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Unprecedented Pentacoordination of Di-2-pyridyl ketone *N*(4)-ethyl thiosemicarbazone Ligand with Formation of Trinuclear Cu(II) Complex

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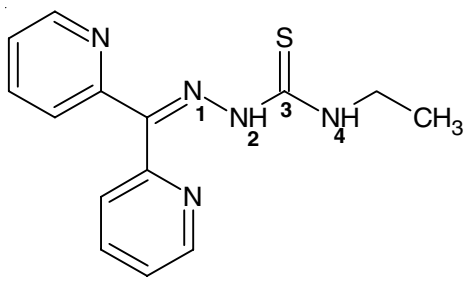
The syntheses and characterization of six copper(II) complexes of di-2-pyridyl ketone *N*(4)-ethylthiosemicarbazone (HDpyETsc) are reported by means of partial elemental analyses, molar conductance measurements, electronic, infrared and EPR spectral studies. The complexes are represented as $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**), $[Cu(DpyETsc)N_3]\cdot H_2O$ (**2**), $[Cu(DpyETsc)Cl]_2\cdot H_2O$ (**3**), $[Cu_2(DpyETsc)_2SO_4]_2\cdot 4H_2O$ (**4**), $[Cu(DpyETsc](ClO_4)_2\cdot H_2O$ (**5**) and $[Cu(DpyETsc)(NCS)]_2$ (**6**). The compound **1** was found to be a trinuclear copper(II) complex with the ligand showing pentacoordination which is unprecedented for this type of ligand. Two centro-symmetric six membered metallocycles are formed and the terminal copper atoms have distorted square pyramidal geometry.

Keywords: Thiosemicarbazone, Cu(II) complex, Di-2-pyridyl ketone, Crystal structure, EPR spectra.

INTRODUCTION

Thiosemicarbazide and thiosemicarbazone complexes of copper have attracted particular attention over the past decades in the context of their wide spectrum of biological activity and applications as radiopharmaceuticals. Thiosemicarbazones are versatile ligands that can coordinate as neutral ligands or in their deprotonated form [1,2]. The activity of thiosemicarbazones depends very much on the parent aldehyde or ketone and is affected also by *N*(4) substitution [3]. Thiosemicarbazones derived from di-2-pyridyl ketone are potentially tetradentate. However in majority of cases they function as tridentate ligands only.

Thiosemicarbazone is emerging moiety with wide spectrum of biological activity and having sound scope in research and developing process in pharmaceutical and medicinal chemistry [4]. Copper(II) is a biologically active, essential ion; its chelating ability and positive redox potential allow participation in biological transport reactions. Copper(II) also forms the active centers of more than a dozen metalloproteins. Further, copper(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents. The chemistry of polynuclear copper complexes has become a fascinating area of research in contemporary coordination chemistry following the discovery of multicopper active sites in several blue copper oxidases and development of novel functional materials showing molecular ferromagnetism and specific catalytic properties [5]. Additionally, polynuclear copper compounds have attracted much attention due to their ability to perform DNA strand cleavage [6]. On this basis, the present communication reports on the optimal conditions for synthesis of six copper complexes with the ligand, di-2-pyridyl ketone *N*(4)-ethyl thiosemicarbazone (HDpyETsc) and their characterization by physicochemical methods, together with X-ray crystal structure of one of the copper complexes, *viz.* $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$.



Structure of HDpyETsc

EXPERIMENTAL

Di-2-pyridyl ketone, *N*(4)-ethyl thiosemicarbazide, copper(II) nitrate trihydrate, copper(II) acetate monohydrate, copper(II) chloride dihydrate, copper(II) sulphate pentahydrate, copper(II) perchlorate hexahydrate, sodium azide and

potassium thiocyanate, ethanol and methanol were used as supplied. Caution: Azide and perchlorate complexes of metals with organic ligands are potentially explosive and should be handled with care.

Synthesis of ligand: The thiosemicarbazone ligand was synthesized according to the reported procedure [7].

Syntheses of complexes: Complexes **1**, **3**, **4** and **5** were prepared by the direct reaction of the appropriate copper salts with the ligand. Ethanolic solution of the ligand HDpyETsc (1 mmol) and the ethanolic solution of the corresponding copper salt (1 mmol) were mixed. The mixture was refluxed for 4 h and allowed to stand at room temperature. The complexes formed were filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}. The compounds **2** and **6** were prepared by a metathetical displacement of the acetate anion of the copper acetate complex, by azide and thiocyanate ion, respectively. The azide complex was obtained by stirring the reaction mixture of the ligand and copper(II) acetate in ethanol after adding 1 mmol of NaN_3 in water and the thiocyanate complex by refluxing the reaction mixture of the ligand and copper(II) acetate in ethanol after adding 1 mmol of KNCS in ethanol. The complexes obtained were filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}. XRD quality single crystals of compound **1** were obtained by the slow evaporation of its ethanol solution in air. Attempts were made to crystallize other complexes also, but unfortunately failed.

