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Structural, spectral and antimicrobial studies of copper(II) complexes of 2-benzoylpyridine $N(4)$-cyclohexyl thiosemicarbazone

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Abstract

Six new copper(II) complexes of 2-benzoylpyridine $N(4)$-cyclohexyl thiosemicarbazone (HL) have been synthesized and characterized by different physicochemical techniques like molar conductivity measurements, magnetic studies and electronic, infrared and EPR spectral studies. Five of the complexes have been found to possess the stoichiometry [CuLX], where X = Cl (**1**), Br (**2**), NO$_3$ (**3**), NCS (**4**), N$_3$ (**5**). The complex prepared from copper sulfate has the composition [Cu$_2$L$_2$SO$_4$]·(H$_2$O)$_2$ (**6**). In all the complexes the deprotonated ligand, L and the anion (Cl⁻, Br⁻, NO$_3$⁻, NCS⁻, N$_1$⁻, SO$_4^{2-}$) were found to be coordinated to the Cu(II) ion. The terdentate nature of the ligand is evident from the IR spectra. The metal ligand bonding parameters evaluated from the EPR spectra indicate strong in-plane σ and in-plane π bonding. The magnetic and spectroscopic data indicate a square planar geometry for complexes **1, 3, 4** and **5**, while the complexes **2** and **6** are assigned a square pyramidal geometry. Crystal structure of the complex [CuLCl] reveals two molecules per asymmetric unit of a monoclinic lattice, with space group symmetry $P2_1/n$. The complexes [{CuLBr}$_2$] (**2**) and [CuLNCS] (**4**) crystallized into triclinic lattices with space group $P1$. Compound **2** exists as a thiolate bridged copper(II) dimer. The antimicrobial activity of the ligand and the copper complexes were tested against five types of bacteria isolated from clinical samples. The complexes were found to be active against *Bacillus* sp., *Vibrio cholera O1*, *Staphylococcus aurus* and *Salmonella paratyphi*.

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1. Introduction

Thiosemicarbazones and their metal complexes exhibit a wide range of biological applications. The biological activity of certain thiosemicarbazones is due to their ability to form terdentate chelates with transition metal ions bonding through oxygen, nitrogen and sulfur

atoms, O—N—S or sulfur and two nitrogen atoms, N—N—S. Some thiosemicarbazones and a few of their metal complexes have shown antibacterial, antitumour, antituberculostatic and antifungal activities, which substantiate the relevance of the coordination chemistry of thiosemicarbazones.

Thiosemicarbazones derived from 2-formyl- and 2-acetylpyridine have been extensively studied, but much less attention has been given to those derived from 2-benzoylpyridine, though there are some reports on the studies of some $N(4)$-substituted 2-benzoylpyridine thiosemicarbazones and their metal complexes

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. There are also some recent reports on structural studies and spectral characteristics of N(4)-phenyl 4-benzoylpyridine thiosemicarbazone . It was found that the presence of a bulky group at the terminal nitrogen N(4) considerably increased the activity . We have recently reported structural and spectral studies of copper(II) complexes of 2-benzoylpyridine N(4),N(4)-(butane-1,4-diyl)thiosemicarbazone . In addition, iron(III) complexes of 2-acetylpyridine-N(4),N(4)-(butane-1,4-diyl) thiosemicarbazone are also reported . This paper describes the syntheses, structural, spectral and antimicrobial studies of six new Cu(II) complexes of 2-benzoylpyridine N(4)-cyclohexyl thiosemicarbazone (HL).

2. Experimental

Cyclohexyl isothiocyanate (Fluka), hydrazine hydrate (Lancaster), 2-benzoylpyridine (Lancaster) were used as received. The HL was prepared by a reported procedure .

2.1. Synthesis of complexes

To a methanolic solution of cupric chloride (2 mmol), a methanolic solution of HL (2 mmol) was added and refluxed for 4 h to prepare [CuLCl] (1). The resulting solution, on cooling, yielded blue coloured crystals, which were filtered, washed with methanol and ether and dried over P_4O_{10} in vacuo. [{CuLBr}$_2$] (2), [CuLNO$_3$] (3), [CuL$_2$SO$_4$]·2H$_2$O (6) were prepared by similar method using the appropriate copper salts. Compounds [CuLNCS] (4) and [CuLN$_3$]·3H$_2$O (5) were prepared by a metathetical displacement of the acetate anion of the copper acetate complex by the addition of 1 mmol each of the methanolic solutions of KCNS and NaN$_3$, respectively, to the reaction mixture containing the ligand and copper acetate in methanol. The resulting solution was refluxed for 3 h and left overnight. The solids, which separated were filtered, washed with methanol and ether and dried over P_4O_{10} in vacuo.

2.2. Physical methods

Carbon, hydrogen and nitrogen analyses of the ligand and the complexes were done on a Heraeus elemental analyser at CDRI, Lucknow, India. The IR spectra were recorded on a Shimadzu DR 8001 series FT-IR instrument using KBr pellets in the range 400–4000 cm^{-1} and far IR spectra were recorded in the range 50–500 cm^{-1} on a Nicolet Magna 550 FT-IR spectrometer using polyethylene pellets at RSIC, IIT, Bombay, India. The solid-state reflectance spectra of the ligand and the complexes were recorded on an Ocean Optics, Inc. SD2000 Fibre Optic Spectrometer. Electronic spectra of the lig-

and and the complexes in DMF solution were recorded on a Shimadzu 160A UV Vis. spectrophotometer. The EPR spectra of the complexes were recorded in a Varian E-112 Spectrometer using TCNE as the standard at RSIC, IIT, Bombay. The magnetic susceptibility measurements were carried out at the Indian Institute of Technology, Roorkee, at room temperature in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 K Oersted field strength. The molar conductances of the complexes of the solutions in dimethylformamide (ca. 10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

