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Copper(II) complexes of *N*(4)-substituted thiosemicarbazones derived from pyridine-2-carbaldehyde: Crystal structure of a binuclear complex

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Abstract

Ten copper(II) complexes {[CuL^{1}Cl] (**1**), [CuL^{1}NO$_3$]$_2$ (**2**), [CuL^{1}N$_3$]$_2$ · 2/3H$_2$O (**3**), [CuL^1]$_2$(ClO$_4$)$_2$ · 2H$_2$O (**4**), [CuL^{2}Cl]$_2$ (**5**), [CuL^{2}N$_3$] (**6**), [Cu(HL^2)SO$_4$]$_2$ · 4H$_2$O (**7**), [Cu(HL^2)$_2$] (ClO$_4$)$_2$ · 1/2EtOH (**8**), [CuL^{3}Cl]$_2$ (**9**), [CuL^{3}NCS] · 1/2H$_2$O (**10**)} of three NNS donor thiosemicarbazone ligands {pyridine-2-carbaldehyde-*N*(4)-*p*-methoxyphenyl thiosemicarbazone [HL^1], pyridine-2-carbaldehyde-*N*(4)-2-phenethyl thiosemicarbazone [HL^2] and pyridine-2-carbaldehyde *N*(4)-(methyl), *N*(4)-(phenyl) thiosemicarbazone [HL^3]} were synthesized and physico-chemically characterized. The crystal structure of compound **9** has been determined by X-ray diffraction studies and is found that the dimer consists of two square pyramidal Cu(II) centers linked by two chlorine atoms.

Keywords: Thiosemicarbazone; Cu(II) complex; Pyridine-2-carbaldehyde; Crystal structure

1. Introduction

The coordination chemistry involving heterocyclic thiosemicarbazones has been interesting research area in the last 30 years because of their well-documented biological activities. Thiosemicarbazone derivatives have considerable antibacterial, antimalarial, antiviral and antitumor activities [1]. Complexation of such thiosemicarbazone ligands with metal ions has been found to produce synergistic effects on the antiproliferative activities of the parent ligands [2]. It has been reported that copper(II) complexes of heterocyclic *N*(4)-substituted thiosemicarbazones exercise bio-activity through a mechanism involving either inhibition of the enzyme ribonucleotide reductase, or creation of lesions in DNA strands. Studies have also shown that, for these ligands, nature of substitution on the terminal N(4) atom is crucial for the antifungal activity [3].

Pyridine-2-carbaldehyde thiosemicarbazone was the first α-(*N*)-heterocyclic carboxaldehyde thiosemicarbazone, reported to have carcinostatic effects [4]. This thiosemicarbazone ligand coordinates to the metal ions in both the anionic (L$^-$) and neutral (HL) forms. The anionic L$^-$ form is usually present in [CuLX]$_2$ dimers in which, the metal centers can either be bridged through the thiolate sulfur or the non-thiosemicarbazone co-ligand X (X = Cl, N$_3$, NCS, etc.) [5]. It is reported that the formation of complexes with S-bridge or X-bridge depends on the nature of the non-thiosemicarbazone ligands. However, the actual underlying reasons for the formation of S- over X-bridged systems are not clear to date [6]. On the basis of these findings, the present communication reports on the optimal conditions for synthesis of ten copper(II) complexes with three ligands, viz., pyridine-2-carbaldehyde *N*(4)-paramethoxyphenyl thiosemicarbazone (HL^1), pyridine-2-carbaldehyde *N*(4)-phenethyl thiosemicarbazone (HL^2) and pyridine-2-carbaldehyde *N*(4)-methyl *N*(4)-phenyl thiosemicarbazone (HL^3) and their characterization

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by physicochemical methods, together with X-ray crystal structure of one of the copper compounds, viz. $[CuL^3Cl]_2$.

2. Experimental

2.1. Materials

Pyridine-2-carbaldehyde (Aldrich), 2-phenylethylamine (Fluka) and *p*-anisidine (Fluka) were used as received. The metal salts copper(II) nitrate trihydrate, copper(II) chloride dihydrate, copper(II) acetate monohydrate, copper(II) perchlorate hexahydrate, copper(II) sulphate pentahydrate, sodium azide and potassium thiocyanate (Merck) were used as supplied. 4-Methyl-4-phenyl-3-thiosemicarbazide was prepared as reported previously [7] and solvents were purified by standard procedures before use. *Caution!* Azide and perchlorate complexes of metals with organic ligands are potentially explosive and should be handled with care.

2.2. Synthesis of ligands

The thiosemicarbazones were obtained by adopting and modifying a reported procedure of Scovill et al. [7]. The synthesis and crystal structure of HL^1 have been published earlier [8]. The structure of the three ligands are given in Scheme 1.

2.2.1. Synthesis of HL^1 and HL^3

HL^1 was synthesized by refluxing a solution of 1.00 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide in 5 ml of MeCN with 0.679 g (5.52 mmol) of 4-methoxyaniline (*p*-anisidine) and 0.591 g (5.52 mmol) of pyridine-2-carbaldehyde for 1.5 h. HL^3 was synthesized by a similar procedure without the addition of an amine. The solutions were chilled (overnight) and the crystals that formed were collected and washed well with MeCN. The compounds were recrystallized from ethanol and dried *in vacuo* over P_4O_{10}.

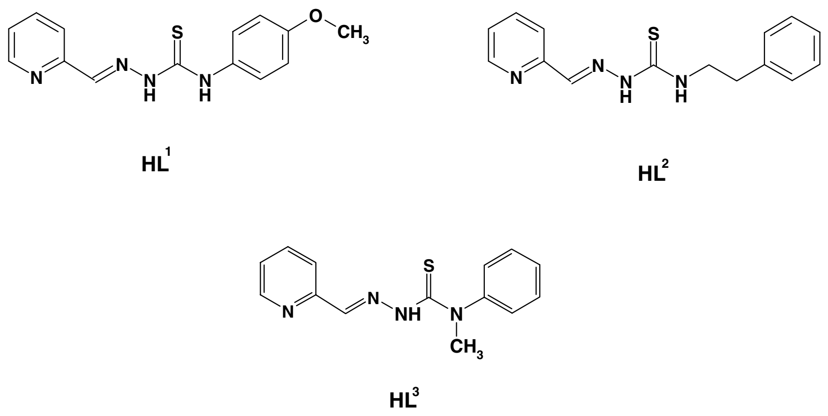
We have reported the syntheses of ligands HL^1 and HL^3 along with the crystal structure of HL^3 recently [9].