Physical measurements: Elemental analyses of the ligand and the complexes were done on a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared 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 Spectro UV-VIS Double Beam UVD-3500 spectrometer in the 200-900 nm range from solutions in acetonitrile. The EPR spectra of the complexes were recorded on a Varian E-112 spectrometer using TCNE as the standard at SAIF, IIT, Mumbai, India. The molar conductances of the complexes in dimethylformamide solutions (10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

X-ray crystallography: Single crystals of compound **1** of X-ray diffraction quality were grown from its ethanol solution by slow evaporation at room temperature in air. The crystallographic data and structure refinement parameters for the compound **1** are given in Table-1. Diffraction data for **1** were collected at 150(2) K using a CrysAlis CCD, Oxford Diffraction Ltd. at the National Single Crystal X-Ray Diffraction facility, IIT, Bombay, India. The trial structure was solved using SHELXS-97 [8] and refinement was carried out by full-matrix least square method based on F^2 (SHELXL-97) [8]. Molecular graphics employed were diamond and mercury [9].

TABLE-1
CRYSTAL REFINEMENT PARAMETERS OF $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**)

Formula	$C_{28}H_{34}N_7O_{15}S_2Cu_3$
Formula weight (M)	1079.44
Temperature (T) K	150(2)
Wavelength (MoK_α) (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Lattice constants	
a (Å); b (Å); c (Å)	8.072(4); 9.661(11); 14.290(8)
α (°); β (°); γ (°)	70.459(17); 79.148(3); 74.522(3)
Volume V ($Å^3$)	1006.1(8)
Z	1
Calculated density (ρ) ($Mg\ m^{-3}$)	1.782
Absorption coefficient (μ, mm^{-1})	1.763
F(000)	549
Crystal size (mm^3)	0.33 × 0.23 × 0.19
θ Range for data collection	2.98-24.99
Limiting indices	$-9 \le h \le 9$; $-11 \le k \le 11$; $-16 \le l \le 16$
Reflections collected	8952
Independent Reflections	3525 [R(int) = 0.0691]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3525/0/304
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0750$, $wR_2 = 0.2001$
R indices (all data)	$R_1 = 0.1097$, $wR_2 = 0.2196$
Largest difference peak and hole (e $Å^{-3}$)	1.083 and -2.445

RESULTS AND DISCUSSION

In all the complexes, the thiosemicarbazone deprotonates and chelates in thiolate form as evidenced by the IR spectra. The elemental analyses suggest the general empirical formula [Cu(DpyETsc)X] where X = N_3, Cl, ClO_4 and NCS for all complexes except **1** and **4**. Complex **1** turned out to be $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]$ and complex **4** to be $[Cu_2(DpyETsc)_2SO_4]$. The complexes are appreciably soluble in methanol, ethanol, DMF and DMSO.

The colours, partial elemental analyses and molar conductivities of the metal complexes are shown in Table-2. The green and brown colours are common to complexes involving thiosemicarbazone coordination due to the sulfur-to-metal charge-transfer bands, which dominate their visible spectra [10]. The molar conductivity values of the compounds **1**, **2**, **3**, **4** and **6**

TABLE-2
COLOURS, PARTIAL ELEMENTAL ANALYSES AND MOLAR CONDUCTIVITIES OF THE Cu(II) COMPLEXES

Compound	Colour	Elemental analysis (%): Found (calcd.)			Λ_M^*
		C	H	N	
$[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]H_2O$ (**1**)	Brown	31.68 (31.09)	3.23 (3.11)	18.47 (18.38)	11
$[Cu(DpyETsc)N_3]\cdot H_2O$ (**2**)	Green	41.03 (41.22)	3.70 (3.95)	27.41 (27.47)	6
$[Cu(DpyETsc)Cl]_2\cdot H_2O$ (**3**)	Green	42.38 (42.86)	3.27 (3.85)	17.88 (17.85)	10
$[Cu_2(DpyETsc)_2SO_4]_2\cdot 4H_2O$ (**4**)	Green	40.00 (40.62)	3.25 (3.90)	16.83 (16.92)	9
$[Cu_2(DpyETsc)_2](ClO_4)_2\cdot H_2O$ (**5**)	Green	36.56 (36.85)	2.93 (3.31)	15.44 (15.35)	155
$[Cu(DpyETsc)NCS]_2$ (**6**)	Brown	44.00 (44.38)	3.11 (3.48)	20.63 (20.70)	18

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

in 10^{-3} M solution in DMF show that they are nonconductors [11]. But the molar conductivity value of compound **5** suggests that it is 1:2 electrolyte.