2.3. X-ray crystallography

Single crystals of compound 1 for X-ray analysis were grown by slow evaporation of the complex in a chloroform methanol mixture. A deep blue monoclinic crystal of compound [CuLCl] (1) was mounted on a glass fibre using epoxy cement. The X-ray diffraction data were measured in frames with increasing θ (width of 0.3°/frame) at room temperature (293 K) using a Bruker SMART APEX CCD diffractometer, equipped with a fine focus sealed tube X-ray source. The SMART software was used for data acquisition and the SAINT software for data extraction . Empirical absorption corrections were made on the intensity data . The structure was solved by the heavy atom method and refined by full-matrix least squares using the SHELX system of programs and the graphics tool was PLATON for windows . All non-hydrogen atoms of the complex cations were refined anisotropically. Few hydrogen atoms were located from the difference Fourier map and the rest were generated, assigned isotropic thermal parameters and refined using a riding model. The hydrogen atoms were used for structure factor calculation only. Similarly, a deep blue crystal of [{CuLBr}$_2$] (2) and a light green coloured crystal of [CuLNCS] (4) were analysed and the crystallographic data along with the structural refinements are given in .

2.4. Antimicrobial activity

For antimicrobial activity, two Gram positive and three Gram negative bacteria were used as test organisms. The disc diffusion method was used for screening the antimicrobial property and determining the MIC (minimum inhibitory concentration) of the compounds.

3. Results and discussion

3.1. Synthesis of the complexes

All the complexes were synthesized by refluxing HL with the corresponding copper salt in ethanol. The col-

Table 1
Colours and partial elemental analysis data of the complexes

Compound	Color	Found (Calc.)%			μ (B.M.)
		C	H	N	
[CuLCl] (1)	blue	52.62 (52.29)	4.94 (4.82)	12.72 (12.84)	1.52
[{CuLBr}$_2$] (2)	blue	47.16 (47.45)	4.55 (4.37)	11.70 (11.65)	1.80
[CuLNO$_3$] (3)	green	49.35 (49.29)	4.62 (4.54)	14.73 (15.13)	1.62
[CuLNCS] (4)	green	52.40 (52.33)	4.70 (4.58)	15.03 (15.26)	1.94
[CuLN$_3$]·3H$_2$O (5)	blue	45.46 (45.96)	4.94 (5.43)	20.14 (19.74)	1.97
[Cu$_2$(L)$_2$SO$_4$]·2H$_2$O (6)	dark green	48.87 (48.87)	5.03 (4.93)	11.99 (12.00)	1.66

ours, stoichiometries, elemental analyses and magnetic moments of the Cu(II) complexes are given in. All the Cu(II) complexes prepared are either blue or green in colour. The elemental analysis data of all the compounds suggest a formula [MLX], where X is Cl, Br, NO$_3$, NCS, N$_3$ and L is the deprotonated ligand. However, the sulfato complex is found to have the formula [Cu$_2$(L)$_2$SO$_4$]·2H$_2$O. The compounds 5 and 6 contain water molecules and the IR data suggest that the water molecules are not coordinated, but exist as lattice water.

All the complexes are found to be non-conductors in DMF solution. These facts along with the elemental analysis data indicate that the anion and the deprotonated ligand are coordinated to the central Cu(II). Magnetic moments of the complexes are calculated from magnetic susceptibility measurements and the values of all the Cu(II) complexes at room temperature are found to be in the range 1.5–1.9 B.M. The values of the magnetic moments, which are close to the spin only value of 1.7 B.M. indicate the presence of one unpaired electron.

Table 2
Crystal data and structural refinement for the complexes

Parameters	[CuLCl] (1)	[{CuLBr}$_2$] (2)	[CuLNCS] (4)
Empirical formula	C$_{19}$H$_{21}$ClCuN$_4$S	C$_{19}$H$_{22}$BrCuN$_4$S	C$_{20}$H$_{21}$CuN$_5$S$_2$
Formula weight (M)	436.45	481.92	459.08
Temperature, T (K)	293(2)	293(2)	293(2)
Wavelength, Mo Kα (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Lattice constants			
a (Å)	13.170(3)	9.642(5)	8.679(5)
b (Å)	8.670(2)	10.714(6)	9.376(5)
c (Å)	35.445(9)	10.899(6)	13.280(7)
α (°)	90.00	72.746(9)	80.761(9)
β (°)	98.00	76.413(9)	81.187(9)
γ (°)	90.00	70.887(8)	76.876(9)
Volume, V (Å^3)	4008.1(18)	1004.1(9)	1031.1(10)
Z	8	2	2
Calculated density, ρ (Mg m^{-3})	1.446	1.5940	13.4787
Absorption coefficient, μ (mm^{-1})	1.337	3.191	1.277
F(000)	1800	488	474
Crystal size (mm)	0.40 × 0.35 × 0.30	0.40 × 0.35 × 0.20	0.45 × 0.40 × 0.35
θ range for data collection	2.82–26	2.5–29.59	2.43–28.08
Limiting indices	$-16 \leqslant h \leqslant 16$, $-10 \leqslant k \leqslant 10$, $-43 \leqslant l \leqslant 43$	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 14$	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$
Reflections collected	29 574	12 475	12 440
Unique reflections (R_{int})	7862 (0.0498)	9644 (0.0227)	4951 (0.0220)
Completeness to θ	26.00 (99.6%)	29.59 (91.1%)	28.08 (98.5%)
Absorption correction	none	none	none
Maximum and minimum transmission	0.6898 and 0.6168	0.5678 and 0.3617	none
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	7862/0/637	9644/3/529	4951/0/337
Goodness-of-fit on F^2	1.091	0.955	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0555$, $wR_2 = 0.1041$	$R_1 = 0.0362$, $wR_2 = 0.0899$	$R_1 = 0.0406$, $wR_2 = 0.0926$
R indices (all data)	$R_1 = 0.0932$, $wR_2 = 0.1158$	$R_1 = 0.0577$, $wR_2 = 0.1014$	$R_1 = 0.0547$, $wR_2 = 0.0982$
Largest difference peak and hole (e Å^{-3})	0.417 and -0.291	0.736 and -0.499	0.549 and -0.202