2.3. Synthesis of complexes

Refluxing/stirring of alcoholic solution of the ligand with the alcoholic/ aqueous alcoholic solution of the corresponding copper salt yielded the compounds **1**, **2**, **4**, **5**, **7**, **8** and **9** whereas compounds **3**, **6** and **10** were prepared by the metathetical displacement of acetate ion by azide and thiocyanate ion, respectively. Complexes **1**, **5** and **9** were synthesized by refluxing (1 h) 1.5 mmols each of the respective ligands dissolved in 20 ml hot ethanol with 1 mmol of $CuCl_2 \cdot 2H_2O$. In a similar method, complexes **4** and **8** were synthesized by using respective ligands and $Cu(ClO_4)_2 \cdot 6H_2O$ whereas complex **2** was obtained by stirring a hot solution of HL^1 (1.5 mmol) in ethanol (20 ml) with $Cu(NO_3)_2 \cdot 3H_2O$ (1.5 mmol). For the synthesis of **3**, **6** and **10**, the acetate complexes were first prepared by refluxing (15 min) 1.5 mmols each of the respective ligands dissolved in 20 ml hot ethanol with 1.5 mmol of $Cu(OAc)_2 \cdot H_2O$ and the acetate ion was then displaced by azide ion (**3**, **6**) and thiocyanate ion (**10**) by using NaN_3 and KCNS, respectively. The complex **7** was prepared by refluxing (4 h) a mixture of HL^2 (1.5 mmol) and $CuSO_4 \cdot 5H_2O$ (1.5 mmol) in a mixture of ethanol (20 ml) and water (20 ml). Upon evaporation of the solvent, the complexes were precipitated as green or brown solids. The complexes formed were filtered, washed with water, ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.4. Physical measurements

Elemental analyses of the ligand and the complexes were done on a Heracus elemental analyzer at CDRI, Lucknow, India, and on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR Spectrophotometer with KBr pellets at SAIF, Kochi. Electronic spectra were recorded on a Cary 5000, version 1.09 UV–Vis–NIR Spectrophotometer from a solution in $CHCl_3$. The EPR spectra of the complexes were recorded on a Varian E-112 Spectrometer using TCNE as the standard at SAIF, IIT, Bombay, India. The magnetic susceptibility



Scheme 1. The thiosemicarbazones HL^1, HL^2 and HL^3.

measurements were carried out at the Indian Institute of Technology, Roorkee, India, at room temperature in the polycrystalline state on a PAR model 155 Vibrating sample magnetometer at 5 kOe field strength. The molar conductances of the complexes in dimethylformamide solutions (10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

2.5. X-ray crystallography

Single crystals of compound **9** of X-ray diffraction quality were grown from its methanol solution by slow evaporation at room temperature in air. The crystallographic data and structure refinement parameters are given in Table 1. The data were collected using a CrysAlis CCD, Oxford Diffraction Ltd., version 1.171.29.2 with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation on a triclinic single crystal of dimension 0.25 × 0.20 × 0.20 mm with $P\bar{1}$ symmetry at the National Single Crystal X-ray Diffraction Facility, IIT, Bombay, India. The unit cell dimensions and intensity data were measured at 293 K. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The trial structure was solved using SHELXS-97 [10] and refinement was carried out by full-matrix least squares on F^2 (SHELXL) [10]. Molecular graphics employed were ORTEP-III [11] and PLATON [12].

Table 1
Crystal refinement parameters of compound **9**

Parameters	$[CuL^3Cl]_2$ (**9**)
Empirical formula	$C_{28}H_{26}Cl_2Cu_2N_8S_2$
Formula weight (M)	736.71
Temperature (T) K	293(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Lattice constants	
a (Å)	9.2246(18)
b (Å)	9.468(3)
c (Å)	10.714(3)
α (°)	69.41(2)
β (°)	83.157(17)
γ (°)	59.45(2)
V (Å^3)	752.3(3)
Z	1
(ρ_{calc}) (Mg m^{-3})	1.626
Absorption coefficient, μ (mm^{-1})	1.765
F(000)	374
Crystal size (mm)	0.25 × 0.20 × 0.20
θ Range for data collection (°)	3.16–30.14
Limiting indices	$-13 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$
Reflections collected	10909
Independent reflections (R_{int})	4439 (0.0185)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4439/0/190
Goodness-of-fit on F^2	0.987
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0708$
R indices (all data)	$R_1 = 0.0428$, $wR_2 = 0.0743$
Largest difference peak and hole (e Å^{-3})	0.410 and −0.215

3. Results and discussion

In all the compounds except **7** and **8** the thiosemicarbazones deprotonate and chelate in thiolate form as evidenced by the IR spectra. The elemental analyses suggest the general empirical formula [CuLX] where X = Cl, NO_3, N_3, ClO_4 and NCS for complexes except **7** and **8**, but the complex **7** turned out to be $[Cu(HL)SO_4]$ and complex **8** to be $[Cu(HL)_2](ClO_4)_2$ with the perchlorate ion out of the coordination sphere. The complexes are appreciably soluble in methanol, ethanol, DMF and DMSO.

The colors, partial elemental analyses, molar conductivities and magnetic susceptibilities of the metal complexes are shown in Table 2. The green and brown colors are common to complexes involving thiosemicarbazone coordination due to the sulfur-to-metal charge-transfer bands, which dominate their visible spectra [13]. The molar conductivity values of the compounds **1**, **2**, **3**, **5**, **6**, **7**, **9** and **10** in 10^{-3} M solution in DMF show that they are nonconductors [14] indicating that the anion and the ligand are coordinated to the central copper(II). But the molar conductivity values of compounds **4** and **8** suggest that they are 2:1 electrolytes. The magnetic susceptibilities at room temperature per copper atom of the complexes except **6**, **8** and **10** suggest interaction between metal centers [15].

