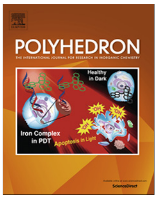
Polyhedron 75 (2014) 50–56

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis and spectral characterization of copper(II) complexes derived from 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone: Crystal structure of a binuclear complex

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ARTICLE INFO

Article history:
Received 13 December 2013
Accepted 28 February 2014
Available online 12 March 2014

Keywords:
2-Benzoylpyridine
Thiosemicarbazone
Copper(II) complex
EPR
X-ray crystal structure

ABSTRACT

Six copper(II) complexes $[Cu_2(L)_2SO_4]\cdot H_2O$ (**1**), $[Cu_2(L)_2(OAc)_2]\cdot H_2O$ (**2**), $[Cu(L)NO_3]_2$ (**3**), $[Cu(L)N_3]_2\cdot H_2O$ (**4**), $[Cu(L)NCS]\cdot H_2O$ (**5**) and $[Cu(L)I]$ (**6**) of 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone (HL) were prepared and characterized using partial elemental analysis, magnetic susceptibility, conductivity measurements, FT-IR, UV–Vis and EPR studies. The molecular structure of $[Cu_2(L)_2(OAc)_2]$ (**2a**) was resolved using single crystal X-ray diffraction studies and it was found to have distorted square pyramidal geometry with the basal plane occupied by thiosemicarbazone and the acetate oxygen O2. The compound crystallized in monoclinic space group $P2_1/n$ and formed a centrosymmetric dimer, bridged through oxygen of the acetate moiety. From the physicochemical studies, it was found that thiosemicarbazone coordinates through one of the pyridyl nitrogen, azomethine nitrogen and thioiminolate sulfur atoms. Binuclear nature of some of the complexes was confirmed from EPR parameters and magnetic moment values. In all complexes g values in frozen DMF, indicate the presence of the unpaired electron residing in the $d_{x^2-y^2}$ orbital.

1. Introduction

Thiosemicarbazones are versatile class of ligand systems formed by the condenzation of thiosemicarbazides with aldehydes or ketones. The remarkable features lie in their wide range of biological applications such as antitumor [1], antibacterial [2], anti-viral [3] and anticarcinogenic properties [4] and structural diversity due to their variable coordinative abilities [5,6]. 2-Benzoylpyridine thiosemicarbazone was proved as a novel reagent for the single pot synthesis of dinuclear Cu(I)–Cu(II) complexes with stable copper(II)–iodide bonds [7]. This paper reports the synthesis and spectral characterization of copper(II) complexes derived from 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone along with the crystal structure of a binuclear copper(II) complex.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and purchased from commercial sources. The solvents were purified according to standard procedures. 2-Benzoylpyridine (Aldrich), N^4,N^4-dimethyl-3-thiosemicarbazide (Aldrich), $CuSO_4\cdot 5H_2O$, $CuNO_3\cdot 5H_2O$, $Cu(CH_3COO)_2\cdot H_2O$, NaN_3, KSCN, NaI (all are BDH, AR quality) were used as received. Caution! Metal complexes with organic ligands containing azide are potentially explosive. So they should be prepared in small quantities and handled with care.

2.2. Synthesis of the thiosemicarbazone HL and its copper(II) complexes

2.2.1. Synthesis of thiosemicarbazone HL

The thiosemicarbazone was synthesized according to the reported procedure [8] and its crystal structure has been published [9]. The structural formula of the ligand (HL) is represented in the Scheme 1.

HL: Yield: 70%; M.P. 140 °C; $C_{15}H_{16}N_4S$; C 63.35 (63.85); H 5.67 (5.86); N 19.70 (20.01); S 11.28 (11.00); IR (cm^{-1}): 1575s, ν(C=N); 1115s, ν(N–N); 1420s, 805s, ν(C=S); 699s, ν(py(ip)); 3055 m, ν(^{2}N–H); Mass to charge ratio (m/z): 285.2 (M+1); ^{1}H NMR (δ ppm in $CDCl_3$): 14.365 (1H, b), 8.753–7.347 (aromatic protons), 3.452 (6H, s).