3.2. Crystal structures of [CuLCl], [{CuLBr}₂] and [CuLNCS]

The structures of [CuLCl] (**1**), [{CuLBr}₂] (**2**) and [CuLNCS] (**4**) along with the atom labelling are shown in   , respectively. Crystal data are given in   and a comparison of selected bond lengths and bond angles of H₂L, with compounds **1**, **2** and **4**, is summarized in

3.2.1. [CuLCl]

The compound CuLCl (**1**) crystallizes into a monoclinic lattice with a $P2_1/n$ space group symmetry. There are two crystallographically independent molecules, A and B, in the asymmetric unit of the compound, with bond lengths and angles, which agree with each other and are within normal ranges. The compound shows a square planar geometry with the Cu atom lying in an approximate plane with the N1, N3, S1 and Cl1 atoms. Due to coordination, the C13–S1 bond length of the thiosemicarbazone moiety approaches the value corresponding to a C–S single bond, as evident from the increased value of 1.746(3) Å in the complex, compared to 1.675(15) Å in the ligand. The C13–S1 distance in **1** compares well with those reported for the related thiosemicarbazone complexes, in which the coordination by the thiolate tautomers has been definitely established by X-ray structural determinations   . A slight distortion from the square planar geometry is evidenced by the bond angles, N1–Cu1–N2 (80.31(9)°), N2–Cu1–S1 (84.21(7)°), N1–Cu1–Cl1 (98.15(7)°) and Cl1–Cu1–S1

(97.22(4)°). The bonding parameters reveal that the Cu1–N1 (2.036(2) Å) and Cu1–N2 (1.966(2) Å) bond lengths are much smaller than the Cu1–Cl1 (2.2099(10) Å) bond length. This implies stronger Cu–N bonds compared to the Cu–Cl bond, indicating the domination of the thiosemicarbazone moiety in the bonding. The repeating unit in the crystal packing consists of three molecules where two of them set in an offset fashion are self-assembled by the intermolecular (N2H⋯S1) hydrogen bonding interactions, while the third molecule is arranged in a face to face manner with the neighbouring molecule. The repeating units are packed in an offset fashion and a three dimensional packing is effected by the π–π stacking, ring–metal and Cl–π interactions.

3.2.2. [{CuLBr}₂]