3.1. Crystal structure of $[CuL^3Cl]_2$ (9)

The molecular structure of the compound **9** along with atom numbering scheme are given in Fig. 1. The asymmetric unit is formed by one half of the molecule and the other half is related by a center of inversion in the Cu(1)–Cl(1)–Cu(1a)–Cl(1a) ring. The coordination geometry at each Cu(II) is square pyramidal. The ligand HL^3 coordinates the metal in a tridentate manner through its pyridyl nitrogen, azomethine nitrogen and thiolate sulfur, after enolization and deprotonation, to form the basal plane along with one chlorine atom. The basal chlorine atom takes the axial position of the adjacent monomer like its counterpart to result in two distorted square pyramids. The Cu–Cu separation is found to be 3.5330(11) Å. The τ value [16] of 0.139 at metal centers indicates slight distortion from perfect square pyramidal geometry. Thus, the two metal centers are bridged via chlorine atoms resulting in the formation of four five membered rings in which one copper atom is shared by two fused rings. A four membered ring involving the copper atoms and the chlorine atoms is also formed. The five membered ring Cu(1), N(1), C(5), C(6), N(2) is approximately planar with a maximum deviation of 0.0135(18) Å for C5, but Cu(1), N(2), N(3), C(7), S(1) ring is slightly distorted as evidenced by the maximum deviation of 0.1349(18) Å for C7; likewise for their counterpart rings. The four membered ring Cl(1), Cu(1), Cl(1a), Cu(1a) makes an angle of 83.62(3)° with the mean plane of bicyclic

Table 2
Colors, partial elemental analyses, magnetic susceptibilities and molar conductivities of the complexes

Compound	Color	Found (Calc.)%				μ (BM)	Λ_M[a]
		C	H	N	S		
$[CuL^1Cl]$ (**1**)	Brown	43.65(43.75)	3.48(3.41)	14.32(14.58)	8.20(8.34)	1.54	5
$[CuL^1NO_3]_2$ (**2**)	Green	41.12(40.92)	3.17(3.19)	16.97(17.04)	16.97(17.04)	1.14	51
$[CuL^1N_3]_2 \cdot 2/3H_2O$ (**3**)	Brown	42.36(42.36)	3.18(3.47)	24.83(24.70)	8.10 (8.08)	1.39	18
$[CuL^1]_2(ClO_4)_2 \cdot 2H_2O$ (**4**)	Brown	35.85 (36.06)	3.31(3.24)	11.84(12.01)	6.76 (6.88)	0.86	160
$[CuL^2Cl]_2$ (**5**)	Green	47.54(47.12)	4.01(3.95)	14.88(14.65)	8.35 (8.39)	0.99	6
$[CuL^2N_3]$ (**6**)	Brown	46.43(46.32)	3.63(3.89)	25.08(25.21)	8.14(8.24)	2.14	51
$[Cu(HL^2) SO_4]_2 \cdot 4H_2O$ (**7**)	Green	37.78(37.53)	4.06(4.20)	11.42 (11.67)	13.01(13.36)	1.41	48
$[Cu(HL^2)_2] (ClO_4)_2 \cdot 1/2EtOH$ (**8**)	Green	43.73(43.81)	4.17(4.37)	13.17(12.77)	7.00(7.31)	1.74	132
$[CuL^3Cl]_2$ (**9**)	Green	45.17(45.65)	3.48(3.56)	15.26(15.21)	8.75(8.71)	1.52	7
$[CuL^3NCS] \cdot 1/2H_2O$ (**10**)	Green	44.94 (45.04)	3.13(3.53)	17.4 (17.51)	15.50(16.03)	1.74	11

[a] Molar conductivity of 10^{-3} M DMF solution, in Ω^{-1} cm^2 mol^{-1}.

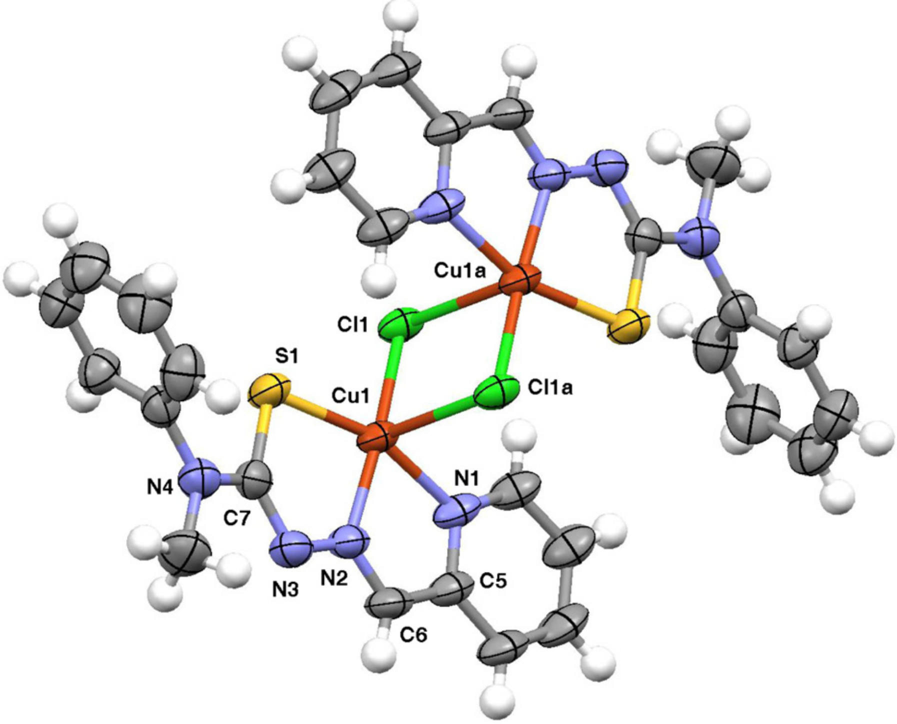


Fig. 1. ORTEP diagram of $[CuL^3Cl]_2$ (**9**) in 50% probability ellipsoids.

chelate system N(1), C(5), C(6), N(2), N(3), C(7), S(1), Cu(1) which is slightly distorted from planarity with a maximum deviation of −0.1979(18) Å for C5. Relevant bond lengths and angles are featured in Table 3. The bridging chlorine atoms are positioned at distances of 2.2587(7) Å for Cl(1) and 2.7245(12) Å for Cl(1a) and make an angle of 90.20(3)° at each metal centers and are in agreement with previous reports [17,18]. The Cu–$N_{azomethine}$ bond length [1.9784(14) Å] is lesser by 0.0541(19) Å compared to Cu–$N_{pyridine}$, indicates the strength of former bond than the latter [18,19].

The ligand HL^3 suffers a structural reorientation upon complexation. The N3 and C5 atoms were in *Z* configuration about the azomethine bond in its metal free form of ligand, is now in *E* form to coordinate the metal as NNS donor ligand. Coordination lengthens the thiosemicarbazone moiety's C(7)–S(1) bond length by 0.0645(22) Å and shortens N(3)–C(7) by 0.0384(18) Å, suggesting deprotonation after enolization. A comparison of the changes in bond lengths and angles are given in Table 3.