Crystal structure of $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (1): The structure consists of symmetrical Cu_3L_2 core with the centrally interlocked copper ion as the inversion center. The DIAMOND drawing and atom labeling scheme of the complex is shown in Fig. 1 and selected geometrical parameters are given in Table-3. C12–S1 bond length of 1.718(8) Å indicates that the sulphur to be in deprotonated thiolate form [12,13].

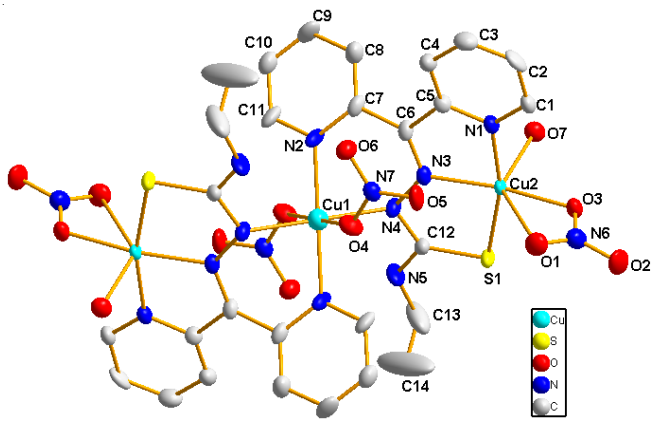


Fig. 1. Diamond diagram of $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**) along with the atom numbering scheme. The hydrogen atoms and water molecule are omitted for clarity

TABLE-3
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF $[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**)

Bond lengths (Å)		Bond angles (°)	
Cu(1)–N(4)	2.058(7)	N(4)–Cu(1)–N(2)	81.8(3)
Cu(1)–N(2)	2.073(7)	N(4)#1–Cu(1)–N(4)	180.00(1)
Cu(1)–O(4)	2.398(6)	N(4)–Cu(1)–N(2)#1	98.2(3)
Cu(2)–N(3)	1.977(6)	N(2)#1–Cu(1)–N(2)	180.00(4)
Cu(2)–N(1)	1.983(7)	N(4)#1–Cu(1)–O(4)	89.5(2)
Cu(2)–O(1)	2.760(7)	N(4)–Cu(1)–O(4)	90.5(2)
Cu(2)–O(3)	2.002(6)	N(2)#1–Cu(1)–O(4)	79.80(2)
Cu(2)–S(1)	2.250(3)	N(2)–Cu(1)–O(4)	100.2(2)
Cu(2)–O(7)	2.255(8)	N(4)–Cu(1)–O(4)#1	89.5(2)
S(1)–C(12)	1.718(8)	N(2)–Cu(1)–O(4)#1	79.8(2)
N(3)–C(6)	1.308(11)	O(4)–Cu(1)–O(4)#1	180.00(1)
N(4)–C(12)	1.368(10)	N(3)–Cu(2)–N(1)	80.0(3)
N(5)–C(12)	1.312(11)	N(3)–Cu(2)–O(3)	170.1(2)
Cu(1)···Cu(2)	4.7079(21)	N(1)–Cu(2)–O(3)	100.8(3)
		N(3)–Cu(2)–S(1)	85.2(2)
		O(3)–Cu(2)–S(1)	93.34(19)
		N(3)–Cu(2)–O(7)	102.5(3)
		N(1)–Cu(2)–O(7)	86.9(3)
		O(3)–Cu(2)–O(7)	87.4(3)
		S(1)–Cu(2)–O(7)	98.8(3)

Three copper centers are arranged in a linear fashion with a Cu1–Cu2 distance of 4.7079(21) Å. A polymeric Cu thiosemicarbazone complex with bridging of S and Cl is found to have a Cu–Cu distance of 3.790 Å [14]. The binuclear complex of $[Cu_2(dyapm)_2(C_2O_4)(NO_3)_2(C_3H_7NO)_2]$ is found to have a Cu–Cu distance of 5.737(2) Å [15]. There is no direct covalent linkage between Cu2 and Cu2′ and the *trans* arrangement of the chelating donors at the central copper ion leads these metals to be separated by a distance of 9.4158(41) Å. In the trinuclear unit Cu1 is found to have a six coordinated distorted octahedral geometry with two unidentate nitrate groups and each Cu2 a chelating bidentate nitrate group.