2.2.2. Synthesis of copper(II) complexes

*2.2.2.1. Synthesis of $[Cu_2(L)_2SO_4]\cdot H_2O$ (**1**), $[Cu_2(L)_2(OAc)_2]\cdot H_2O$ (**2**), $[Cu(L)NO_3]_2$ (**3**).* A solution of thiosemicarbazone, HL (0.284 g,

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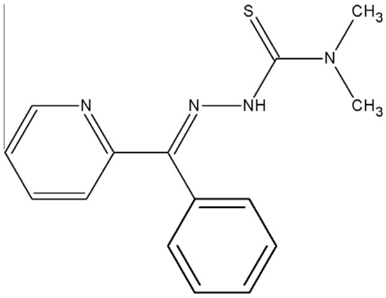
http://dx.doi.org/10.1016/j.poly.2014.02.042
0277-5387/



Scheme 1. Structure of 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone.

1 mmol) in 10 mL of methanol was mixed and refluxed with methanolic solution (10 mL) of appropriate copper(II) salt (1 mmol) for 4 h. On cooling, the complexes formed was filtered, washed with few drops of methanol and ether and dried *in vacuo* over P_4O_{10}.

*2.2.2.2. Synthesis of [Cu(L)N₃]₂·H₂O (**4**) and [Cu(L)NCS]·H₂O (**5**).* A solution of thiosemicarbazone, HL (0.284 g, 1 mmol) in 10 mL of hot methanol was treated with aqueous solution of $Cu(OAc)_2 \cdot H_2O$ (0.199 g, 1 mmol). To this 1 mmol NaN_3/KSCN was added and refluxed for 4 h. On cooling, the compounds separated was filtered, washed with few drops of methanol and ether and dried over P_4O_{10} *in vacuo.*

*2.2.2.3. Synthesis of [Cu(L)I] (**6**).* For the synthesis of this complex, a solution of $CuNO_3 \cdot 5H_2O$ (0.246 g, 1 mmol) in 10 mL of methanol and a solution of NaI (0.1525 g, 1 mmol) in 10 mL of methanol were mixed and boiled for 15 min and then chilled in ice. The precipitated CuI was filtered and CuI was treated with a solution of thiosemicarbazone, HL (0.284 g, 1 mmol) in 10 mL hot methanol and refluxed for 4 h and cooled. The dark green shining crystals formed were filtered, washed with few drops of methanol and ether and dried over P_4O_{10} *in vacuo.*

2.3. Physical measurements

The partial elemental analyses of the thiosemicarbazone and its complexes were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. IR spectra were recorded on a JASCO FT-IR-5300 spectrometer in the range 4000–400 cm^{-1} using KBr pellets. Electronic spectra were recorded on a Cary 5000, version 1.09 UV–Vis–NIR spectrophotometer using acetonitrile solutions. Magnetic susceptibility measurements were made in the polycrystalline state in a simple Gouy balance using cobaltmercuric thiocyanate, $Hg[Co(SCN)_4]$ at room temperature at the Department of Applied Chemistry, CUSAT, Kochi, India. The EPR spectra were recorded in a Varian E-112 X-band spectrometer using TCNE ($g = 2.00277$) as standard at the SAIF, IIT, Bombay, India. The molar conductivities of the complexes in DMF solutions (10^{-3} M) at room temperature were measured using a direct reading conductivity meter.

2.4. X-ray crystallography

Single crystals of complex $[Cu_2(L)_2(OAc)_2]$ (**2a**) suitable for X-ray diffraction studies were obtained by slow evaporation of its methanolic solution over a period of one week at room temperature. A single crystal of dimensions 0.36 × 0.20 × 0.20 mm^3 was selected and mounted on a Bruker SMART APEX diffractometer, equipped with a graphite crystal incident-beam monochromator, and a fine focus sealed tube with Mo Kα ($\lambda = 0.71073$ Å) as the X-ray source. The unit cell dimensions were measured and the data collection was performed at 293(2) K. Bruker SMART software was used for data acquisition and Bruker SAINT software for data integration [10]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [11]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXL-97 software package [12]. The graphics tool used was DIAMOND version 3.2 g [13]. All non hydrogen atoms were refined anisotropically and positions of hydrogen atoms were derived from Fourier difference maps and were placed geometrically and refined with a riding model. The crystallographic data along with details of structure solution refinements are given in Table 1.

3. Results and discussion

The copper(II) complexes **1**, **2** and **3** were prepared by the reaction of the thiosemicarbazone, HL with appropriate copper(II) salts in 1:1 M ratio. The complexes **4** and **5** were prepared by refluxing the thiosemicarbazone with copper(II) acetate and NaN_3 or KSCN in 1:1:1 M ratio. For the synthesis of complex **6**, metathetical replacement was used. Binuclearity of some complexes was confirmed from EPR studies.