Compound **2** is a thiolate bridged copper(II) dimer complex crystallized into a triclinic lattice with $P\bar{1}$ symmetry. Thiolate bridging by sulfur ligands are well reported   , and recently the metal complexes of Schiff bases   and thiosemicarbazone involving phenolate oxygen bridging are reported. Each CuLBr unit in the molecule assembles into a symmetric binuclear complex by bridging through the thiolate sulfur atom of the adjacent thiosemicarbazone via axial ligation. Thus, the Cu(II) ions reveal a distorted pentacoordinated viz. (4 + 1) (N1N2SBr + S′) square-based pyramidal geometry in the complex. The basal plane is occupied by the thiolate sulfur, azomethine nitrogen, pyridyl nitrogen and the bromine atoms. The bond lengths Cu1–S1 (2.289(2) Å), Cu1–N2 (1.978(4) Å),
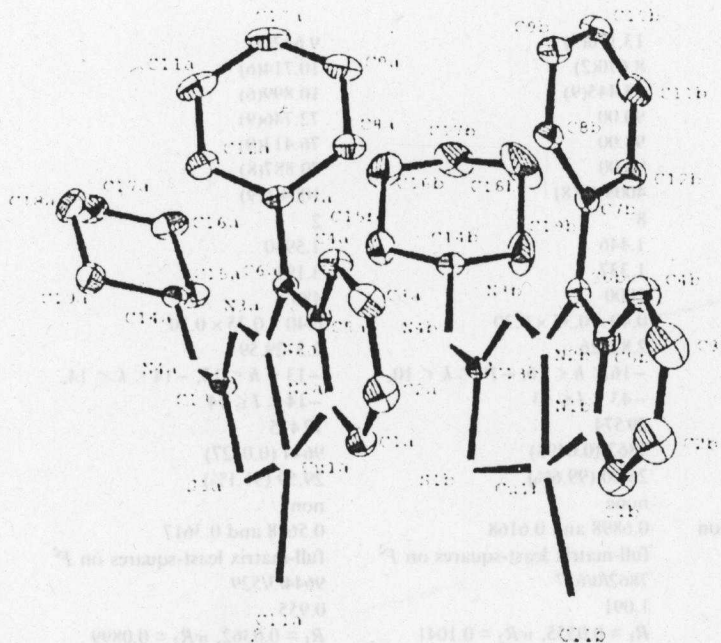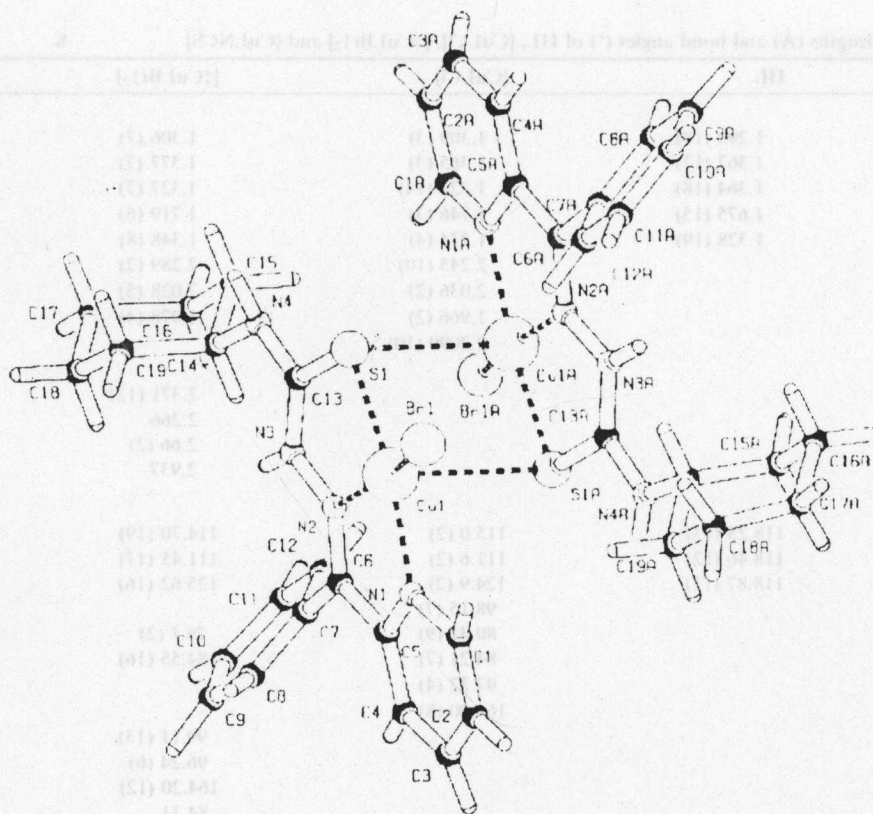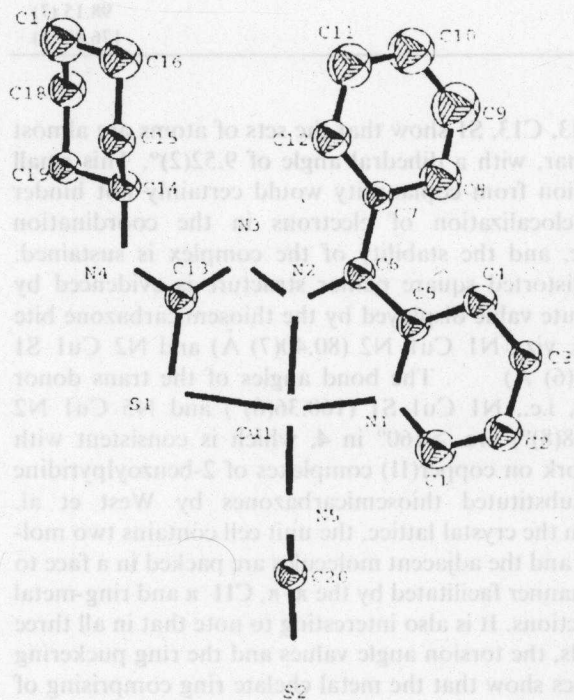

Fig. 1. ORTEP diagram for CuLCl (**1**), displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

Fig. 2. PLATON diagram for [½CuLBr]₂ (2).

Fig. 3. ORTEP diagram for CuLNCS (4), displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

Cu1–N1 (2.028(5) Å) and Cu1–Br1 (2.371(12) Å) are consistent with the other similar bond distances of square pyramidal copper complexes . The apical position of the square pyramid is occupied by the thiolate sulfur of the second unit, at a Cu–Cu distance of ca. 3.523 Å with the Cu1–S1–Cu1A or Cu1–S1A–Cu1A angle being ca. 84.47°. In the Cu₂S₂ plane, the Cu1–S1 or Cu1A–S1A and Cu1–S1A or Cu1A–S1 bond lengths are ca. 2.266 and 2.937 Å, respectively, and the non-equivalent bonds give rise to the asymmetric binuclear thiolate double bridged structure. The basal planes around Cu1 and Cu1A are essentially planar with mean deviations being 0.1905(5) and 0.1891(5) Å, respectively. The significantly longer Cu–S axial bond length of ca. 2.937 Å is likely to reduce the spin–spin coupling between Cu1 and Cu1A centres. The Cu₂S₂ unit in the complex is planar with a mean deviation of 0.0073(5) Å. The Cu₂S₂ plane is observed at angles of 81.76(2)° and 80.60(2)°, respectively, with the basal planes around Cu1 and Cu1A. The crystal packing is effected by the wide network of CH–π interactions and the π–π stacking interactions involving the phenyl, pyridyl and metal chelate rings. The thiolate bridging structure is further stabilized by the comparatively stronger π–π interactions between the centroids Cg(3) and Cg(9) consisting of Cu(1), S(1), Cu(1A), S(1A) and Cu(1A), N(1A),

Table 3
Comparison of selected bond lengths (Å) and bond angles (°) of HL, [CuLCl], [{CuLBr}$_2$] and [CuLNCS]

