdot H_2O$ (**2**). In complex **2**, the ligand moieties are coordinated as monoanionic (HL^-) ones. Two of the complexes $[CuL^1dmbipy]\cdot H_2O$ (**3**) and $[CuL^2dmbipy]$ (**5**) have been found to possess the stoichiometry [CuLB], where B = 4,4′-dimethyl-2,2′-bipyridine (dmbipy). The coordination geometry around copper(II) in **5** is trigonal bipyramidal distorted square based pyramidal (TBDSBP), as obtained by X-ray diffraction studies.

Keywords: Salicylaldehyde; Phenyl thiosemicarbazide; Cyclohexyl thiosemicarbazide; Copper(II) complexes; 4,4′-Dimethyl 2,2′-bipyridine; X-ray crystallography

1. Introduction

Thiosemicarbazones of aromatic *o*-hydroxyaldehydes and ketones have recently attracted considerable attention because of their potential biological properties. These aromatic thiosemicarbazones most often coordinate as the dianion on deprotonation of the ring hydroxyl group and loss of the N(2) hydrogen of the thiosemicarbazone moiety to form mononuclear as well as binuclear metal complexes. Such types of tridentate ONS donor thiosemicarbazones and their copper complexes have been studied in recent years owing to their pharmacological interest [1]. Spectral and structural studies of a series of biologically active heterocyclic base adducts of copper(II) complexes of salicylaldehyde N(4)-substituted thiosemicarbazones have been reported [2]. Similarly, the binuclear copper(II) complexes of N(4)-substituted thiosemicarbazones have also been investigated recently [3,4]. Here, we also report the synthesis, spectral, structural and EPR studies of some mono- and bi-nuclear complexes of two salicylaldehyde N(4)-substituted thiosemicarbazones.

2. Experimental

2.1. Materials

All compounds used for the synthesis of the thiosemicarbazone ligands were purified by standard methods and solvents were purified by distillation. 4,4′-Dimethyl-2,2′-bipyridine (dmbipy) (Sigma Aldrich) and $Cu(OAc)_2\cdot H_2O$ (Fluka) were used as received.

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2.2. Synthesis of the ligands and their copper(II) complexes

Salicylaldehyde N(4)-phenyl and N(4)-cyclohexyl thiosemicarbazones (H_2L^1 and H_2L^2, respectively) were synthesized by the earlier reported method [2,5] (Fig. 1).

2.2.1. $[(CuL^1)_2] \cdot \frac{1}{2}H_2O$ (**1**)

This complex was synthesized by refluxing an ethanolic solution of H_2L^1 (1 mmol, 0.271 g) with an aqueous solution of $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 0.1996 g) for 4 h. The complex formed was filtered, washed with ethanol and finally with ether and dried over P_4O_{10} in vacuo.

2.2.2. $[Cu(HL^1)_2] \cdot H_2O$ (**2**)

This complex was synthesized by refluxing an ethanolic solution of H_2L^1 (2 mmol, 0.542 g) with an aqueous solution of $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 0.1996 g) for 4 h. The complex formed was filtered, washed with ethanol and finally with ether and dried over P_4O_{10} in vacuo.

2.2.3. $[CuL^1dmbipy] \cdot H_2O$ (**3**)

This complex was synthesized by refluxing an ethanolic solution of H_2L^1 (1 mmol, 0.271 g) and heterocyclic base dmbipy (1 mmol, 0.184 g) with an aqueous solution of $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 0.1996 g) for 4 h. The complex formed was filtered, washed with ethanol and finally with ether and dried over P_4O_{10} in vacuo.

2.2.4. $[(CuL^2)_2]$ (**4**)

This complex was prepared by a similar method of the complex **1** by using H_2L^2.

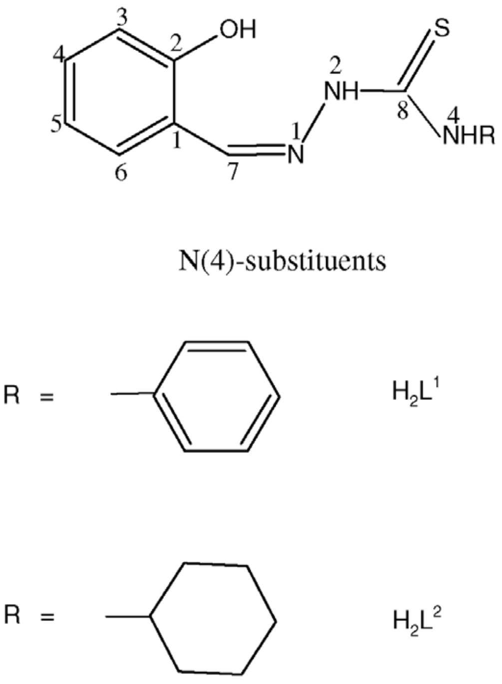

Fig. 1. Formulae of thiosemicarbazone ligands.