Molar conductance of the complexes measured using 10^{-3} M DMF solutions showed that all the complexes except **3** are found to be non electrolyte in nature [14]. Higher conductance of the complex **3** is due to the partial ionization of complex in the DMF solvent. Magnetic moments of the complexes were calculated from magnetic susceptibility measurements. Copper(II) complexes formulated as mononuclear exhibit magnetic moments in the range 1.60–1.78 B.M., which are close to the spin only value [15]. The magnetic moments of the binuclear complexes were found to be in the range 1.37–1.63 B.M. These low magnetic moments may be attributed to the presence of a strong antiferromagnetic interaction. All complexes except **5** and **6** are binuclear in nature. The analytical data of the complexes are listed in Table 2.

3.1. Crystal structure of [Cu₂L₂(OAc)₂] (**2a**)

The molecular structure of the compound along with atom numbering scheme is given in Fig. 1 and selected bond lengths (Å) and bond angles (°) are shown in Table 3.

Even though the compound is isolated as monohydrate, the single crystals do not have any water of hydration. This compound crystallized in monoclinic space group $P2_1/n$ and it is a dimer bridged through oxygen of the acetate moiety. The asymmetric unit is formed by one half of the molecule and the other half is generated by a center of inversion.

The structure contains two copper centers where each copper(II) center is pentacoordinated with azomethine nitrogen N2, pyridyl nitrogen N1, thioiminolate sulfur S1 of thiosemicarbazone moiety and oxygens (O2, O2A) from two acetate groups. The trigonality index τ is calculated using the equation $\tau = (\beta - \alpha)/60$ [16] (for perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity respectively). The value of τ for the molecule is 0.217 which shows that the compound exhibits a distorted square pyramidal geometry with the basal plane occupied by thiosemicarbazone and the acetate oxygen O2.

The oxygen O2A from acetate group of the adjacent monomer plugs into the axial position resulting in a dimer with a Cu···Cu separation of 3.500 Å. The four coplanar basal atoms show a significant distortion from a square geometry as indicated by the N1–Cu1–S1 bond angle of 163.20(5)°. The deviation of the central copper atom from the basal plane in the direction of the axial oxygen is evident from the bond angles of N2–Cu1–O2, 176.22(6)° and N1–Cu1–O2, 96.85(7)°. Most of the angles involving the central copper atoms are widely different from 90° and 180°,

Table 1
Crystal refinement parameters of $[Cu_2(L)_2(OAc)_2]$ (**2a**).

Empirical formula	$C_{34}H_{36}Cu_2N_8O_4S_2$
Formula weight	811.91
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.808(2)
b (Å)	16.589(5)
c (Å)	12.391(3)
α (°)	90
β (°)	93.909(10)
γ (°)	90
V (°)	1806.3(8)
Z	2
Calculated density (Mg/m^3)	1.493
Absorption coefficient (mm^{-1})	1.342
F(000)	836
Crystal size (mm)	0.30 × 0.20 × 0.20
θ (°)	2.05–28.05
Limiting indices	$-11 \leqslant h \leqslant 11$, $-21 \leqslant k \leqslant 21$, $-15 \leqslant l \leqslant 16$
Reflections collected/unique (R_{int})	21166/4381 (0.0290)
Completeness to θ (%)	25.00 (100.0)
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.801 and 0.722
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4381/0/229
Goodness-of-fit (GOF) on F^2	1.035
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0831$
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.0902$
Largest difference in peak and hole (e Å^{-3})	0.281 and −0.269

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

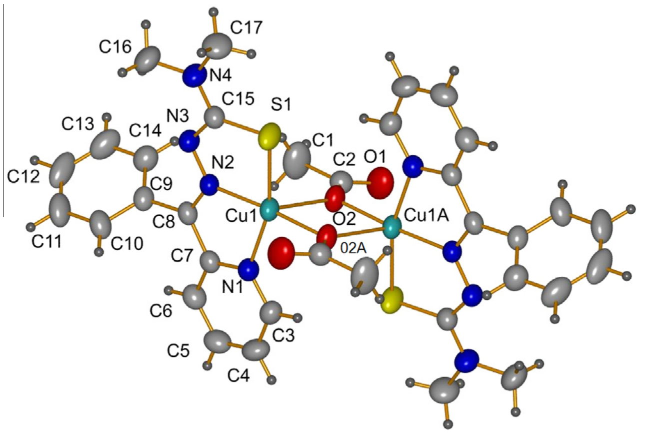


Fig. 1. The molecular structure of $[Cu_2(L)_2(OAc)_2]$ (**2a**) along with the atom numbering scheme.