	HL	[CuLCl]	[{CuLBr}$_2$]	[CuLNCS]
Bond lengths				
C(6)–N(2)	1.290 (18)	1.309 (3)	1.306 (7)	1.299 (3)
N(2)–N(3)	1.367 (17)	1.365 (3)	1.377 (7)	1.366 (2)
N(3)–C(13)	1.364 (18)	1.323 (14)	1.327 (7)	1.325 (3)
S(1)–C(13)	1.675 (15)	1.746 (3)	1.719 (6)	1.746 (2)
C(13)–N(4)	1.328 (19)	1.334 (4)	1.348 (8)	1.339 (3)
Cu(1)–S(1)		2.245 (10)	2.289 (2)	2.261 (12)
Cu(1)–N(1)		2.036 (2)	2.028 (5)	2.016 (2)
Cu(1)–N(2)		1.966 (2)	1.978 (4)	1.962 (19)
Cu(1)–Cl(1)		2.2099 (10)		
Cu(1)–N(5)				1.924 (2)
Cu(1)–Br(1)			2.371 (12)	
Cu(1A)–S(1A)			2.266	
Cu(1A)–S(1A)			2.66 (2)	
Cu(1A)–S(1)			2.937	
Bond angles				
N(1)–C(5)–C(6)	118.25 (13)	115.0 (2)	114.70 (19)	114.60 (5)
N(2)–N(3)–C(13)	118.46 (12)	111.6 (2)	111.45 (17)	112.20 (4)
N(3)–C(13)–S(1)	118.87 (11)	124.9 (2)	125.62 (16)	126.20 (5)
N(1)–Cu(1)–Cl(1)		98.15 (7)		
N(1)–Cu(1)–N(2)		80.31 (9)	79.7 (2)	80.40 (7)
N(2)–Cu(1)–S(1)		84.21 (7)	84.55 (16)	84.43 (6)
S(1)–Cu(1)–Cl(1)		97.22 (4)		
N(2)–Cu(1)–Cl(1)		164.00 (8)		
N(1)–Cu(1)–Br(1)			99.11 (13)	
S(1)–Cu(1)–Br(1)			96.24 (6)	
N(2)–Cu(1)–Br(1)			164.20 (12)	
Cu(1)–S(1)–Cu(1A)			84.11	
Cu(1A)–S(1A)–Cu(1)			84.47	
S(1)–Cu(1A)–S(1A)			95.56	
S(1A)–Cu(1)–S(1)			95.89	
N(1)–Cu(1)–N(5)				97.44 (9)
S(1)–Cu(1)–N(5)				98.15 (7)
N(2)–Cu(1)–N(5)				176.88 (8)

C(5A), C(6A), N(2A), respectively, which is observed at a remarkably shorter distance of 2.7632(3) Å.

3.2.3. [CuLNCS]

The crystal is developed into a triclinic lattice with P$\bar{1}$ symmetry and it reveals a distorted square planar N$_3$S coordination sphere with the copper centre. The thiosemicarbazone ligand occupies three positions and the thiocyanate nitrogen the fourth position of an approximate square plane. The C13–S1 bond length of 1.675(15) Å in the ligand HL is an evidence for the thione form in the solid state, which is shifted to 1.746(2) Å in the complex, confirming the coordination via the thiolate sulfur in **4**. The N2–N3 bond length of 1.367(17) Å in the uncomplexed thiosemicarbazone is found to remain unchanged in the complex, whereas, the C13–N3 bond length of 1.364(18) Å in HL is shifted to 1.325(3) Å in **4**. This is in support for the shifting of the thione form of the thiosemicarbazone to the thiol form during complexation. The ligand is deprotonated at N3 and the complex carries two five-membered chelate rings. The two planes through Cu1, N1, C5, C6, N2 and Cu1,

N2, N3, C13, S1 show that the sets of atoms are almost coplanar, with a dihedral angle of 9.52(2)°. This small deviation from coplanarity would certainly not hinder the delocalization of electrons in the coordination sphere, and the stability of the complex is sustained. The distorted square planar structure is evidenced by the acute value displayed by the thiosemicarbazone bite angles, viz., N1–Cu1–N2 (80.40(7) Å) and N2–Cu1–S1 (84.43(6) Å) . The bond angles of the trans donor atoms, i.e., N1–Cu1–S1 (160.36(6)°) and N5–Cu1–N2 (176.88(8)°) are ≥160° in **4**, which is consistent with the work on copper(II) complexes of 2-benzoylpyridine N(4)-substituted thiosemicarbazones by West et al. . In the crystal lattice, the unit cell contains two molecules and the adjacent molecules are packed in a face to face manner facilitated by the π–π, CH–π and ring-metal interactions. It is also interesting to note that in all three crystals, the torsion angle values and the ring puckering analyses show that the metal chelate ring comprising of Cu1, S1, C13, N3 and N2 adopts an envelope conformation, whereas the cyclohexyl ring exists in the chair form. Atoms C14, C16, C17 and C19 constitute the best-fitting

plane of the cyclohexyl ring, while the atoms C15 and C18 deviate by 1.2415(6) and −1.2491(6) Å, respectively, on either side of the plane.