2.2.5. $[CuL^2dmbipy]$ (**5**)

The complex **5** was prepared by a similar method of the complex **3** by using H_2L^2.

2.3. Physical measurements

Elemental analyses were performed on a Vario ELIII elemental analyzer at SAIF, Cochin University of Science and Technology, Kochi 22, India. Magnetic susceptibility measurements were performed on a Vibrating Sample Magnetometer using $Hg[Co(SCN)_4]$ as a calibrant. Diamagnetic corrections for various atoms and structural units were computed from Pascal's constants. The FT-IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS FTIR spectrometer using KBr pellets in the range 4000–400 cm^{-1} at SAIF, Cochin University of Science and Technology, Kochi 22, India and far IR spectra were recorded in the range 500–50 cm^{-1} on a Nicolet Magna 550 FT-IR spectrophotometer using polyethylene pellets at SAIF, IIT, Bombay, India. Electronic spectra of the ligands and the complexes were recorded on a GENESYS™ 10 Series spectrophotometers in DMF solvent. The EPR spectra were recorded on a Varian E-112 spectrometer using TCNE as the standard at SAIF, IIT, Bombay, India.

2.4. X-ray crystallography

A dark green crystal of the compound **5** having approximate dimensions 0.35 × 0.30 × 0.30 mm was sealed in a

Table 1
Crystal data and structure refinement parameters for $[CuL^2dmbipy]$

Empirical formula	$C_{26}H_{29}CuN_5OS$
Formula weight	523.14
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	25.6690(19)
b (Å)	14.4860(8)
c (Å)	15.6400(10)
α (°)	90
β (°)	95.678(6)
γ (°)	90
Volume (Å^3)	5787.1(7)
Z	8
D_{calc} (Mg/m^3)	1.201
Absorption coefficient (mm^{-1})	0.851
F(000)	2184
Crystal size (mm)	0.35 × 0.30 × 0.30
θ Range for data collection (°)	2.03–24.98
Index ranges	$0 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 17$, $-18 \leqslant l \leqslant 18$
Reflections collected	5160
Independent reflections [R_{int}]	5041 [0.0361]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5041/0/313
Goodness-of-fit on F^2	0.981
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1291$
R indices (all data)	$R_1 = 0.1830$, $wR_2 = 0.1619$
Largest difference in peak and hole (e A^{-3})	0.401 and −0.320

glass capillary. The X-ray diffraction data were measured at room temperature (293 K), data acquisition and cell refinement were done using the Argus (Nonius, MACH3 software) [6]. The Maxus software package (Nonius) was used for data reduction [7]. The structure was solved by direct methods and full-matrix least-squares refinement using SHELX 97 [8] package. The positions of all the non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELX 97 program and all the hydrogen atoms were fixed in calculated positions. There were two potentially solvent accessible areas that can be spotted by PLATON [9]. However, we could not figure out any chemically reasonable solvent molecules in the void. Hence program SQUEEZE had been applied and the new file formed has been without solvent molecule. The structure of the compound **5** was plotted using the program DIAMOND Version 3.0 [10]. The final refinement cycle was based on all 5041 independent reflections and 313 variables, the $R_1 = 0.0586$, $wR_2 = 0.1291$. The crystallographic data and structure refinement parameters for the complex at 293 K are given in Table 1.

3. Results and discussion

3.1. Synthesis of the complexes

The complexes **1** and **4** were readily formed by refluxing ethanolic solutions of their respective ligand and Cu-$(OAc)_2 \cdot H_2O$ in 1:1 ratio. The complex **2** was formed by using the ligand H_2L^1 and $Cu(OAc)_2 \cdot H_2O$ in 1:2 ratio. The complexes **3** and **5** were prepared by adding their respective ligands, metal salt and polypyridyl base 4,4′-dimethyl 2,2′-bipyridine (dmbipy) in 1:1:1 ratio. After double deprotonation, thiosemicarbazones coordinate as tridentate ligands in the thiolate form (L^{2-}) in all the complexes, except in complex **2**. In complex **2**, it is coordinated as monoanionic (HL^-) form. The elemental analyses of the complexes are in agreement with the general formula $[(ML)_2]$ (for complexes **1** and **4**); $[M(HL)_2]$ (for complex **2**) and [MLB] (for the complexes **3** and **5**) (Table 2). An X-ray quality single crystal of the compound **5** was obtained by slow evaporation of its ethanol solution over a period of 7 days.