The molecules are packed along the *a*-axis directed by the C3–H3···Cl1 intermolecular hydrogen bonding interaction (Table 4). This intermolecular hydrogen bond links the molecules to form one-dimensional polymeric chains (Fig. 2). The aromatic π···π stacking interactions between pyridyl rings (symmetry code: 2 − *x*, 1 − *y*, 1 − *z* and a Cg–Cg distance of 3.8896 Å) reinforces crystal structure cohesion in molecular packing in the crystal lattice.

Table 3
Selected bond lengths (Å) and bond angles (°) of HL^3 and $[CuL^3Cl]_2$ (**9**)

	HL^3	$[CuL^3Cl]_2$ (**9**)
S(1)–C(7)	1.6750(14)	1.7395(18)
N(2)–C(6)	1.285(2)	1.287(2)
N(2)– N(3)	1.3613(17)	1.352(2)
N(3)–C(7)	1.3644(18)	1.326(2)
N(4)–C(7)	1.345(2)	1.352(2)
Cu(1)–S(1)		2.2481(6)
Cu(1)–N(1)		2.0325(14)
Cu(1)–N(2)		1.9784(14)
Cu(1)–Cl(1)		2.2587(7)
Cu(1)–Cl(1a)		2.7245(12)
C(6)–N(2)–N(3)	117.75(13)	121.34(14)
N(2)–N(3)–C(7)	120.25(12)	111.73(13)
N(4)–C(7)–N(3)	113.87(12)	116.42(15)
N(3)–C(7)–S(1)	122.89(12)	124.89(14)
N(4)–C(7)–S(1)	123.22(11)	118.69(13)
S(1)–Cu(1)–N(1)		162.41(5)
N(1)–Cu(1)–N(2)		80.52(6)
S(1)–Cu(1)–N(2)		83.78(5)
N(1)–Cu(1)–Cl(1)		96.93(5)
N(2)–Cu(1)–Cl(1)		170.75(4)
S(1)–Cu(1)–Cl(1)		97.32(2)
N(1)–Cu(1)–Cl(1a)		90.46(5)
N(2)–Cu(1)–Cl(1a)		98.68(5)
S(1)–Cu(1)–Cl(1a)		99.74(3)
Cl(1)–Cu(1)–Cl(1a)		90.20(3)

Table 4
H-bonding interactions in compound **9**

D–H···A	D–H (°)	H···A (°)	D···A (°)	D–H···A (Å)
C(1)–H(1)···Cl(1)[a]	0.93	2.81	3.3611	119
C(3)–H(3)···Cl(1)[b]	0.93	2.76	3.5754	148

D, donor, A, acceptor, equivalent position codes.

[a] *x*, *y*, *z*.

[b] 1+ *x*, *y*, *z*.

3.2. Infrared spectra

The IR bands most useful for the determination of the mode of coordination are presented in Table 5. The far IR assignments are shown in Table 6. The strong bands at 3310 and 3374 cm^{-1} in the spectra of HL^1 and HL^2 have been assigned to $\nu(^4N–H)$. In the complexes these bands shift to both higher and lower energies, suggesting differences in hydrogen bonding of N(4)H between the uncomplexed and complexed thiosemicarbazone [20]. A medium band in the range 3129–3158 cm^{-1} in the free ligands due to $\nu(^2N–H)$ vibration disappears in the spectra of complexes except **7** and **8**, providing a strong evidence for the ligand coordination around copper(II) ion in the deprotonated form. In the spectra of **7** and **8**, $\nu(^2N–H)$ bands appear at 3219 and 3206 cm^{-1}, respectively, but ν(S–H) band at 2570 cm^{-1} is absent showing that the ligand is in the thione form in these complexes [21]. The intense bands at 1584, 1586 and 1590 cm^{-1} in the spectra of HL^1, HL^2, and HL^3, respectively have been assigned to ν(C=N) of the thiosemicarbazone moiety. These bands are shifted to lower energies in the spectra of the complexes (1553–1573 cm^{-1}), indicating azomethine nitrogen coordination [22]. The presence of bands in the 402–415 cm^{-1} range is assigned to $\nu(Cu–N_{azomethine})$ agree well with previous studies of metal complexes of 2-formylpyridine *N*(4)-substituted thiosemicarbazones [23]. Strong bands found at 1024–1079 cm^{-1} in the ligands are assigned to the ν(N–N) band of the thiosemicarbazone. The increase in the frequency of this band in the spectra of complexes is due to the increase in the bond strength, again confirming the coordination via the azomethine nitrogen [24]. For the complexes containing the anionic ligands, a second band due to ν(N=C) is often resolved, but a number of complexes show only a single, broad band for both ν(C=N) and ν(N=C) modes [25]. The complexes **1**, **2**, **3**, **4**, **5**, **6**, **9** and **10** show bands corresponding to ν(N=C) in the range 1588–1615 $cm^{-1}$where as these bands are not present in the spectra of the complexes **7** and **8**.

The two bands appearing at the frequencies 1334, 1324 and 1307 cm^{-1} [$\nu(CS) + \nu(CN)$] and 837, 897 and 779 cm^{-1} (thioamide IV band), respectively, in the spectra of HL^1, HL^2, and HL^3 have been shifted to lower frequencies in the ranges 1289–1367 and 773–897 cm^{-1}, respectively indicating coordination of the thione/thiolato sulfur [26]. The presence of new bands in the range 323–344 cm^{-1} which is assignable to ν(Cu–S) is another indication of sulfur coordination which is found to be consistent with earlier reports [27]. Coordination of the pyridine nitrogen is indicated by a positive shift of the in-plane ring deformation band at 613, 622 and 614 cm^{-1} in the spectra of HL^1, HL^2, and HL^3 to 617–646 cm^{-1} in the spectra of the complexes. Out-of-plane ring deformation bands at 401, 406, and 421 cm^{-1} in the spectra of HL^1, HL^2 and HL^3 are also shifted to higher frequencies [28]. Pyridine nitrogen coordination is further proved by strong bands observed in the region 262–313 cm^{-1} assignable to ν(Cu–N) of pyridine ring as suggested by Clark and Williams [29]. Based on the above spectral evidences, it is confirmed that the ligands HL^1, HL^2, and HL^3 are tridentate, coordinating via the azomethine nitrogen, the pyridyl nitrogen and thione/thiolate sulfur.