The metal ion Cu2 (and symmetry related Cu2′) is coordinated by the pyridine N[Cu2–N1 = 1.983(7) Å], azomethine N [Cu2–N3 = 1.977(6) Å] and the thiolato sulphur [Cu2–S1 = 2.250(3) Å] from the ligand. The remaining positions are occupied by oxygens of the chelating nitrate group [Cu2–O3 = 2.002(6) Å] and [Cu2–O1 = 2.760(7) Å]. This is found to be less than the distance observed for Cu–ONO_2 being 2.786(2) Å in $[Cu_2(dyapm)_2(C_2O_4)(NO_3)_2(C_3H_7NO)_2]$ [15]. The coordination is completed by oxygen of the water molecule at a distance of 2.255(8) Å.

The central Cu1 located at the inversion center of the molecule attains an axially elongated octahedral geometry being surrounded in the equatorial plane by two pyridine nitrogens [Cu1–N2= 2.073(7) Å] and two nitrogens adjacent to the azomethine nitrogens [Cu1–N4 = 2.058(7) Å] and at the axial positions by two nitrate oxygens [Cu1–O4 = 2.398(6) Å]. The variations in the N2–Cu1–N4 [81.8(3)] and N2–Cu1–O4 bond angles [100.2(2)] from 90.0 cause distortion to the octahedral geometry. However this leads to a stable six membered Cu1–N2–C(7)–C6–N3–N4 metallocycle. The centrosymmetric metallocycle with respect to Cu1 atom is depicted in Fig. 2.

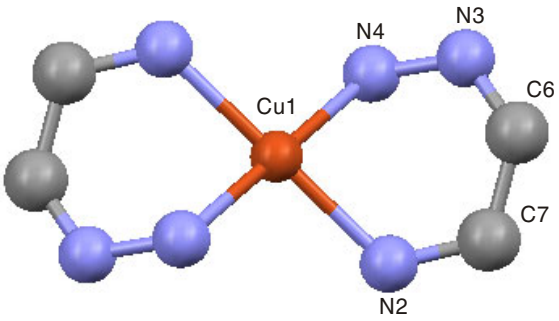


Fig. 2. Centrosymmetric six membered metallocycle formed along Cu(1) centre

In the solid state, the complex shows a variety of H–bonding interactions involving amino nitrogen and the nitrato oxygen. Two different hydrogen-bonding motifs are present in the molecule. Intramolecular hydrogen bonding interactions are observed between the amino nitrogen N5 of one ligand with the nitrato oxygen O6 at a distance of 2.895(10) Å. Another intramolecular metal-hydrogen interaction is observed between Cu1 and N5H at a distance of 2.83 Å. The Cu2 bound water molecule is hydrogen bonded to nitrato oxygen O6 and O111 of the water molecule [2.813(12) Å and 2.779(14) Å] by intermolecular interaction. H111 and H222 of the same water molecule is hydrogen bonded to adjacent O2 nitrato group coordinated to Cu2 at a distance of 2.847(13) and 2.813(12) Å. These type of hydrogen bonding interactions are found to be very important in active species of several multinuclear metalloenzymes [16]. The lattice water held among the units are depicted as in Fig. 3.

The ring puckering analysis show that the ring Cg(3) consisting of atoms Cu2–N1–C5–C6–N3 adopts an envelope on N3 [Q(2) =0.147(7)] [17]. The packing diagram along c axis

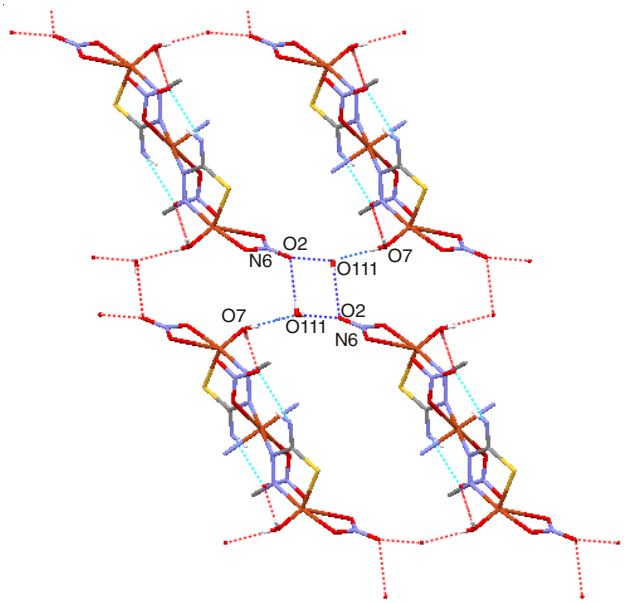


Fig. 3. A view of the hydrogen bonding interactions in compound **1**. (dipyridyl portions omitted for clarity)

(Fig. 4) shows the diverse π–π stacking and CH–π and N–O–π interactions giving rise to a supramolecular three-dimensional net work. When viewed along the a and b axes units are arranged in superimposing layers as in Fig. 5.