Magnetic moments of the complexes were calculated from magnetic susceptibility measurements. The complexes **2**, **3** and **5** exhibit magnetic moments in the range 1.5–1.9 BM, which are close to the spin-only value. The magnetic moments of the complexes **1** and **4** at room temperature were found to be at ca. 1.25 BM. This low magnetic moments may arise due to the antiferromagnetic spin-spin interaction between the neighboring Cu(II) centers [11].

3.2. X-ray diffraction studies of the compound [CuL^2dmbipy]

The molecular structure of the compound **5** along with atom numbering scheme is given in Fig. 2 and selected bond lengths and bond angles are summarized in Table 3. Compound **5** crystallizes in the monoclinic space group $C2/c$. The copper atom in [CuL^2dmbipy] (**5**) is coordinated by phenolato oxygen, O(1), azomethine nitrogen, N(1), thiolato sulfur, S(1), of the thiosemicarbazone and the pyridine nitrogen, N(4) and N(5) of bipyridine derivative and is having an approximately trigonal bipyramidal geometry in which the equatorial positions are occupied by S(1), O(1) and N(5) and the axial positions by N(1) and N(4) [Cu(1)–N(1), 1.951(4) Å, Cu(1)–N(4), 2.016(4) Å] with the N(1)–Cu(1)–N(4) angle of 177.94(16)° being close to the ‘ideal’ value of 180° which is usual for such systems. In a five-coordinate system, the angular structural parameter (τ) is

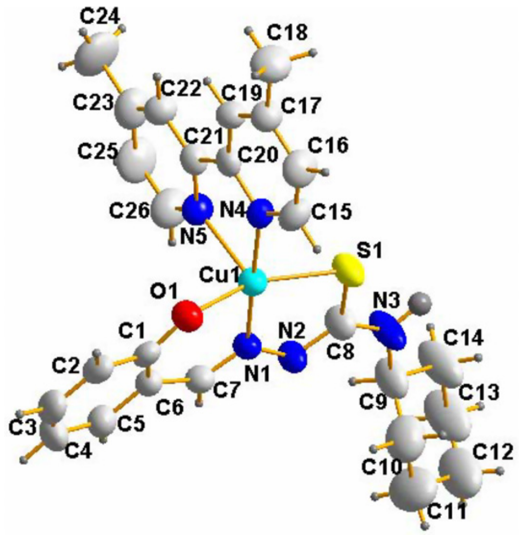

Fig. 2. Structure and labelling scheme for [CuL^2dmbipy].

Table 2
Analytical data of the ligands and their Cu(II) complexes

Compound	Colour	μ_{eff} (BM)	Calculated (found) %		
			C	H	N
H_2L^1	yellow		61.97(62.21)	4.83(5.13)	15.49(15.50)
$[(CuL^1)_2] \cdot \frac{1}{2}H_2O$ (**1**)	brown	1.24	49.84(49.80)	3.44(3.32)	12.46(13.03)
$[Cu(HL^1)_2] \cdot H_2O$ (**2**)	brown	1.51	54.05(54.54)	4.21(4.20)	13.51(13.50)
[CuL^1dmbipy] $\cdot H_2O$ (**3**)	green	1.72	58.36(58.08)	4.71(4.79)	13.09(12.98)
H_2L^2	white		59.65(59.48)	6.97(7.06)	14.91(14.95)
$[(CuL^2)_2]$ (**4**)	brown	1.25	49.61(49.43)	5.06(5.23)	12.40(12.22)
[CuL^2dmbipy] (**5**)	green	1.82	59.69(60.57)	5.59(6.12)	13.39(12.72)

Table 3
Selected bond lengths (Å) and bond angles (°) for [CuL^{2}dmbipy]