The chloro complex **1** shows ν(Cu–Cl) band at 304 cm^{-1}, which is similar to its assignment for terminal chloro ligands in other thiosemicarbazone complexes [30]. In the chloro complexes **5** and **9**, the strong bands observed at 329 and 315 cm^{-1} together with bands at 162 and 164 cm^{-1} have been assigned to the ν(Cu–Cl) in a bridging mode [18]. The crystal structure of **9** confirms the presence of two bridging chlorine atoms.

The nitrato complex **2** has two strong bands at 1287 and 1412 cm^{-1} with a separation of 125 cm^{-1} corresponding to ν_1 and ν_4 and a medium band at 1016 cm^{-1} corresponding to ν_2 of the nitrato group indicating the presence of a terminal monodentate nitrato group [31]. The $\nu_1 + \nu_4$combination bands considered as diagnostic for the monocordinated nitrato group are observed at 1734 and

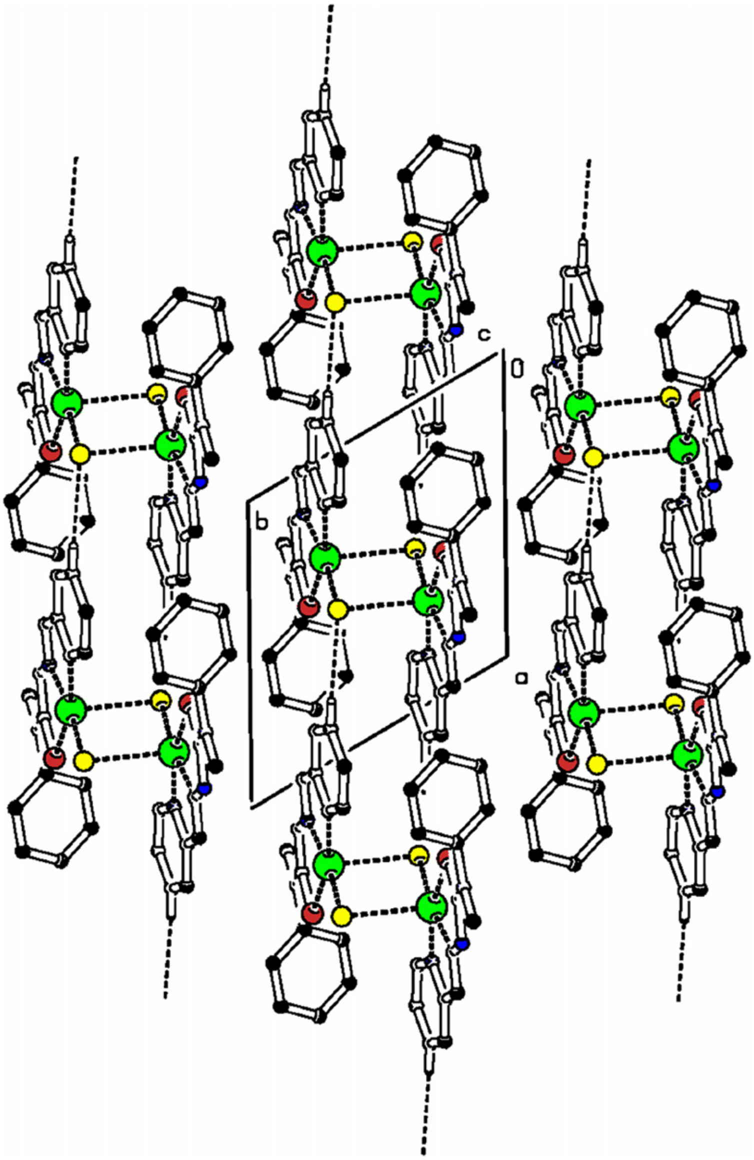


Fig. 2. A view of the unit cell packing of the molecule (**9**) showing hydrogen bonding interactions producing polymeric chains.

Table 5
Infrared spectra (cm^{-1}) of *N*(4)-substituted thiosemicarbazones and their copper complexes

Compounds	$\nu C{=}N$	$\nu N{=}C$	$\nu N–N$	$\nu/\delta C–S$	py(ip)	py(op)	$\nu^2 N–H$	$\nu^4 N–H$
HL^1	1584		1024	1334,837	613	401	3134	3310
$[CuL^1Cl]$ (**1**)	1558	1596	1133	1307,826	646	409		3340
$[CuL^1NO_3]_2$ (**2**)	1564	1597	1135	1308,830	617	417		3321
$[CuL^1N_3]_2 \cdot 2/3H_2O$ (**3**)	1561	1606	1135	1301, 829	617	413		3251
$[CuL^1]_2(ClO_4)_2 \cdot 2H_2O$ (**4**)	1560	1609	1121	1300,837	636	409		3286
HL^2	1586		1079	1324,897	622	406	3129	3374
$[CuL^2Cl]_2$(**5**)	1560	1588	1138	1335,889	628	414		3443
$[CuL^2N_3]$ (**6**)	1573	1592	1083	1313,867	626	412		3446
$[Cu(HL^2)SO_4]_2 \cdot 4H_2O$ (**7**)	1560		1165	1361,890	618	412	3219	3403
$[Cu(HL^2)_2](ClO_4)_2 \cdot 1/2EtOH$ (**8**)	1565		1139	1367, 886	635	419	3206	3330
HL^3	1590		1035	1307, 779	614	421	3158	
$[CuL^3Cl]_2$ (**9**)	1553	1615	1138	1289, 775	636	449		
$[CuL^3NCS] \cdot 1/2H_2O$ (**10**)	1558	1607	1140	1291, 773	631	453		

1749 cm^{-1}. ν_3, ν_5 and ν_6 are observed at 743, 712 and 803 cm^{-1}, respectively [32]. Besides, in the far IR spectrum of the complex, the band observed at 255 cm^{-1} can be assigned to $\nu(Cu–ONO_2)$ consistent with the bands at 253–280 cm^{-1} reported earlier for $\nu(Cu–ONO_2)$ in metal complexes [33].