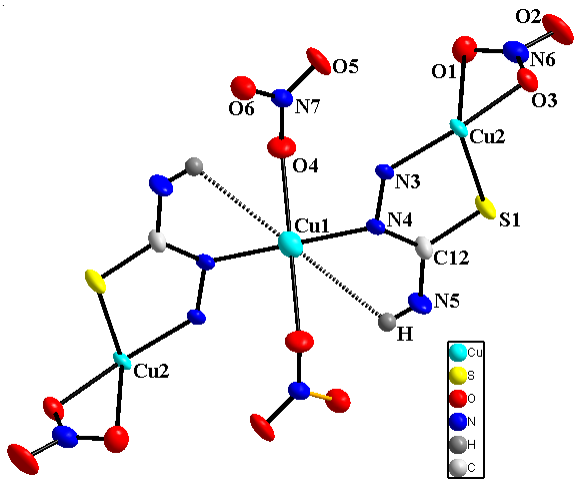


Fig. 4. Compound **1** showing Cu(1)–N5(H) interactions and Cu(1)–N(4) coordination (dipyridyl portions omitted for clarity)

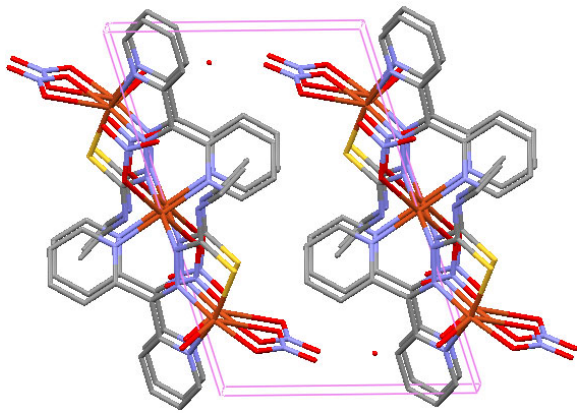


Fig. 5. Packing diagram along b axis of compound **1**

A very interesting aspect observed is the pentadentate coordination shown by the ligand which is usually tridentate. The usual coordinating sites (NNS) are coordinated to Cu2 while the unusual sites *i.e.* N2 (second pyridine N) and N4 to the central Cu1. This type of Cu1–N4 coordination is first observed according to the best of our knowledge. Another feature observed is the metal-hydrogen interaction observed.

TABLE-4
H-BONDING, π–π, CH–π AND N–O–π
INTERACTION PARAMETERS OF COMPOUND **1**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (Å)
N(5)–H(5)···O(6)[a]	0.88	2.12	2.895	147
O(7)–H(101)···O(111)[b]	0.71	2.07	2.779	172
O(7)–H(102)···O(6)[c]	0.56	2.26	2.813	169
O(111)–H(111). .O(2)[d]	0.68	2.21	2.847(13)	158
O(111)–H(222)···O(2)[e]	0.57	2.26	2.818	167
π–π interactions				
Cg(I)–Res(I)···Cg(J)	Cg–Cg (Å)		α (°)	β (°)
Cg(2) [1] -> Cg(7)[a]	4.795(5)		45.51	44.00
Cg(6) [1] -> Cg(6)[g]	4.701(6)		0.00	45.24
CH–π interactions				
X--H(I) Res(I) Cg(J)	H..Cg (Å)		X-H..Cg (°)	X..Cg(Å)
C(11)-H(11) [1] -> Cg(2)[a]	2.94		132	3.638(10)
N–O–π interaction				
Y--X(I) Res(I) Cg(J)[f]	X..Cg (Å)		Y-X..Cg (°)	Y..Cg(Å)
N(7) -O(5) [1] -> Cg(3)	3.123(8)		85.0(5)	3.251(8)
Metal-H interaction (Å)				
Cu(1). ... H(5)[a]	2.83			

Equivalent position code a = -x,2-y,1-z; b = 1-x,2-y,1-z;
c = 1+x,y,z; d = 1-x,1-y,1-z; e = x,y,1+z; f = x,y,z; g = -x,2-y,-z.
Cg(2) = Cu(2) --> S(1)-->C(12)--> N(4)-->N(3)-->
Cg(3) = Cu(2)--> N(1) --> C(5) --> C(6) --> N(3) -->
Cg(6) = N(1) --> C(1) -->C(2) -->C(3) -->C(4) -->C(5) -->
D, donor; A, acceptor; Cg, centroid; α, dihedral angles between planes I and J; β, angles between Cg(I) and Cg(J)