Bond lengths			
Cu(1)–N(1)	1.951(4)	C(3)–C(4)	1.372(8)
Cu(1)–S(1)	2.272(15)	O(1)–C(1)	1.301(6)
Cu(1)–N(4)	2.016(4)	N(1)–N(2)	1.387(5)
Cu(1)–O(1)	1.965(3)	N(4)–C(15)	1.330(7)
N(3)–C(8)	1.343(7)	N(5)–C(26)	1.315(8)
C(1)–C(2)	1.404(7)	C(2)–C(3)	1.381(8)
C(4)–C(5)	1.372(8)	S(1)–C(8)	1.732(6)
Cu(1)–N(5)	2.226(5)	C(5)–C(6)	1.396(7)
N(1)–C(7)	1.291(6)	N(2)–C(8)	1.325(6)
N(3)–C(9)	1.467(7)	N(4)–C(20)	1.366(6)
N(5)–C(21)	1.352(6)	C(1)–C(6)	1.429(7)
Bond angles			
N(1)–Cu(1)–O(1)	92.28(16)	O(1)–Cu(1)–N(4)	89.94(15)
O(1)–Cu(1)–N(5)	96.36(16)	N(1)–Cu(1)–S(1)	84.88(13)
N(4)–Cu(1)–S(1)	93.41(12)	C(8)–S(1)–Cu(1)	94.53(19)
C(7)–N(1)–N(2)	113.5(4)	N(2)–N(1)–Cu(1)	122.3(3)
C(8)–N(3)–C(9)	124.2(5)	C(15)–N(4)–Cu(1)	124.5(4)
C(26)–N(5)–C(21)	117.5(5)	C(21)–N(5)–Cu(1)	112.5(4)
O(1)–C(1)–C(6)	124.0(5)	C(3)–C(2)–C(1)	122.2(6)
C(1)–C(6)–C(7)	122.9(5)	N(2)–C(8)–S(1)	125.6(4)
N(3)–C(9)–C(14)	109.9(5)	N(1)–Cu(1)–N(4)	177.94(16)
N(1)–Cu(1)–N(5)	102.14(18)	N(4)–Cu(1)–N(5)	77.23(18)
O(1)–Cu(1)–S(1)	156.71(12)	N(5)–Cu(1)–S(1)	106.84(12)
C(1)–O(1)–Cu(1)	125.6(3)	C(7)–N(1)–Cu(1)	124.0(4)
C(8)–N(2)–N(1)	112.2(4)	C(15)–N(4)–C(20)	116.4(4)
C(20)–N(4)–Cu(1)	119.1(4)	C(26)–N(5)–Cu(1)	130.1(4)
O(1)–C(1)–C(2)	119.6(5)	C(2)–C(1)–C(6)	116.4(5)
C(5)–C(6)–C(7)	117.6(5)	N(1)–C(7)–C(6)	126.3(5)
N(3)–C(8)–S(1)	117.4(4)	N(3)–C(9)–C(10)	111.1(6)

used to propose an index of trigonality. The value of τ is defined by an equation represented by $\tau = (\beta - \alpha)/60$, where β is the greatest basal angle and α is the second greatest angle; τ is 0 for rectangular pyramidal forms and 1 for trigonal bipyramidal forms [12,13]. However, in the case of the five-coordinate system, the structure varies from near regular trigonal bipyramidal (RTB) to near square based pyramidal (SBP). The value of τ for the compound **5** is 0.35, indicates that the coordination geometry around Cu(II) is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP) [14] with copper displaced 0.2174 Å above the N(1), N(4), S(1) and O(1) coordination plane and towards the elongated apical N(5) atom, at a larger distance of 2.226(5) Å. This value is larger than the normal Cu–N bond lengths reported [15,16]. One of the reasons for the deviation from an ideal stereochemistry is the restricted bite angle imposed by both the L^{2-} and dmbipy ligands. The bite angle around the metal viz, N(4)–Cu(1)–N(5) of 77.23(18)° may be considered normal, when compared with an average value of 77° cited in the literature [17–19]. The O(1)–Cu(1)–N(5) bond angle, 96.36(16), and S(1)–Cu(1)–N(5) bond angle, 106.84(12), indicate a slight tilting of the axial Cu(1)–N(5) bond in the direction of the O(1)–Cu(1) bond and away from S(1)–Cu(1) bond. The dihedral angle formed by the least square plane Cg(4) and Cg(5) is 6.13° for the compound **5**. Ring puckering analyses and least-square plane calculations show that the Cg(3) ring comprising of atoms Cu(1), O(1), C(1), C(6), C(7) and N(1) adopts a screw-boat conformation and Cg(7) ring comprising of atoms C(9), C(10), C(11), C(12), C(13) and C(14) adopts a chair conformation.