Table 6
Far infrared spectra (cm^{-1}) of the copper complexes

Compound	νCu–N$_{\text{azo.}}$	νCu–N$_{\text{py}}$	νCu–S	νCu–Cl	νCu–N$_{\text{azido}}$	νCu–N$_{\text{(NCS)}}$	νCu–O$_{\text{nitrato}}$
[CuL^{1}Cl] (**1**)	415	250	325	304			
[CuL^{1}NO$_3$]$_2$ (**2**)	415	313	323				255
[CuL^{1}N$_3$]$_2$ · 2/3H$_2$O (**3**)	407	272	332		429		
[CuL^1]$_2$(ClO$_4$)$_2$ · 2H$_2$O (**4**)	412	271	325				
[CuL^{2}Cl]$_2$ (**5**)	415	275	344	329 162			
[CuL^{2}N$_3$] (**6**)	402	262	338		435		
[Cu(HL^2)SO$_4$]$_2$ · 4H$_2$O (**7**)	415	280	324				
[Cu(HL^2)$_2$](ClO$_4$)$_2$ · 1/2EtOH (**8**)	414	276	325				
[CuL^{3}Cl]$_2$ (**9**)	413	297	325	315 164			
[CuL^{3}NCS] · 1/2H$_2$O (**10**)	413	297	325			314	

The azido complexes **3** and **6** show sharp bands at 2056 and 2038 cm^{-1} and strong bands at 1243 and 1356 cm^{-1}, respectively. These are assigned to ν_a and ν_s of the coordinated azido group. The broad bands observed at 647 cm^{-1} for both complexes are assigned to δ(N–N–N). ν(Cu–N$_{\text{azido}}$) bands are observed at 446 and 435 cm^{-1}, respectively, for **3** and **6**.

The perchlorate complexes **4** and **8** show single broad bands at 1121 cm^{-1} and strong bands at 626 and 624 cm^{-1}, indicating the presence of ionic perchlorate. The bands at 1121 cm^{-1} are assignable to ν_3(ClO$_4$) and the unsplit bands at 626 and 624 cm^{-1} assignable to ν_4(ClO$_4$). In the spectrum of the compound **4**, a medium band at 926 cm^{-1} may be due to ν_1(ClO$_4$) suggesting that ionic perchlorate is distorted from tetrahedral symmetry due to lattice effects or hydrogen bonding by the NH functions of the coordinated ligand [34]. However, no band assignable to ν_1(ClO$_4$) is observable in the spectrum of compound **8**. This along with unsplit ν_3 and ν_4 bands show exclusive presence of non-coordinated perchlorate group.

For the sulfato complex **7**, strong bands at 1116 and 1028 cm^{-1} are assignable to ν_3 of the mono coordinated sulfato group. Medium bands at 939 cm^{-1} (ν_1) and 644 cm^{-1} (ν_4) further confirm the unidentate behaviour of sulfato group [31].

Thiocyanato complex **10** exhibits a strong and sharp band at 2079 cm^{-1}, a weak band at 773 cm^{-1} and another weak band at 484 cm^{-1} which can be attributed to ν(CN), ν(CS) and δ(NCS), respectively. These values are typical for N-bonded thiocyanate complexes. A medium band at 325 cm^{-1} corresponds to ν(Cu–N$_{\text{thiocyanato}}$) vibrations which is in agreement with the reported values [35].

3.3. Electronic spectra

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The tentative assignments of the significant electronic spectral bands of ligands and their copper(II) complexes are presented in Table 7. The electronic spectra in CHCl$_3$ solution of HL^1, HL^2 and HL^3 show the following intraligand absorption maxima: for HL^1, two bands corresponding to $\pi \rightarrow \pi^*$ of the pyridyl ring, benzene ring and imine function of the thiosemicarbazone moiety are observed at 42 730 and 38 760 cm^{-1}; the $n \rightarrow \pi^*$ transitions of the pyridyl ring and imine function of the thiosemicarbazone moiety are observed at 30 770 cm^{-1}; for HL^2, these bands are observed at 42 190, 36 630 and 30 960 cm^{-1}, respectively, and for HL^3 they are observed at 43 290, 38 610 and 30 840 cm^{-1} [36]. The

Table 7
Electronic spectra (cm^{-1}) of *N*(4)-substituted thiosemicarbazones and their copper complexes

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	CT	d–d
HL^1	42 730, 38 760	30 770		
[CuL^{1}Cl] (**1**)	41 840, 36 230	31 150	22 990, 27 700	16 420
[CuL^{1}NO$_3$]$_2$ (**2**)	42 190, 37 490	35 460	23 150, 27 850	14 880
[CuL^{1}N$_3$]$_2$ · 2/3H$_2$O (**3**)	42 020, 37 050	34 280	23 510	16 190
[CuL^1]$_2$(ClO$_4$)$_2$ · 2H$_2$O (**4**)	41 670, 37 880		24 040	15 290
HL^2	42 190, 36 630	30 960		
[CuL^{2}Cl]$_2$ (**5**)	42 190, 38 610	33 000	23 420, 29 150	16 230
[CuL^{2}N$_3$] (**6**)	42 120, 38 790	33 210	23 310	16 270
[Cu(HL^2) SO$_4$]$_2$ · 4H$_2$O (**7**)	41 840	33 110	23 870, 28 980	16 080
[Cu(HL^2)$_2$](ClO$_4$)$_2$ · 1/2EtOH (**8**)	42 190, 38 760	32 570	22 880	16 780
HL^3	43 290, 38 610	30 842		
[CuL^{3}Cl]$_2$ (**9**)	42 190, 38 760	32 470	23 200	16 370
[CuL^{3}NCS] · 1/2H$_2$O (**10**)	42 270, 38 620	31 440	23 760	16 150

$\pi \rightarrow \pi^*$ transitions are not significantly altered on complex formation. In the spectra of the complexes in chloroform solutions the $n \rightarrow \pi^*$ transitions associated with the pyridine ring observed above 30 000 cm^{-1} in the spectra of the thiosemicarbazones are shifted to higher energies, the blue shift indicating coordination *via* the pyridyl nitrogen [17]. Strong bands in the range 22 880–24 040 cm^{-1} observed in the spectra of all Cu(II) complexes are assigned to $S \rightarrow Cu$ and $py \rightarrow Cu$ charge-transfer bands [26]. For the chloro complexes **1** and **5**, the $Cl \rightarrow Cu(II)$ charge transfer bands are found at 27 700 and 29 150 cm^{-1}, respectively, and band at 27 850 cm^{-1} in the spectrum of nitrato complex (**2**) is attributable to nitrato $O \rightarrow Cu(II)$ ligand to metal charge transfer transition [37].