Infrared spectra: The characteristic IR bands of the complexes differ from their free ligand HDpyETsc and provide significant indications regarding the coordination and bonding sites of the ligand. Relevant characteristic bands of all the compounds are listed in Table-5. The strong band at 3199 cm^{-1} in the spectrum of HDpyETsc has been assigned to $\nu(^4N–H)$. In the complexes these bands shift to higher energies, suggesting differences in hydrogen bonding of N(4)H between the uncomplexed and complexed thiosemicarbazone [18]. The IR spectrum of the ligand exhibits a medium band at 2979 cm^{-1} assigned to $\nu(^2N–H)$ vibration, disappears in the spectra of all the complexes providing strong evidence for ligand coordination to the copper(II) ion in the deprotonated thiolate form [19]. On coordination of the azomethine nitrogen, ν(C=N) band shifts to lower wave numbers in the spectra of the complexes [20]. The ν(Cu–N) stretching frequencies for the azomethine nitrogen are observed around 400 cm^{-1}. Strong band found at 1109 cm^{-1} in the ligand is 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 [21]. The IR spectra of the complexes show a new sharp band at about 1520 cm^{-1} which is assigned to the newly formed ν(N=C). This indicates that the ligand enolizes and

TABLE-5
INFRARED SPECTRA (cm^{-1}) OF HDpyETsc AND ITS COPPER COMPLEXES

Compounds	$\nu(^4N–H)$	ν(C=N)	ν/δ(C–S)	ν(N–N)	CuN	py(op)
HDpyETsc	3199	1585	1431, 799	1109	--	615
$[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$(**1**)	3205	1524	1340, 796	1157	415	635
$[Cu(DpyETsc)N_3]\cdot H_2O$ (**2**)	3341	1517	1334, 788	1118	408	652
$[Cu(DpyETsc)Cl]_2\cdot H_2O$ (**3**)	3269	1518	1333, 783	1152	407	644
$[Cu_2(DpyETsc)_2SO_4]_2\cdot 4H_2O$ (**4**)	3255	1525	1337, 785	1157	412	686
$[Cu_2(DpyETsc)_2](ClO_4)_2\cdot H_2O$ (**5**)	3308	1518	1307, 788	1168	412	623
$[Cu(DpyETsc)NCS]_2$ (**6**)	3241	1512	1338, 781	1130	410	666

coordinates in the thiolate form. Coordination *via* thiolate sulfur is also indicated by the ν(CS) and δ(CS) bands found at about 1335 and 780 cm^{-1}, respectively The out-of-plane bending vibrations of the pyridine ring in uncomplexed ligands shift to higher frequencies on complexation, confirming the coordination of the ligands to the metal *via* the pyridine nitrogen [22].

The nitrato complex **1** has three strong bands at 1275, 1384 and 1036 cm^{-1} corresponding to ν_1, ν_4 and ν_2 of unidentate nitrato groups with a separation of 109 cm^{-1} for ν_1 and ν_4 indicating the presence of a terminally bonded monodentate nitrato group. ν_3, ν_5 and ν_6 are observed at 748, 731 and 822 cm^{-1}, respectively [23].

The spectrum of complex **2** showed a strong band at 2051 cm^{-1} due to asymmetric $\nu(N_3)$ mode. The band associated with the symmetric $\nu(N_3)$ mode is located at 1378 cm^{-1}. The broad band observed at 687 cm^{-1} are assigned to δ(N–N–N) vibration.

The sulfato complex **4** exhibits four fundamental vibrations *i.e.*, 975 cm^{-1} due to ν_1, a medium band at 450 cm^{-1} due to ν_2, medium and weak bands at 1267, 1181 and 1120 cm^{-1} corresponding to ν_3 and medium and weak bands at 653, 612 and 580 cm^{-1} due to ν_4, which are assigned to the bidentately coordinated sulfato group [24].

The perchlorato complex **5** shows a single broad band at 1090 cm^{-1} and another strong band at 636 cm^{-1}, indicating the presence of ionic perchlorate. The band at 1090 cm^{-1} is assignable to $\nu_3(ClO_4)$ and the unsplit band at 636 cm^{-1} assignable to $\nu_4(ClO_4)$. Also in the spectrum of the compound, a medium band at 963 cm^{-1} may be due to $\nu_1(ClO_4)$ suggesting that ionic perchlorate is distorted from tetrahedral symmetry due to lattice effects or hydrogen bonding by the NH functions of the coordinated ligand [25].

Thiocyanato complex **6** has a very strong and sharp band at 2075 cm^{-1}, a medium band at 748 cm^{-1} and a weak band at 470 cm^{-1} corresponding to ν(CN), ν(CS) and δ(NCS) modes of the NCS group, respectively [26]. The intensity and position of these bands indicate the unidentate coordination of the thiocyanate group through the nitrogen.