Fig. 3 shows the contents of the unit cell along the *b* axis. The assemblage of molecules in the respective manner in the unit cell is resulted by the H bonding, π–π and CH–π interactions as depicted in Table 4. The centroid Cg(4) is involved in π–π interaction with pyridyl ring of the neighboring unit at the distance of 3.7197 Å, the CH–π interactions of the rings Cg(6) and Cg(1) with the neighboring molecules and also intermolecular hydrogen bonding interactions between N(3)–H(3N) and S(1) contribute stability to the unit cell packing.

3.3. IR and electronic spectra

The infrared spectral data of the complexes **1**–**5** are presented in Table 5 with their tentative assignments. On coordination of azomethine nitrogen, *ν*(C═N) shifts to lower wavenumbers by 10–20 cm^{-1}, as the band shifts from 1613 cm^{-1} in the uncomplexed thiosemicarbazone spectrum to ca. 1596 cm^{-1} in the spectra of the complexes. In all the five Cu(II) complexes, another strong band is found at ca. 1530–1555 cm^{-1}, which may be due to the newly formed *ν*(N═C) bond, resulting from enolization of the principal thiosemicarbazone ligand. Coordination of azomethine nitrogen is confirmed with the presence of new bands in the range 420–470 cm^{-1}, assignable to *ν*(Cu–N) for these complexes. For complexes **1**–**5**, *ν*(Cu–N) bands are at ca. 427 cm^{-1}. The *ν*(N–N) of the thiosemicarbazones H$_2$L^1 and H$_2$L^2 are found at 1149 and 1111 cm^{-1} respectively. The increase in the frequency of this band in the spectra of the complexes, due to the increase in the bond strength, again confirms the coordination *via* the azomethine nitrogen [20]. The decrease in the stretching frequency of C–S bond from ca. 865 cm^{-1} in the thiosemicarbazones by 50–70 cm^{-1} upon complexation indicates coordination *via* its thiolate sulfur. The presence of a new band in the 320–340 cm^{-1} range assignable to *ν*(Cu–S), is another indication of the involvement of sulfur coordination. In all the five complexes, except in the complex **2**, phenolic oxygen coordinated to copper by loss of the OH proton. A new band in the range 380–395 cm^{-1} in the spectra of the complexes **3** and **5** are assignable to *ν*(Cu–O). The IR spectra of the complexes **3** and **5** display bands characteristic of coordinated heterocyclic base [21].

The electronic spectra of the complexes in DMF solution are presented in Table 6. Each thiosemicarbazone and its copper(II) complexes have a ring π → π* bands in the range 32 000–38 000 cm^{-1} and n → π* bands in the range 28 000–32 000 cm^{-1}. Two ligand to metal charge transfer bands are found in 24 000–28 000 cm^{-1} range. In accordance with studies of previous copper(II) thiosemicarbazone complexes [22,23], the higher energy bands in the range 26 000–27 000 cm^{-1} is assigned to S → Cu^{II} transitions. The bands in the