Table 3
Selected bond lengths (Å) and bond angles (°) of $[Cu_2(L)_2(OAc)_2]$ (**2a**).

Cu(1)–N(1)	2.0227(17)
Cu(1)–N(2)	1.9651(16)
Cu(1)–O(2)	1.9432(13)
Cu(1)–S(1)	2.2601(8)
C(15)–S(1)	1.730(2)
C(8)–N(2)	1.299(2)
C(15)–N(3)	1.328(3)
N(2)–N(3)	1.357(2)
Cu1···Cu1A	3.500
O(2)–Cu(1)–N(2)	176.22(6)
O(2)–Cu(1)–N(1)	96.85(7)
N(2)–Cu(1)–N(1)	80.26(7)
O(2)–Cu(1)–S(1)	98.56(5)
N(2)–Cu(1)–S(1)	84.04(5)
N(1)–Cu(1)–S(1)	163.20(5)

indicating significant distortion from the square pyramidal geometry.

Weak non-classical intramolecular hydrogen bonding interactions (Fig. 2) make the molecule more rigid and the two types of C–H···π interactions mainly involve in interconnecting the neighboring molecules with H···Cg distances of 3.2523 and 3.3856 Å (Table 4). Very weak π···π interactions are also present in the crystal system.

3.2. IR spectra

The tentative assignments of the significant IR spectral bands of HL and its copper(II) complexes are presented in Table 5. The ν(C=N) band at 1575 cm^{-1} is shifted to lower energies in the spectra of the complexes indicating coordination through azomethine nitrogen [17]. The strong band at 1115 cm^{-1} is assigned to ν(N–N) band of the thiosemicarbazone. In complexes, the frequency of this band was found to increase and may be due to the increase in the bond strength, confirming the coordination *via* the azomethine nitrogen [17]. In the spectrum of HL, two strong bands at 1420 and 805 cm^{-1} are assigned to ν(C=S), whereas in the complexes these bands are found to shift to lower frequencies in the ranges 1340–1310 and 796–777 cm^{-1} respectively. This characteristic shift of the ν(C=S) in the complexes confirms the coordination *via* the thioiminolate sulfur atom. Formation of a new band at *ca.* 1510 cm^{-1} assigned to ν(C = N) bond and disappearance of medium band at 3055 cm^{-1} assigned to $\nu(^2$N–H) vibration provides a strong evidence for the ligand coordination around Cu(II) ion in the deprotonated form. Coordination of pyridine ring nitrogen in the complexes is indicated by a shift of in-plane and out-of-plane ring deformation bands [18]. Based on the above spectral evidence,

Table 2
Colors, partial elemental analyses and magnetic moments of 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone and its copper(II) complexes.

Compounds	Color	Found (Calc.)%				μ (B.M.)	Λ^*_M
		C	H	N	S		
HL	yellow	63.85 (63.35)	5.86 (5.67)	20.01 (19.70)	11.00 (11.28)		
$[Cu_2(L)_2SO_4]\cdot H_2O$ (**1**)	black	44.75 (44.60)	4.18 (3.99)	13.60 (13.87)	12.00 (11.91)	1.38	5.8
$[Cu_2(L)_2(OAc)_2]\cdot H_2O$ (**2**)	black	48.55 (49.20)	4.77 (4.62)	12.97 (13.50)	7.23 (7.73)	1.37	1.6
$[Cu(L)NO_3]_2$ (**3**)	black	43.94 (44.06)	3.77 (3.70)	17.14 (17.13)	8.08 (7.84)	1.52	71
$[Cu(L)N_3]_2\cdot H_2O$ (**4**)	brown	45.33 (45.27)	3.84 (4.05)	24.68 (24.68)	8.50 (8.06)	1.63	3
$[Cu(L)NCS]\cdot H_2O$ (**5**)	brown	45.27 (45.43)	3.39 (4.05)	17.46 (16.56)	14.48 (15.16)	1.60	14.2
$[Cu(L)I]$ (**6**)	black	38.09 (38.02)	3.60 (3.19)	11.78 (11.82)	6.31 (6.77)	1.78	4.5

* 10^{-3} M solutions in DMF.