Electronic spectra: The significant electronic absorption bands in the spectra of the ligand and complexes are presented in Table-6. The spectrum of HDpyETsc show the intraligand absorption maxima at 34720 and 29400 cm^{-1}. These bands are due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of the thiosemicarbazone ligand. Strong bands in the range 23000–24500 cm^{-1} observed in the spectra of all Cu(II) complexes are assigned to S→Cu and py→Cu charge-transfer bands [27].

All complexes exhibit a *d-d* band as weak shoulders in the visible region in the range 16500-18500 cm^{-1}. For the square planar complexes 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} ($^2A_{1g}\rightarrow {}^2B_{1g}$, $^2B_{2g}\rightarrow {}^2B_{1g}$ and $^2E_g\rightarrow {}^2B_{1g}$) 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 [28-30]. Since the four *d* orbitals lie very close together, each transition cannot be distinguished by their energy and hence it is difficult to resolve the three bands into separate components.

EPR spectra: The EPR spectra of the complexes in the polycrystalline state at 298 K and in solution at 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 the Table-7. 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 frequency, 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 [31]:

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

TABLE-6
ELECTRONIC SPECTRA (cm^{-1}) OF HDpyETsc AND ITS COPPER(II) COMPLEXES

Compound	$\pi\rightarrow\pi^*$	$n\rightarrow\pi^*$	C T	d-d
HDpyETsc	34560	29410	–	–
$[Cu_3(DpyETsc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**)	34250	29330	24270	15380
$[Cu(DpyETsc)N_3]\cdot H_2O$ (**2**)	33670	28330	23810	18520
$[Cu(DpyETsc)Cl]_2\cdot H_2O$ (**3**)	32790	28010	23640	17010
$[Cu_2(DpyETsc)_2SO_4]_2\cdot 4H_2O$ (**4**)	33330	28410	23640	17180
$[Cu_2(DpyETsc)_2](ClO_4)_2\cdot H_2O$ (**5**)	33110	28650	23810	16450
[Cu(DpyETsc)NCS] (**6**)	34010	29760	23980	17450

TABLE-7
EPR SPECTRAL PARAMETERS OF THE COPPER(II) COMPLEXES

	1	**2**	**3**	**4**	**5**	**6**
Polycrystalline (298 K)						
$g_{\parallel}$	–	–	2.1848	–	–	2.1515
$g_{\perp}$	–	–	2.0635	–	–	2.0705
g_{iso} or g_{av}	2.0951	2.1348	–	2.0839	2.0730	
DMF (77 K)						
$g_{\parallel}$	2.1741	2.1581	2.1591	2.1745	2.1766	2.1693
$g_{\perp}$	2.0594	2.0441	2.0518	2.0531	2.0577	2.0500
$A_{\parallel}$	196.6	186.6	182.6	195.0	196.6	196.6
α^2	0.7483	0.7349	0.7282	0.7830	0.7923	0.7795
β^2	0.8429	0.8967	0.8699	0.8523	0.8291	0.8497
γ^2	0.9692	0.9239	0.9736	0.9228	0.9322	0.9050
$K_{\parallel}$	0.6307	0.6590	0.6375	0.6673	0.6569	0.6623
$K_{\perp}$	0.7253	0.6798	0.7095	0.7225	0.7386	0.7054

The EPR spectra of compounds **1**, **3**, **4** and **5** in the polycrystalline state (298 K) show only one broad signal at 2.13, 2.09, 2.08 and 2.09, 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. This type of spectra unfortunately give no information on the electronic ground state of the Cu(II) ion present in the complexes. However the spectra of compounds **2** and **6** show typical axial behaviour (Fig. 6) with well defined $g_{\parallel}$ and $g_{\perp}$ features. The variation in the g values indicates that the geometry of the compound is affected by the nature of the coordinating anions. 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: $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$. If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex [24].