3.3. Vibrational spectra

The tentative assignments of the significant IR spectral bands of HL and its copper(II) complexes are presented in . The $v(C=N)$ band of the thiosemicarbazone at 1582 cm^{-1} is found to be shifted to lower energies in the spectra of the complexes indicating coordination via the azomethine nitrogen. This is confirmed by the bands in the range 440–464 cm^{-1}, which have been assigned to the $v(Cu-N)$ bond . The $v(N-N)$ of the thiosemicarbazone is found at 1118 cm^{-1}. The increase in frequency of this band in the spectra of complexes is due to the increase in bond strength, again confirming the coordination via the azomethine nitrogen. In the uncomplexed thiosemicarbazone, a strong band at 833 cm^{-1} is assigned to $v(C=S)$, whereas in the complexes, this band is found to be shifted to lower frequencies in the range 783–794 cm^{-1}. This negative shift of the $v(C=S)$ band in the complexes is indicated by the coordination via the thiolate sulfur atom. Strong bands observed in the region 340–353 cm^{-1} have been assigned to the $v(Cu-S)$ band. In all the copper complexes a strong band is observed in the region 266–280 cm^{-1}, which is consistent with the $v(Cu-N)$ of pyridine as suggested by Clark and Williams . Based on the above spectral evidences, it is confirmed that the ligand is coordinated to the Cu(II) ion as a tridentate anion, coordinating via the azomethine nitrogen, pyridyl nitrogen and thiolate sulfur. In the chloro complex, a strong band observed at 304 cm^{-1} has been assigned to the $v(Cu–Cl)$ band. The $v(Cu–Br)$ frequency is observed at 247 cm^{-1} in the bromo complex. The $v(Cu–Br)$ and $v(Cu–Cl)$ frequencies are consistent with terminal chloro and bromo ligands. In the IR spectrum of the complex containing nitrate as the gegenion, the band observed at 268 cm^{-1} can be assigned to $v(Cu–ONO_2)$, consistent with the bands at 253–280 cm^{-1} reported earlier for Cu–ONO$_2$ in metal complexes . Moreover, in the nitrato complex of HL, two strong bands at 1280 and 1410 cm^{-1} corresponding to v_1 and v_4 modes of nitrato groups with a separation of 130 cm^{-1} indicate

the presence of a terminally bonded monodentate nitrate group . In the azido complex, a strong band observed at 2037 cm^{-1} is assigned to v_a of the azide group, indicative of azide coordination . Other bands due to N$_3$ such as v_s(NNN) are difficult to assign because of the richness of the spectrum of the complex. In the thiocyanato complex, the very strong band observed at 2093 cm^{-1} corresponds to $v(C=N)$. Bands observed at 783, 481 and 461 cm^{-1} are assigned to $v(C=S)$, δ(NCS) and $v(Cu-N)$, respectively. These facts indicate that thiocyanate group is N-coordinated to copper . In the sulfato complex, the fourth coordination position is occupied by the oxygen atom of the sulfate ion which belongs to the high symmetry point group T_d. The symmetry of the sulfate is reduced to C_{2v} when it functions as a bidentate ligand in the complex. The IR spectrum of compound 6 contains strong bands at 1002, 1117, 1204 cm^{-1} due to v_3, 960 cm^{-1} due to v_1 and 465 cm^{-1} due to v_2, and these can be assigned to a bridging bidentate sulfato group . This type of bidentate bridging by a sulfato group has been proved by a single crystal X-ray diffraction study for a thiosemicarbazone derived from di-2-pyridyl ketone . According to Stefov et al. , coordinated water should exhibit frequencies at 825, 575 and 500 cm^{-1}. The absence of spectral bands in these regions in the spectra of complexes 3 and 6 indicates that the water molecules in these complexes are not coordinated but are present as lattice water.

3.4. Electronic spectra

The energies of the electronic transitions for the thiosemicarbazone HL and its Cu(II) complexes (solid state and DMF solution) are listed in . The solid-state electronic spectra of the thiosemicarbazone HL consists of a broadband at ca. 29000 cm^{-1} which is the n → π* band of the pyridine ring. Another n → π* band of the thiosemicarbazone moiety is present in the 24000 cm^{-1} region . The molar absorptivity for n → π* transitions for the solution spectrum is >10^4, which is consistent with the previously studied heterocyclic thiosemicarbazones . The electronic spectra of the Cu(II) complexes consist of a n → π* band of the pyridine ring at ca. 30000 cm^{-1}. Additional bands observed in the range 23000–25000 cm^{-1} are assigned to S → Cu

Table 4
IR spectral assignments (cm^{-1}) of HL and the Cu(II) complexes

Compound	$v(C=N)$	$v(N-N)$	$v(C-S)$	ρ(py)	$v(Cu-N)$	$v(Cu-Npy)$	$v(Cu-S)$	$v(Cu-X)$
HL	1582m	1118s	1370w, 833m	607w				
[CuLCl]	1582s	1150m	1337m, 785m	642w	460m	280s	349m	304s
[{CuLBr}$_2$]	1544s	1150m	1336m, 794m	644m	443s	282s	353s	247s
[CuLNO$_3$]	1543w	1138m	1279s, 786w	646m	459m	268s	352s	268s
[CuLNCS]	1542s	1138s	1331s, 783w	642m	461s	266m	350s	350s
[CuLN$_3$]·3H$_2$O	1540m	1131	1324m, 788s	644s	464s	278m	351w	
[Cu$_2$(L)$_2$SO$_4$]·2H$_2$O	1544m	1130s	1332m, 789m	641m	463s	280s	352s	397s

Table 5
Electronic spectral assignments (cm⁻¹) (log ε in parentheses) of HL and the Cu(II) complexes

Compound	Mode	d → d	L → M	n → π*	π → π*
HL	solid			28735, 24390sh	38610
	DMF			29411 (4.13), 26315 (3.32)	39010 (4.20)
[CuLCl]	solid	18691, 15313	24509, 31250sh	30030, 26809sh	38967
	DMF	17452 (2.602)	22830 (4.14)	27624 (3.83)	39062 (4.41)
[{CuLBr}₂]	solid	18080sh, 16129	24937	31645	37453sh
	DMF	18080 (2.41)	24860 (3.21)	31620 (4.12)	37560sh (4.25)
[CuLNO₃]	solid	16590sh, 15455	24937	32382	35714
	DMF	18350 (2.51)	23510 (4.13)	32310 (4.10)	36810 (4.61)
[CuLNCS]	solid	17761sh, 15308	24213	32362	38314sh
	DMF	17568sh (2.61)	22831 (3.81)	28571 (4.34)	37965 (4.06)
[CuLN₃]·3H₂O	solid	18691sh, 17123	24213	32362	37453sh
	DMF	17110sh (2.34)	22727 (4.35)	28409 (4.21)	37013sh (4.01)
[Cu₂(L)₂SO₄]·2H₂O	solid	17355sh, 15220	24570	31645	37453sh
	DMF	15980 (2.5)	24087 (4.30)	32467 (4.43)	37700 (4.21)

and py → Cu charge-transfer bands . . . . In the chloro complex (1), a shoulder observed at 31250 cm⁻¹ is assigned to the Cl → Cu charge-transfer transition. The solid state spectra of all the Cu(II) complexes have a broadband in the region 15000–19000 cm⁻¹. This is consistent with a broad structured band for square planar complexes in the range 13000–20000 cm⁻¹ .