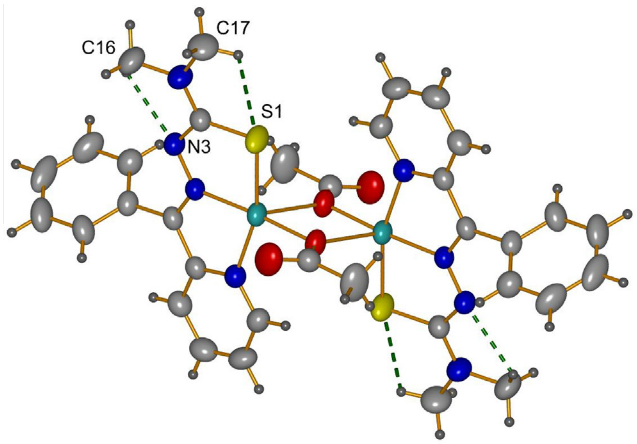


Fig. 2. Molecular structure showing intramolecular hydrogen bonding interactions.

Table 4
Hydrogen bonding interactions.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
C(16)–H(16C)···N(3)	0.9602	2.3131	2.670(3)	101.13
C(17)–H(17A)···S(1)	0.9609	2.4833	2.982(3)	112.19
X–H(I)···Cg(J)	H···Cg (Å)		X···Cg (Å)	∠X–H···Cg (°)
C–H···π interactions				
C(16)–H16B···Cg(1)[a]	3.2523		3.657(3)	107.43
C(16)–H16B···Cg(1)[a]	3.3856		4.179(3)	141.35

Equivalent position code: $a = -1 + x, y, z$.
Cg(1) = N1, C3, C4, C5, C6, C7.
D, donor; A, acceptor; Cg, centroid;

it is confirmed that the thiosemicarbazone HL is tridentate in nature coordinating *via* the azomethine nitrogen, the pyridyl nitrogen and thioiminolate sulfur.

Sulfato complex **1** showed strong band at 1029 cm^{-1} due to ν_1 and weak band at 962 cm^{-1} due to ν_3 can be assigned to the sulfato anion existing in the bridged bidentate form [19]. This type of sulfato complex with bridged bidentate nature has been proved for copper complex derived from di-2-pyridyl ketone thiosemicarbazone [20]. The bands at 1551 [ν_a(COO)] and 1387 cm^{-1} [ν_s(COO)] support the bridging nature of acetate group in complex **2** [21]. In the nitrato complex **3**, three strong bands at 1459, 1392 and 1140 cm^{-1} indicates the ν_4, ν_1 and ν_2 modes of the nitrato group and it confirms the presence of terminal monodentate nitrato group [19]. The azido complex **4** shows a single strong band at 2055 cm^{-1} due to the asymmetric stretching mode and the band associated with symmetric stretching mode is located at 1386 cm^{-1} [22]. Thiocyanato complex **5** exhibit strong band at 2073 cm^{-1} and weak bands at 747 and 489 cm^{-1}, which can be attributed to ν(CN), ν(CS), and ν(NCS) respectively. These values are typical for unidentate N-bonded thiocyanate complexes [23]. The presence of lattice water was confirmed from the broad band obtained above 3400 cm^{-1} [24].

3.3. Electronic spectra

The electronic spectral data of thiosemicarbazone and its Cu(II) complexes in acetonitrile solution are given in Table 6.

The spectrum of thiosemicarbazone, HL consists of broad band at 36580 cm^{-1}. This band remained almost unshifted in the complexes and is due to π–π^* transition of the thiosemicarbazone. The n–π^* band which is found at 29820 cm^{-1} in the spectrum of thiosemicarbazone was slightly shifted due to complexation. This is an indication of the enolization followed by deprotonation of the ligand during complexation [25]. The charge transfer bands were observed in the 23000–25000 cm^{-1} range, and their broadness can be explained as due to the combination of S → Cu and pyridine N → Cu LMCT transitions [25]. All complexes exhibit *d–d* bands as shoulders in the 14430–18230 cm^{-1} region.

3.4. EPR studies

The EPR spectra of the complexes in polycrystalline state at 298 K and solution state 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 ($g = 2.00277$). The EPR spectra are simulated using EasySpin 4.0.0 package [26] and the experimental (red) and simulated (blue) best fits are included. The EPR parameters of the copper(II) complexes were presented in Table 7.