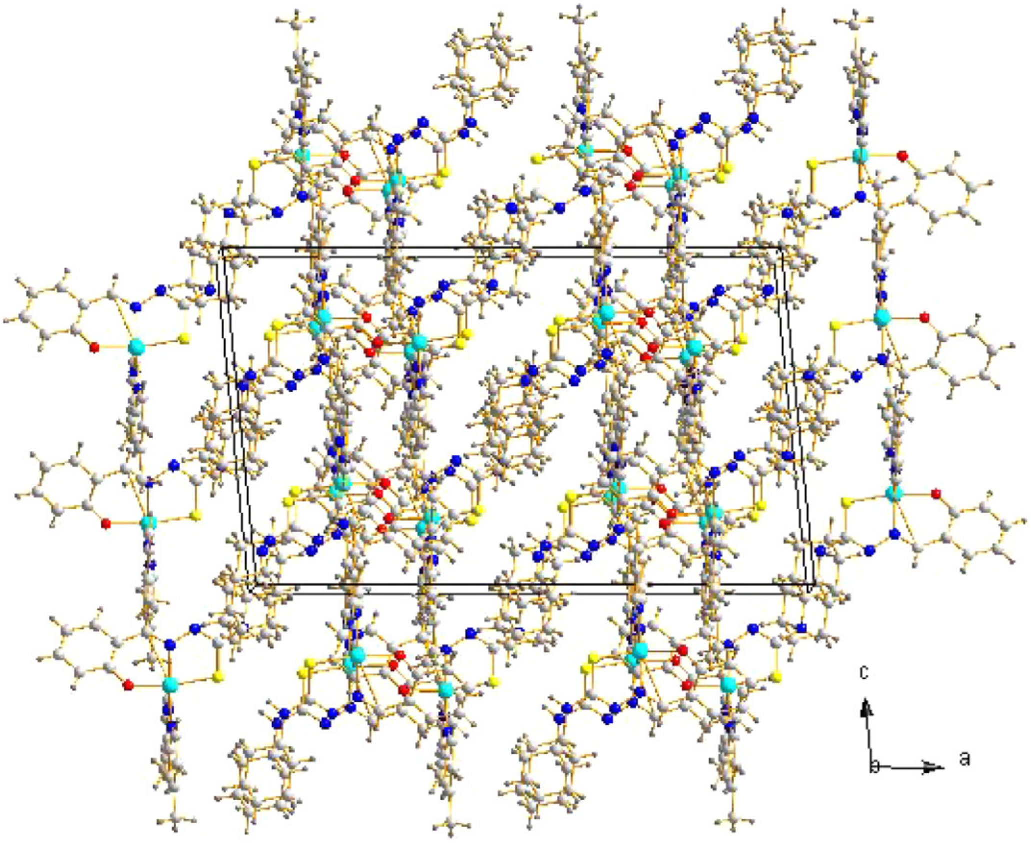

Fig. 3. Unit cell packing diagram of the complex [CuL^{2}dmbipy] viewed along the *b* axis.

Table 4
Interaction parameters of the compound [CuL^{2}dmbipy]

Cg(I)–Res(1)–Cg(J)	Cg–Cg (Å)	α (°)	β (°)	
π–π interactions				
Cg(4) [1] → Cg(5)^a	3.7197	6.13	22.51	
Cg(5) [1] → Cg(4)^a	3.7197	6.13	21.67	
XH(I)–Cg(J)	H···Cg (Å)	X–H···Cg (°)	X···Cg (Å)	
CH–π interactions				
C(18)–H(18)[1] → Cg(6)^b	2.90	176	3.8605	
C(18)–H(18) [1] → Cg(1)^c	2.96	138	3.7250	
C(25)–H(25) [1] → Cg(6)^d	2.97	165	3.8788	
D–H–A	D–H	H–A	D–A	D–H–A
H bonding				
N(3)–H(3N)–S(1)	0.94	2.62	3.5310	165

Equivalent position codes: a = $1/2-x$, $1/2-y$, $-z$. Cg(4) = N(4), C(15), C(16), C(17), C(19), C(20); Cg(5) = N(5), C(21), C(22), C(23), C(25), C(26).
Equivalent position codes: b = $1/2-x$, $1/2-y$, $-z$; c = x, $1-y$, $-1/2+z$; d = $1/2-x$, $-1/2+y$, $1/2-z$.
D, donor; A, acceptor; Cg, centroid, α, dihedral angles between planes I and J, β = angle Cg(1)–Cg(J).

24000–25000 cm^{-1} range are assignable to phenoxy O → Cu^{II} transitions [24]. Each complex has a d–d combination band in the range 14000–16000 cm^{-1}, which appears as a weak shoulder on the intraligand and charge transfer bands.

3.4. EPR spectra

The EPR parameters obtained for the compounds in the polycrystalline state at 298 K and in DMF solution at 77 K are presented in Tables 7 and 8.

The EPR spectra of compounds **1**–**5** in the polycrystalline state at room temperature shows different types of geometrical species. The compounds **1**, **3** and **4** show isotropic spectra with only one broad signal at $g = 2.059$, 2.070 and 2.129, respectively. Spectrum of compound **2** gives three g values indicating rhombic distortion in its geometry. The values g_1 and g_2 are very close to each other in compound **2**, which means that the rhombic distortion is very small. The spectrum of the compound **5** shows a typical axial one with well-defined $g_\parallel$ and $g_\perp$ values at 2.195 and 2.063, respectively. The geometric parameter G, 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 for rhombic spectra $G = (g_3 - 2.0023)/(g_\perp - 2.0023)$, where $g_\perp = (g_1 + g_2)/2$. If $G < 4.0$ considerable exchange interaction is indicated in the solid complex [25,26]. The G value for the compounds **2** and **5** in polycrystalline state at 298 K are 3.55 and 3.17, respectively. In all the copper(II) complexes $g_\parallel > g_\perp > 2.0023$ and G values within the range 2.5–4.0 are consistent with a $d_{x^2-y^2}$ ground state.