3.5. Electron paramagnetic resonance spectra

The EPR spectra of a polycrystalline sample at 298 K and in different solutions at 298 and 77 K were re-corded in the X band, using the 100 KHz field modulation; g factors were quoted relative to the standard marker TCNE (g = 2.00277). The EPR parameters of the Cu(II) complexes are presented in . The EPR spectra of CuLCl and Cu₂(L)₂SO₄ in the polycrystalline state at 298 K show only one broad signal at g = 2.125 and 2.063, respectively. Such isotropic spectra, consisting of a broad signal, and hence only one g value, arise from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. These types of spectra unfortunately give no informa-

Table 6
EPR parameters of the Cu(II) complexes of HL.

Compound	Solid (298 K)		DMF solution (298 K)		DMF solution (77 K)			
	g₁/g₂/g₃	gav	giso	Aiso	g₁/g₂/g₃	gav	A∥	G
[CuLCl]	giso 2.1257		2.0828	84.13	g∥ 2.160, g⊥ 2.046	2.0854	166.39	3.63
[{CuLBr}₂]	g₁ 2.0649, g₂ 2.0710, g₃ 2.1559	2.097	2.1330	79.0	g∥ 2.1270, g⊥ 2.0340	2.065	176.17	3.93
[CuLNO₃]	g∥ 2.1840, g⊥ 2.0510	2.095	2.0807	79.46	g∥ 2.1923, g⊥ 2.0532	2.0995	180.7	3.73
[CuLNCS]	g₁ 2.037, g₂ 2.054, g₃ 2.169	2.086	2.1200	88.80	g₁ 2.0367, g₂ 2.053, g₃ 2.1764	2.0887	168.26	4.14
[CuLN₃]·3H₂O	g∥ 2.2064, g⊥ 2.0993	2.135	2.1456	82.26	g∥ 2.1276, g⊥ 2.0338	2.064	171.1	3.97
[Cu₂(L)₂SO₄]·2H₂O	giso 2.063		2.1152	81.32	g∥ 2.1826, g⊥ 2.0498	2.0940	169.8	3.84

ᵃ A values are given in 10⁻⁴ cm⁻¹.

tion on the electronic ground state of the Cu(II) ion present in the complexes. The spectra of [{CuLBr}$_2$] and [CuLNCS] are rhombic with three g values. The spectra of the other compounds show typical axial spectra with well-defined $g_\parallel$ and $g_\perp$ values. The spectra are often broad because of the broadening resulting from the fast spin–lattice relaxation time and exchange coupling. The geometric parameter G, which is a measure of the exchange interaction between copper centres in the polycrystalline compound, is calculated and the value of G is found to be in the range 2.3–4.0. In all the copper(II) complexes $g_\parallel > g_\perp > 2.0023$ and a G value less than 4.1 is consistent with a $d_{x^2-y^2}$ ground state. The EPR spectral studies are in agreement with the X-ray diffraction studies for complexes 1, 2 and 4. All the complexes in DMF solution at 298 K clearly show four well-resolved hyperfine lines (^{65}Cu, $I = 3/2$). The EPR spectra of the complexes in glassy state at 77 K were recorded in different solvents, such as DMF, CHCl$_3$ and in a 1:1 mixture of CHCl$_3$ and toluene. Solutions of compounds 1 and 2 in chloroform toluene mixture show well-resolved four hyperfine lines corresponding to monomeric Cu(II) complexes. The spectra have five nitrogen superhyperfine lines on the high field copper hyperfine splitting component, which arise from the coupling of the electron spin with the nuclear spin of the two nitrogen atoms. The EPR spectrum of compound 5 shows four well-resolved hyperfine lines with seven nitrogen superhyperfine lines on the high field copper hyperfine splitting component. The seven superhyperfine lines arise from the coupling of the electron spin with the nuclear spin of the three nitrogen atoms, i.e., one azomethine nitrogen, one nitrogen of pyridine ring and one nitrogen from the azido anion coordinated to the Cu(II) centre. The EPR spectra of compounds 3, 4 and 6 in DMF solution at 77 K show four hyperfine lines. The EPR spectra of compounds 1 and 5 are given in respectively.

Fig. 5. EPR spectrum of CuLN$_3$ (5) in DMF solution at 77 K.

The $g_\parallel$ values of all the compounds are found to be almost the same, which indicates that the bonding is dominated by the thiosemicarbazone moiety. Kivelson and Nieman have reported that $g_\parallel$ values less than 2.3 indicate considerable covalent character to M–L bonds, while a value greater than 2.3 indicate ionic character. The $g_\parallel$ values of all the compounds are found to be less than 2.3, which indicates considerable covalent character to the M–L bond.