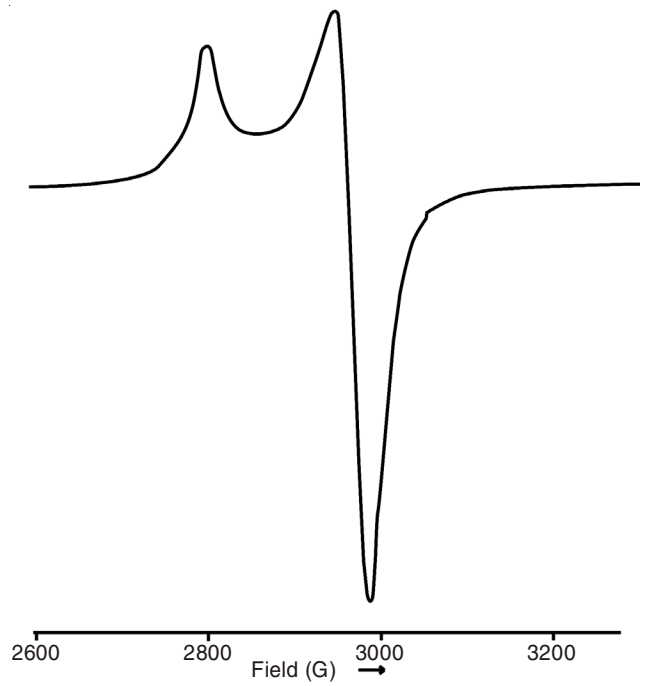


Fig. 6. Solid state EPR spectra of $[Cu(DpyETsc)Cl]_2 \cdot H_2O$ (**3**)

In all the copper(II) complexes $g_{\parallel} > g_{\perp} > 2.0023$ and G values within the range 2.14–2.91 are consistent with a $d_{x^2-y^2}$ ground state [32].

For the spectra of all the complexes in frozen DMF the $g_{\parallel} > g_{\perp}$ values rule out the possibility of a trigonal bipyramidal structure for which $g_{\perp} > g_{\parallel}$ is expected. For the complexes **1**, **2**, **4** and **6**, we obtain well-resolved four hyperfine lines in the parallel region (Fig. 7). But for complex **5**, seven hyperfine lines are obtained, suggesting a dimeric state with two copper centres. The splitting in the perpendicular region of the spectra can be attributed to interaction of an unpaired electron spin with the copper nuclear spin and two ^{14}N (I = 1) donor nuclei. The binuclear nature of **3**, **4**, **5** and **6** was confirmed by the presence of half-field signals ($\Delta M_s = \pm 2$) at about 1600 G (Fig. 8). For **1**, the spectrum shows an axial part with four main hyperfine peaks in the $g_{\parallel}$ region due to the central Cu(II) ion and a signal at g = 4.147 that is attributed to a $\Delta M_s = 2$ transition from the two triplet states formed from the interactions of the central Cu(II) ion with each one of the two terminal copper ions. 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

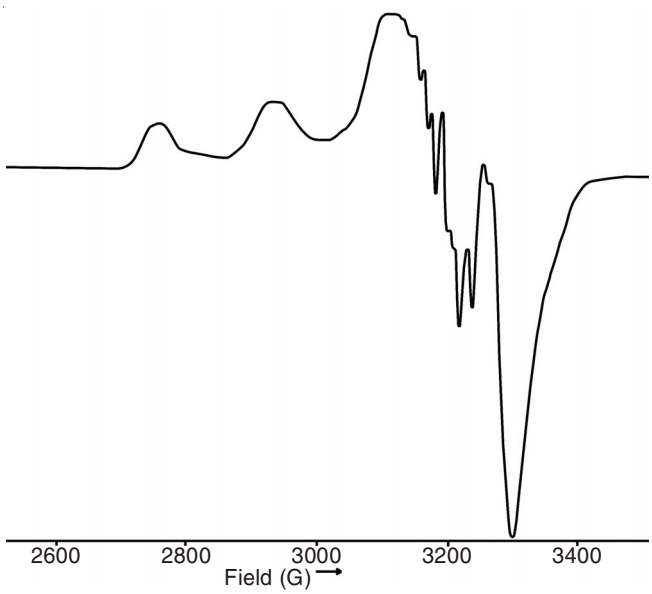


Fig. 7. EPR spectrum of $[Cu(DpyETsc)Cl]_2 \cdot H_2O$ (**3**) at 77 K

Fig. 8. EPR spectrum of compound **5** in DMF at 77 K

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:

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

The orbital reduction factors $K_{\parallel} = \alpha^2 \beta^2$ and $K_{\perp} = \alpha^2\gamma^2$ were calculated using the following expressions [19].

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\Delta E(d_{xy} - d_{x^2-y^2}) / 8\lambda_0$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E(d_{xy,yz} - d_{x^2-y^2}) / 2\lambda_0$$

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

According to Hathaway, $K_{\parallel} = K_{\perp} = 0.77$ for pure σ bonding and $K_{\parallel} < K_{\perp}$ for in-plane π bonding, while for out-of-plane π bonding $K_{\parallel} > K_{\perp}$. In all the copper(II) complexes, it is observed that $K_{\parallel} < K_{\perp}$ 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 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 but are different from that in the solid state. Kivelson and Neiman [31] have reported that $g_{\parallel}$ values less than 2.3 indicate considerable covalent character to M-L bonds and greater than 2.3 indicate ionic character. The $g_{\parallel}$ values of the complexes are found to be less than 2.3, which indicate considerable covalent character to the M-L bond.

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