Table 5
IR spectral assignments for ligands and their Cu(II) complexes

Compound	ν(C=N)	ν(N=C)	ν(N–N)	ν(Cu–N)	ν/δ (C=S)	ν(C–O)	Bands due to heterocyclic base
H_2L^1	1613		1149		1328, 874	1255	
$[(CuL^1)_2]\cdot\frac{1}{2}H_2O$ (**1**)	1594	1555	1153	428	1314, 843	1201	
$[Cu(HL^1)_2]\cdot H_2O$ (**2**)	1599	1540	1153	431	1314, 750	1201	
$[CuL^1dmbipy]\cdot H_2O$ (**3**)	1596	1537	1150	420	1313, 828	1247	1434, 753, 697
H_2L^2	1614		1111		1328, 856	1263	
$[(CuL^2)_2]$ (**4**)	1594	1546	1149	421	1272, 818	1196	
$[CuL^2dmbipy]$ (**5**)	1596	1530	1146	439	1313, 823	1233	1476, 753, 627

Table 6
Electronic spectral assignments for the ligands and their Cu(II) complexes

Compound	π–π^*	n–π^*	LMCT	d–d
H_2L^1	32250	29060		
$[(CuL^1)_2]\cdot\frac{1}{2}H_2O$ (**1**)	33110	31055	27240, 26240	15520
$[Cu(HL^1)_2]\cdot H_2O$ (**2**)	33780	30950, 30300	25970	15640
$[CuL^1dmbipy]\cdot H_2O$ (**3**)	37730, 35080	30950, 30120	25380, 24690	14160
H_2L^2	32150	28730		
$[(CuL^2)_2]$ (**4**)	33000	31250	26310, 24630	16180
$[CuL^2dmbipy]$ (**5**)	34010	31050, 30120	25900, 25120	15430

Table 7
EPR spectral assignments for Cu(II) complexes in polycrystalline state at (298 K) and 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]
$[(CuL^1)_2]\cdot\frac{1}{2}H_2O$ (**1**)	2.059 (g_{iso})	2.195	2.053	2.100	184.5	19.1	71.9
$[Cu(HL^1)_2]\cdot H_2O$ (**2**)	2.030/2.040/2.120 ($g_1/g_2/g_3$)	2.191	2.053	2.099	184.1	14.4	68.6
$[CuL^1dmbipy]\cdot H_2O$ (**3**)	2.070 (g_{iso})	2.169	2.063	2.098	189.0		
$[(CuL^2)_2]$ (**4**)	2.129 (g_{iso})	2.177	2.045	2.089	182.3	14.3	68.1
$[CuL^2dmbipy]$ (**5**)	2.195/2.063 ($g_{\parallel}/g_{\perp}$)	2.167	2.056	2.093	190.5		

[a] Expressed in units of cm^{-1} multiplied by a factor of 10^{-4}.

Table 8
EPR bonding parameters for compounds **1**–**5**

Compound	DMF solution (77 K)									
	G (77 K)	α^2	β^2	γ^2	K	$K_{\parallel}$	$K_{\perp}$	f[a]	P	R[b]
$[(CuL^1)_2]\cdot\frac{1}{2}H_2O$ (**1**)	3.66	0.76	0.88	0.89	0.33	0.67	0.68	119.01	0.0235	
$[Cu(HL^1)_2]\cdot H_2O$ (**2**)	3.59	0.76	0.86	0.90	0.33	0.66	0.69	119	0.0240	0.125
$[CuL^1dmbipy]\cdot H_2O$ (**3**)	2.69	0.75	0.78	0.94		0.59	0.71	114.8		
$[(CuL^2)_2]$ (**4**)	3.89	0.73	0.87	0.86	0.31	0.65	0.64	119.4	0.0236	
$[CuL^2dmbipy]$ (**5**)	2.98	0.75	0.81	0.93		0.61	0.70	114		

[a] Expressed in units of (cm).

[b] Parameter $R = (g_2 - g_1)/(g_3 - g_2)$.

The parameter R {$R=(g_2 - g_1)/(g_3 - g_2)$ for rhombic systems} calculated for the compound **2** is 0.125, i.e., $R < 1$, indicating a $d_{x^2-y^2}$ ground state of the copper(II) ion [27,28]. From the g value of a transition metal complex, we can obtain very important information about the structure of the complex.