The spectra of the complexes **1**, **3**, **5**, **6**, **7**, **9** (Fig. 3) and **10** exhibit weak d–d bands centered around 16 000 cm^{-1}, that of **2** and **4** are at *ca.* 15 000 cm^{-1}. For a square planar complex with $d_{x^2-y^2}$ ground state, three transitions are possible $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ ($^2A_{1g} \leftarrow {}^2B_{1g}$, $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$) and square pyramidal complexes have the $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ transitions [38–40]. Since the four d orbitals lie very close together, each transition cannot be distinguished by their energy and hence it is very difficult to resolve the bands into separate components. The broad band observed at 16 780 cm^{-1} in the electronic spectrum of the complex **8** is assigned to $^2E_g \leftarrow {}^2T_{2g}$ transition [41,42]. However, results obtained from electronic spectra do not permit a structural diagnosis free of uncertainty.

3.4. EPR spectra

The copper(II) ion, with a d^9 configuration, has an effective spin of $S = 1/2$ and is associated with a spin angular momentum, $m_s = \pm 1/2$, leading to a doubly degenerate spin state in the absence of a magnetic field. In a magnetic field the degeneracy is lifted between these states and the energy difference between them is given by $E = h\nu = g\beta H$, where h is Planck's constant, ν is the microwave frequency for transition from $m_s = +1/2$ to $m_s = -1/2$, g is the Lande splitting factor (equal to 2.0023 for a free electron), β is the Bohr magneton and H is the magnetic field. For the case of a $3d^9$ copper(II) ion, the appropriate spin Hamiltonian assuming a B_{1g} ground state is given by

$$\widehat{H} = \beta[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y)$$

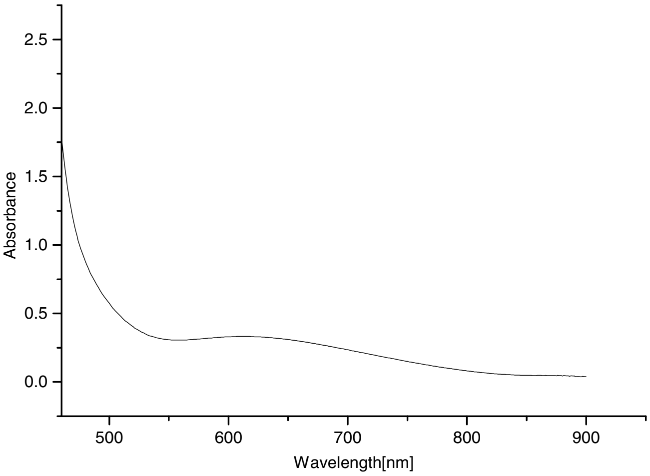


Fig. 3. Electronic spectrum of compound **9** in $CHCl_3$.

The EPR spectra of the complexes in the polycrystalline state at 298 K, in solution at 298 and 77 K were recorded in the X band, using 100 kHz field modulation and the g factors were quoted relative to the standard marker TCNE ($g = 2.00277$). EPR spectral assignments of the copper(II) complexes along with the spin Hamiltonian and orbital reduction parameters are given in Table 8.

The EPR spectra of compounds **8** and **10** in the polycrystalline state (298 K) show only one broad signal at 2.0762 and 2.0765, respectively, due to dipolar broadening and enhanced spin lattice relaxation. The spectra of the compounds **2**, **3**, **4**, **5**, **6**, **7** and **9** show typical axial behavior with slightly different $g_{\parallel}$ and $g_{\perp}$ values. The spectrum of compound **1** gives three g values *viz.* g_1, g_2 and g_3 which indicate rhombic distortion in its geometry. 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, $G = (g_3 - 2)/(g_{\perp} - 2)$ and $g_{\perp} = (g_1 + g_2)/2$. If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex [43]. In all the copper(II) complexes $g_{\parallel} > g_{\perp} > 2.0023$ and G value within the range 2.08–4.49 are consistent with a $d_{x^2-y^2}$ ground state [44]. The solution spectra of complexes were recorded in DMF at 298 K. They are isotropic in nature with well-resolved four hyperfine lines (Fig. 4). The hyperfine splitting is due to the interaction of the electron spin with the copper nuclear spin ($^{63,65}Cu$, $I = 3/2$). The spectra of all the complexes in DMF at 77 K are axial with four copper hyperfine lines in both the parallel and perpendicular regions (Fig. 5). In addition the spectra of some of the complexes show five nitrogen superhyperfine lines in the high field component. For the spectra of all the complexes in frozen DMF the $g_{\parallel} > g_{\perp}$ values rules out the possibility of trigonal bipyramidal structures for which $g_{\perp} > g_{\parallel}$ is expected. The binuclear nature of **2**, **3**, **4**, **7** and **9** was confirmed by the presence of half-field signals ($\Delta M_s = \pm 2$) at *ca.* 1600 G (Fig. 6). However, for **5**, the half-field signal at *ca.* 1600 G is not well resolved. The EPR parameters $g_{\parallel}$, $g_{\perp}$, g_{av}, $A_{\parallel}(Cu)$ and $A_{\perp}(Cu)$ and the energies of d–d transition were used to evaluate the bonding parameters α^2, β^2 and γ^2, which may be regarded as measures of the covalency of the in-plane σ bonds, in-plane π bonds, and out-of-plane π bonds, respectively. The value of in plane sigma bonding parameter α^2 was estimated from the following expression:

$$\alpha^2 = -A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

Table 8
EPR Spectral parameters of the copper(II) complexes

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Polycrystalline (298 K)										
$g_{\|}$	2.1167(g_3)	2.1769	2.1349	2.1931	2.1661	2.1635	2.1806		2.1842	
$g_{\perp}$	2.0341(g_1) 2.0746(g_2)	2.0585	2.0471	2.0501	2.0388	2.0423	2.0879		2.0533	
g_{iso} or g_{av}		2.0979	2.0764	2.0978	2.0812	2.0827	2.1188	2.0762	2.0969	2.0765
DMF (298 K)										
g_{iso}	2.081	2.0955	2.0809	2.0955	2.081	2.0809	2.0955	2.0955	2.081	2.0955
$\mathrm{A_{iso}}$	95.53	88.05	92.29	88.05	95.53	92.29	88.05	88.86	95.53	88.86
DMF (77 K)										
$g_{\|}$	2.1607	2.1787	2.1544	2.1787	2.1625	2.1563	2.1824	2.1697	2.1609	2.1679
$g_{\perp}$	2.0566	2.0585	2.0487	2.0533	2.0533	2.0504	2.0664	2.0469	2.0518	2.0549
$A_{\|}$ (Cu)[a]	186.6	195	187.75	194.9	188.5	187.92	191.9	192.5	186.63	193.99
G	2.19	3.11	2.96	3.99	4.49	4.03	2.08	3.75	3.57	3.15
α^2	0.7400	0.7822	0.7335	0.7797	0.7457	0.7366	0.7785	0.7611	0.7382	0.7670
β^2	0.8468	0.8048	0.8311	0.8184	0.8392	0.8351	0.8493	0.8556	0.8481	0.8283
γ^2	0.9916	0.9085	0.9182	0.8801	0.9479	0.9363	0.9730	0.8833	0.9476	0.9336
K	0.4184	0.4053	0.4067	0.4122	0.4203	0.4069	0.4089	0.3884	0.4141	0.4070
$K_{\|}$	0.6266	0.6295	0.6096	0.6381	0.6258	0.6151	0.6612	0.6512	0.6261	0.6353
$K_{\perp}$	0.7338	0.7106	0.6735	0.6862	0.7069	0.6897	0.7575	0.6723	0.6995	0.7161
P	0.0231	0.0251	0.0229	0.0242	0.0233	0.0207	0.0237	0.0241	0.0229	0.0239