In polycrystalline state at 298 K, compounds **1**, **4** and **5** displayed isotropic spectra with $g_{iso} = 2.080$, 2.053 and 2.060 respectively, arising from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell and enhanced spin lattice relaxation. Unfortunately this type of spectra give no information on the electronic ground state of Cu(II) ion present in the complexes. However the dimeric nature of the complex **1** is evident from the half field signal at 1540 G ($g = 4.200$), with a sevenfold hyperfine splitting.

EPR spectra of compounds **2**, **3** and **6** showed typical axial behavior with slightly different $g_{||}$ and $g_{\perp}$ values in the polycrystalline state. The variation in the $g_{||}$ and $g_{\perp}$ values indicated that the geometry of the compounds in the solid state is affected by the -

Table 6
Electronic spectral assignments, λ (cm^{-1}) for HL and its copper(II) complexes.

Compound	d → d	LMCT	n → π^*	π → π^*
HL	–	–	29820	36580
[$Cu_2(L)_2SO_4$]·H_2O (**1**)	16120	23210	32720	37940
[$Cu_2(L)_2(OAc)_2$]·H_2O (**2**)	16430	23520	32720	37740
[$Cu(L)NO_3$]$_2$ (**3**)	16370	23210	32340	38060
[$Cu(L)N_3$]$_2$·H_2O (**4**)	17310	23210	32910	38000
[Cu(L)NCS]·H_2O (**5**)	16970	23220	32780	37910
[Cu(L)I] (**6**)	15820	23770	31790	40610, 37320

Table 5
Infrared spectroscopic assignments (cm^{-1}) for the 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone and its copper(II) complexes.

Compounds	ν(C=N)	ν(N–N)	ν(C=S)	ν(^{2}NH)	ν(C=N)[a]	ν(Cu–N$_{azo}$)	ν(py(ip))
HL	1575	1115	1420, 805	3055	–	–	699
[$Cu_2(L)_2SO_4$]·H_2O (1)	1551	1122	1340, 796	–	1514	544	670
[$Cu_2(L)_2(OAc)_2$]·H_2O (2)	1545	1140	1315, 784	–	1509	526	655
[$Cu(L)NO_3$]$_2$ (**3**)	1539	1122	1321, 790	–	1514	544	649
[$Cu(L)N_3$]$_2$·H_2O (**4**)	1539	1146	1310, 777	–	1514	532	643
[Cu(L)NCS]·H_2O (5)	1545	1120	1315, 790	–	1502	532	636
[Cu(L)I] (**6**)	1545	1122	1320, 790	–	1514	502	612

[a] Newly formed C=N bond.

Table 7
Spin Hamiltonian and bonding parameters of copper(II) complexes of 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone.

Compounds	Polycrystalline state (298 K)				DMF solution (77 K)											
	g_{iso}	$g_{\|\|}$	$g_{\perp}$	G	$g_{\|\|}/g_3$	$g_{\perp}/g_1, g_2$	g_{av}	$A_{\|\|}$	$A_{\perp}$	A_{av}	α^2	β^2	γ^2	$K_{\|\|}$	$K_{\perp}$	f
$[Cu_2(L)_2SO_4]\cdot H_2O$ (**1**)	2.080				2.200	2.044, 2.090	2.111				0.601	0.529	1.536	0.319	0.924	
$[Cu_2(L)_2(OAc)_2]\cdot H_2O$(**2**)		2.128	2.047	2.812	2.197	2.052	2.100	194	38	90	0.797	0.872	0.881	0.695	0.702	127
$[Cu(L)NO_3]_2$ (**3**)		2.104	2.060	1.763	2.15	2.110	2.123	127			0.587	1.028	1.757	0.604	1.032	168.6
$[Cu(L)N_3]_2\cdot H_2O$ (**4**)	2.053		–	–	2.16	1.970, 2.060	2.063	–	–	–	–	–	–	–	–	–
$[Cu(L)NCS]\cdot H_2O$ (**5**)	2.060	–	–	–	2.192	2.044	2.093	208	38	95	0.827	0.843	0.791	0.697	0.654	104.9
$[Cu(L)I]$ (**6**)		2.073	2.057	1.300	2.204	2.055	2.053	205	38	94	0.835	0.831	0.849	0.694	0.709	107