The EPR spectra of all the compounds in frozen DMF solution at 77 K are axial. Moreover, they show well defined four 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 expected to overlap with the high field component ($g_{\perp}$). However, the half field signal corresponding to the dimer was not observed for the compounds **1** and **4**. 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 [29,30]. For a Cu(II) complex, $g_{\parallel}$ is a parameter sensitive enough to indicate covalence. For a covalent complex, $g_{\parallel} < 2.3$. Here also,

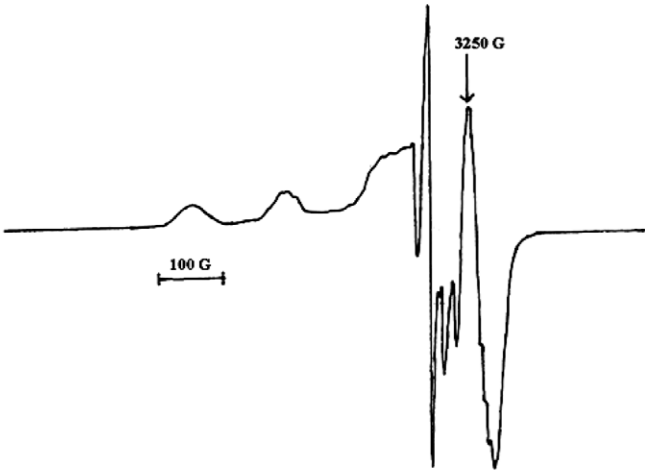

Fig. 4. EPR spectra of the compound **4** in DMF solution (at 77 K).

all the five complexes are covalent in nature. In solution at 77 K, $g_{\|}$ values (2.16–2.19) are almost the same for all the compounds, which indicate similar bonding nature in all of them [31]. In compound **4**, well resolved spectra with four copper hyperfine lines and three superhyperfine lines due to the azomethine nitrogen are observed in DMF (Fig. 4).

The EPR parameters $g_{\|}$, $g_{\perp}$, g_{av}, $A_{\|}$(Cu) and $A_{\perp}$(Cu) and energies of d–d transitions were used to evaluate the bonding parameters α^2, β^2 and γ^2, which may be regarded as measures of covalency of the in-plane σ bonds, in-plane π bonds and out-of-plane π bonds, respectively [32].

The value of in-plane σ bonding parameter α^2 was estimated from the expression [33,34],

$$\alpha^2 = -A_{\|}/0.036 + (g_{\|} - 2.00277) + 3/7(g_{\perp} - 2.00277) + 0.04$$

The following simplified expressions were used to calculate the bonding parameters [35,36]:

$$K_{\|}^2 = (g_{\|} - 2.00277)E_{\mathrm{d\text{–}d}}/8\lambda_0$$
$$K_{\perp}^2 = (g_{\perp} - 2.00277)E_{\mathrm{d\text{–}d}}/2\lambda_0$$

where $K_{\|} = \alpha^2\beta^2$ and $K_{\perp} = \alpha^2\gamma^2$, $K_{\|}$ and $K_{\perp}$ are orbital reduction factors and λ_0 represents the one electron spin–orbit coupling constant which equals $-828\ \mathrm{cm}^{-1}$.

Hathaway [37] pointed out that, for pure σ bonding, $K_{\|} \approx K_{\perp} \approx 0.77$, and for in-plane π bonding, $K_{\|} < K_{\perp}$; while for out-of-plane π bonding $K_{\perp} < K_{\|}$. In all the complexes it is observed that $K_{\|} < K_{\perp}$which indicates the presence of significant in-plane π bonding. The values of the bonding parameters α^2, β^2 and $\gamma^2 < 1.0$ (value of 1.0 for 100% ionic character) indicate significant in-plane π bonding and in-plane σ bonding.

The Fermi contact hyperfine interaction term K may be obtained from [38]

$$K = A_{\mathrm{iso}}/P\beta^2 + (g_{\mathrm{av}} - 2.00277)/\beta^2$$

where P is the free ion dipolar term and its, value is 0.036. K is a dimensionless quantity, which is a measure of the contribution of s electrons to the hyperfine interaction and is generally found to have a value of 0.30. The K values obtained for all the complexes are in good agreement with those estimated by Assour [39] and Abragam and Pryce [40]. The empirical factor $f = g_{\|}/A_{\|}$ (cm^{-1}), is an index of tetrahedral distortion. In all the five compounds, f falls in the range 114–119 cm corresponding to a copper(II) center with medium distortion [41].

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Appendix A. Supplementary material

CCDC 279223 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.040.

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