[a] A values are given in $10^{-4}\ \mathrm{cm}^{-1}$.

Fig. 4. EPR spectrum of **8** in DMF solution at 298 K.

The orbital reduction factors $K_{\|} = \alpha^2\ \beta^2$ and $K_{\perp} = \alpha^2\gamma^2$ were calculated using the following expressions [18]:

$$K_{\|}^2 = (g_{\|} - 2.0023)\Delta E(\mathrm{d}_{xy} - \mathrm{d}_{x^2-y^2})/8\lambda_0$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E(_{\mathrm{d}_{xz,yz}} - \mathrm{d}_{x^2-y^2})/2\lambda_0$$

where λ_0 is the spin orbit coupling constant and has the value $-828\ \mathrm{cm}^{-1}$ for a copper(II) d^9 system.

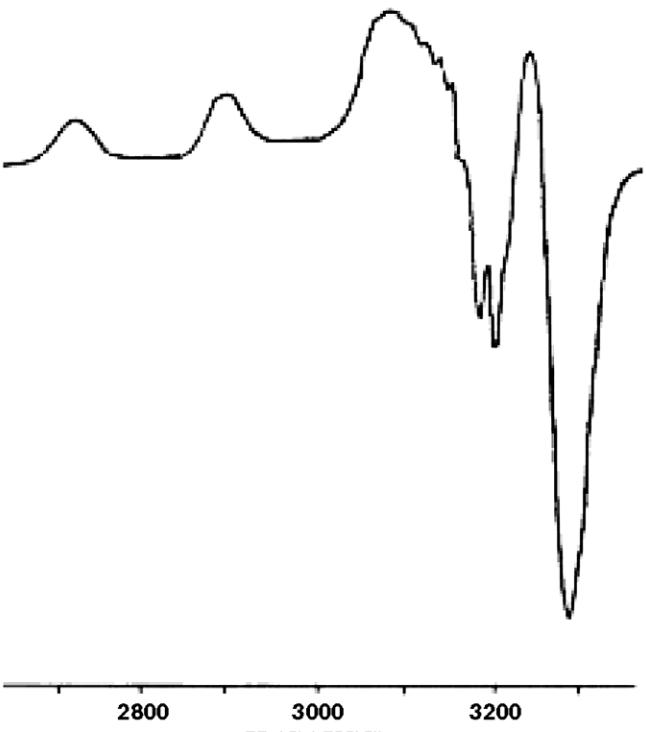


Fig. 5. EPR spectrum of **5** in DMF solution at 77 K.

According to Hathaway [45], $K_{\|} = K_{\perp} = 0.77$ for pure σ bonding and $K_{\|} < K_{\perp}$ for in-plane π bonding, while for out-of-plane π bonding $K_{\|} > K_{\perp}$. In all the copper(II) complexes, it is observed that $K_{\|} < K_{\perp}$ which indicates the presence of significant in-plane π bonding. Furthermore, α^2, β^2 and γ^2 have values less than 1 which is expected

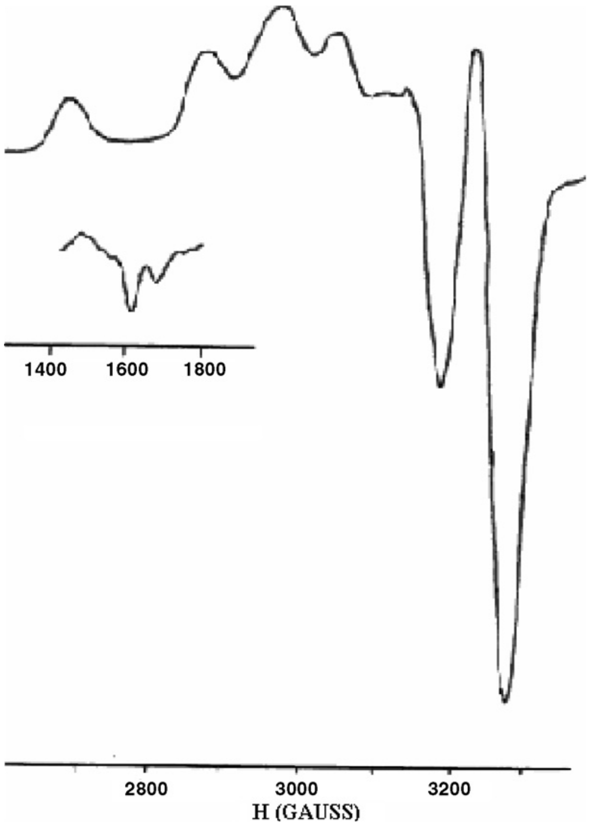


Fig. 6. EPR spectrum of **2** in DMF solution at 77 K.

for 100% ionic character of the bonds and become smaller with increasing covalent bonding. The evaluated values of α^2, β^2 and γ^2 of the complexes are consistent with both strong in plane σ and in plane π bonding. The $g_{\parallel}$ values are nearly the same for all the complexes indicating that the bonding is dominated by the thiosemicarbazone moiety.

The fact that the $g_3/g_{\parallel}$ values are less than 2.3 is an indication of significant covalent bonding in these complexes [46]. The Fermi contact hyperfine interaction term K may be obtained from [47]:

$$K = A_{\mathrm{iso}}/P\beta^2 + (g_{\mathrm{av}} - 2.0023)/\beta^2$$

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. The K values obtained for all the complexes are in agreement with those estimated by Assour [48] and Abragam and Pryce [49].

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Appendix A. Supplementary material

CCDC 613495 contains the supplementary crystallographic data for **9**. 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.2006.09.091.

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