A values in 10^{-4} cm^{-1}.

nature of the coordinating gegenions. The geometric parameter G is a measure of exchange interaction between the copper centres and is calculated for each species using the equation $G = (g_{||}-2.0023)/(g_{\perp}-2.0023)$ for all axial spectra. If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex [27]. The calculated G values are less than 4 which indicate that considerable exchange interaction is present in complexes. The $g_{||}$ values are nearly the same for all the complexes indicating that the bonding is dominated by the thiosemicarbazone moiety. The g_{av} values of all the complexes in the solution state are consistent with the g_{iso} values suggesting that they are not undergoing any kind of dissociation in the solution state. The $g_{||}$ values are less than 2.3 is an indication of significant covalent character to the M–L bond [28]. Although the compounds **1** (Fig. 3) and **4** displayed isotropic nature in polycrystalline state, they show rhombic symmetry with no hyperfine splittings in the parallel and perpendicular regions in the solution at 77 K. For the compound **4**, very weak signal obtained at 1600 G ($g = 4.04$) may be due to the dimeric nature of the compound.

In DMF solution at 77 K, the spectra of compounds **2**, **3** (Fig. 4), **5** and **6** showed axial behavior with well defined $g_{||}$ and $g_{\perp}$ values. For the compounds **2**, **5** and **6**, axial spectra with four hyperfine lines both in the perpendicular and parallel regions were obtained due to the interaction of electron spin with copper(II) nuclear spin. In compounds **2** and **5**, superhyperfine splitting are seen both in the perpendicular and parallel regions which gives an evidence for the coordination of azomethine and pyridyl ring nitrogens in the complexes. For complex **2** the presence of half field ($g = 4$) *ca.* at 1600 G confirms the binuclearity of the complex. Hyperfine splittings are not observed due to high Cu···Cu (3.500 Å) distance separation as obtained from X-ray structural analysis [29].

Even though compound **3** gave axial spectrum in DMF solution at 77 K, the hyperfine structure is not well resolved and this may be due to the poor glass formation. Expected superhyperfine splitting due to nitrogen atoms are missing in this compound. The interesting fact of the spectrum of the compound is that the presence of seven hyperfine splitting for the half field signal, due to the coupling of the electron spin with the nuclear spin of the two copper centers ($2nI + 1 = 2 \times 2 \times 3/2 + 1$).

In frozen state, compound **6** showed two different species due to the formation of solvent coordinated complex along with **6** which is evidenced by seven hyperfine lines at the parallel region. Superhyperfine splittings both in perpendicular and parallel regions were observed. The absence of any half field signals rules out the possibility of any significant coupling between the copper centers.

The EPR parameters $g_{||}$, $g_{\perp}$, g_{av}, $A_{||}$ (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 expression [30]

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

The following simplified expression were used to calculate the bonding parameters

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

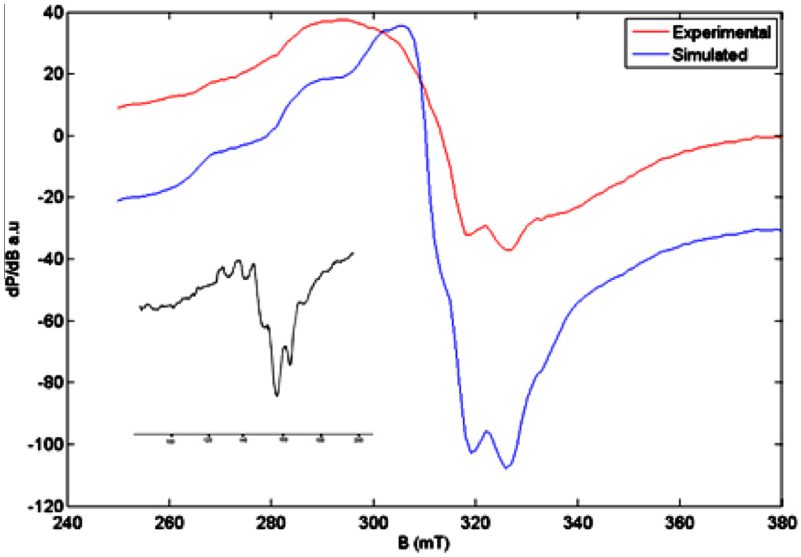


Fig. 3. EPR spectrum of $[Cu_2(L)_2SO_4]\cdot H_2O$ (**1**) in DMF at 77 K.