The EPR parameters $g_\parallel$, $g_\perp$, g_{av}, $A_\parallel$ (Cu) and $A_\perp$ (Cu) and the energies of the 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 the in-plane sigma bonding parameter α^2 was calculated using the expression

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

The orbital reduction factors, $K_\parallel = \alpha^2\beta^2$ and $K_\perp = \alpha^2\gamma^2$ were calculated using the following expressions:

$$K_\parallel^2 = (g_\parallel - 2.0023)E_{d-d}/8\lambda_0,$$

$$K_\perp^2 = (g_\perp - 2.0023)E_{d-d}/2\lambda_0,$$

where λ_0 is the spin–orbit coupling constant, with a value of -828 cm^{-1} for a copper(II) d^9 system.

According to Hathaway , for pure σ bonding, $K_\parallel \approx K_\perp \approx 0.77$, and for in-plane π bonding, $K_\parallel < K_\perp$; while for out-of-plane π bonding, $K_\perp < K_\parallel$. In all the complexes, it is observed that $K_\parallel < K_\perp$ which indicates

Fig. 4. EPR spectrum of CuLCl (1) in DMF solution at 77 K.

Table 7
Bonding parameters and orbital reduction parameters of the Cu(II) complexes of HL

Compound	α^2	β^2	γ^2	$K_{\parallel}$	$K_{\perp}$	K_0	f
[CuLCl]	0.6810	0.9455	0.9862	0.6439	0.6716	0.3283	129.99
[{CuLBr}$_2$]	0.6667	0.8518	0.8590	0.5687	0.5735	0.3312	120.70
[CuLNO$_3$]	0.7537	0.9250	0.9575	0.6972	0.7217	0.3440	121.32
[CuLNCS]	0.7062	0.9226	0.9643	0.6516	0.6810	0.3581	129.30
[CuLN$_3$]·3H$_2$O	0.6538	0.8750	0.8782	0.5720	0.5742	0.2997	124.43
[Cu$_2$(L)$_2$SO$_4$]·2H$_2$O	0.7165	0.9355	0.9600	0.6658	0.6834	0.3394	128.54

the presence of significant in-plane π bonding. This is further confirmed by the bonding parameters α^2, β^2 and γ^2, which are less than 1.0 expected for purely ionic character of the bonds, and decreases with increasing covalent nature of the bonding. Therefore the evaluated values of α^2, β^2 and γ^2 are consistent with both in-plane σ and in-plane π bonding .

The empirical factor $f = g_{\parallel}/A_{\parallel}$ cm^{-1} is an index of tetragonal distortion and its value may vary from 105 to 135 for small to extreme distortion in square planar complexes, and that depends on the nature of the coordinated atom . The f values of the complexes are found to be in the range 121–130, indicating significant distortion from planarity.

Recent studies have shown that biological activity is related to the geometry at the metal sites. Complexes with more tetrahedral distortion are reported to display higher activity . The studies of antimicrobial activity among the six complexes revealed the chloro compound to have the greatest activity, which is consistent with the above statement since compound 1 shows the maximum f value of 129.99. However, compound 4, with almost the same f value (129.30), is found to be less active.

3.6. Antimicrobial activity

The ligand HL and the Cu(II) complexes were tested for their antimicrobial activity. Test substances which produce a zone of inhibition of diameters 9 mm or more are regarded as positive, i.e. having constructive antimicrobial activity; while in those cases where the diameter is below 9 mm, the bacteria are resistant to the sample

tested and the sample is said to have no antimicrobial activity. The following bacteria, isolated from clinical samples, were used as test organisms: (1) *Staphylococcus aureus*, (2) *Bacillus* sp. (Gram positive), (3) *Escherichia coli*, (4) *Salmonella paratyphi*, (5) *Vibrio cholerae O1* (Gram negative).

The disc diffusion method was used for screening the antimicrobial property of the test samples. The MIC (minimum inhibitory concentration) of the compounds showing a positive antimicrobial property was found using the same method. 1% solutions of the samples in DMF were used. The medium used for growing the culture was nutrient agar. The ligand HL was found to be inactive, but all the copper(II) complexes were found to be active ( ). The copper(II) complexes 1 and 3 were found to be active against *Bacillus* sp. *V. cholerae O1* and *S. aureus*. Compound 6 was found to be active against *Bacillus* sp., *V. cholerae O1* and *S. paratyphi*. Compound 5 was found to be active against *V. cholerae O1* and *S. paratyphi* and compounds 2 and 4 were found to be active against *V. cholerae O1*. The MIC values of the complexes are given in .

4. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data centre, CCDC 227455 for compound [CuLCl] (1), CCDC 227456 for compound [CuLNCS] (4) and CCDC 227457 for compound [{CuLBr}$_2$] (2). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge.

Table 8
The antimicrobial activity of the complexes using the disc diffusion method

Compound	Microbial activity inhibition zone				
	Bacillus sp.	*Staphylococcus aureus*	*Vibrio cholera O1*	*Escherichia coli*	*Salmonella paratyphi*
HL					
[CuLCl]	+9 mm	+9 mm	+11 mm		
[{CuLBr}$_2$]			+10 mm		
[CuLNO$_3$]	+11 mm	+10 mm	+11 mm		
[CuL(NCS)]			+10 mm		
[CuLN$_3$]·3H$_2$O			+10 mm		+9 mm
[Cu$_2$(L)$_2$SO$_4$]·2H$_2$O	+10 mm		+14 mm		+9 mm

Table 9
MIC of the Cu(II) complexes

Compound	MIC in µl			
	Bacillus sp.	Vibrio cholerae O1	Salmonella paratyphi	Staphylococcus aureus
[CuLCl]	5	5		4
[{CuLBr}₂]		5		
[CuLNO₃]	5	5		5
[CuLNCS]		5		
[CuLN₃]·3H₂O		5	4	
[Cu₂(L)₂SO₄]·2H₂O	5	5	5	

CB2, 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or   ).

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