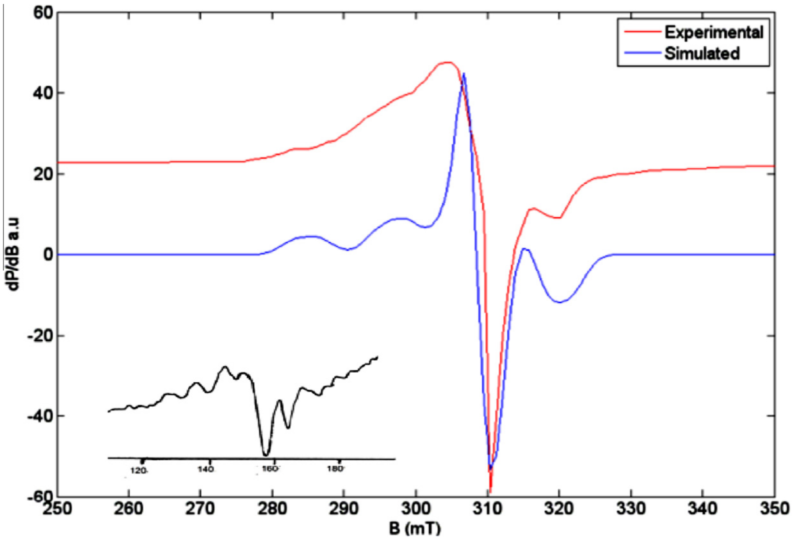


Fig. 4. EPR spectrum of $[Cu(L)NO_3]_2$ (**3**) in DMF at 77 K.

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

$$K_{||}^2 = \alpha^2\beta^2$$

$$K_{\perp}^2 = \alpha^2\gamma^2$$

Where $K_{||}$ and $K_{\perp}$ are orbital reduction factors and λ_0 represents the one electron spin orbit coupling constant which equals $-828\ \text{cm}^{-1}$.

Hathaway [31] has pointed out that for pure sigma bonding $K_{||} \approx K_{\perp} \approx 0.77$, for in plane π -bonding $K_{||} < K_{\perp}$ and for out-of-plane π-bonding, $K_{\perp} < K_{||}$. In all complexes except for **5**, it is observed that $K_{||} < K_{\perp}$.which indicates the presence of significant in plane π-bonding. For complex **5**, $K_{\perp} < K_{||}$ indicates that significant out-of-plane π-bonding is present in complex. The metal–ligand bond is purely ionic, if the value of α^2 is unity and it is completely covalent, if $\alpha^2 = 0.5$ [31]. Here α^2 values calculated for the complexes lie in between 0.5 and 1, which means that the metal–ligand bonds in the complexes under investigation are partially ionic and partially covalent in nature. The empirical factor $f = g_{||}/A_{||}$ is an index of tetragonal distortion. The value may vary from 105–135 for small to medium distortion and depends on the nature of the coordinated atom [32]. High distortion occurs for the nitrato complex ($f = 168$). In all other complexes distortion is medium and is found to be in the range 105–130 cm [33].

4. Conclusion

Copper(II) complexes of 2-benzoylpyridine-N^4,N^4-dimethyl-3-thiosemicarbazone (HL) were synthesized and characterized using various physicochemical techniques. The NNS chelating mode of the thiosemicarbazone was proved in one complex. The molecular structure of $[Cu_2(L)_2(OAc)_2]$ (**2a**) showed that each copper center have distorted square pyramidal geometry. Presence of half field signal with sevenfold splittings at EPR spectra confirmed the binuclearity of some complexes. For all complexes, $g_{||} > g_{\perp} > 2.0023$ showed that single electron of copper(II) nucleus resides in the $d_{x^2-y^2}$ orbital which is the ground state.

Acknowledgments

K. Jayakumar thanks the University Grants Commission, Bangalore, India for financial support. A.A. Aravindakshan gratefully acknowledges CSIR for the award of Junior Research Fellowship. The authors are thankful to the Sophisticated Analytical Instrumentation Facility, IIT Madras, India for single crystal X-ray diffraction measurements and SAIF Kochi for IR, UV-Vis studies and IIT Bombay for providing EPR results.

Appendix A. Supplementary data

CCDC 904873 contains the supplementary crystallographic data for $[Cu_2(L)_2(OAc)_2]$. 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, IEZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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