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Synthesis, spectral characterization and crystal structure of copper(II) complexes of 2-benzoylpyridine-*N*(4)-phenylsemicarbazone

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ABSTRACT

An interesting series of nine new copper(II) complexes $[Cu_2L_2(OAc)_2]\cdot H_2O$ (**1**), [CuLNCS]·½H_2O (**2**), [CuL-NO_3]·½H_2O (**3**), $[Cu(HL)Cl_2]\cdot H_2O$ (**4**), $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ (**5**), $[CuLClO_4]$·½H_2O (**6**), [CuLBr]·2H_2O (**7**), $[CuL_2]\cdot H_2O$ (**8**) and $[CuLN_3]\cdot CH_3OH$ (**9**) of 2-benzoylpyridine-*N*(4)-phenyl semicarbazone (HL) have been synthesized and physico-chemically characterized. The tridentate character of the semicarbazone is inferred from IR spectra. Based on the EPR studies, spin Hamiltonian and bonding parameters have been calculated. The *g* values, calculated for all the complexes in frozen DMF, indicate the presence of the unpaired electron in the $d_{x^2-y^2}$ orbital. The structure of the compound, $[Cu_2L_2(OAc)_2]$ (**1a**) has been resolved using single crystal X-ray diffraction studies. The crystal structure revealed monoclinic space group $P2_1/n$. The coordination geometry about the copper(II) in **1a** is distorted square pyramidal with one pyridine nitrogen atom, the imino nitrogen, enolate oxygen and acetate oxygen in the basal plane, an acetate oxygen form adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

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1. Introduction

Semicarbazones are molecules of great interest due to their potential pharmacological properties such as antibacterial, antifungal, antihypertensive, hypolipidemic, antineoplastic, hypnotic and anticonvulsant [1–4]. A variety of semicarbazones and their metal complexes possess anti-protozoa activity also. These properties are due to wide variation in their stereochemistry and modes of bonding through oxygen and azomethine nitrogen atoms [1]. There has been considerable amount of interest in the studies of semicarbazones recently due to their unusual coordination modes when bound to metals, high pharmacological potentiality and good chelating property.

Semicarbazones are compounds with adaptable structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. The coordination possibilities in semicarbazones are increased by introducing different substituted aldehydes or ketones witch include additional donor atoms [5,6].

In present study, we have chosen the studies of Cu(II) complexes of 2-benzoylpyridine-*N*(4)-phenylsemicarbazone. It is mainly due to the fact that the heteroaromatic moiety of 2-benzoylpyridine can provide a further binding site for metal cations [7] and provides an aromatic nitrogen whose unshared electron pairs are well placed to act courteously in binding metal ions. Further more, semicarbazones derived from 2-benzoylpyridine have a small negative charge resides on the nitrogen atom of the pyridine ring which enhances its biological activity [8]. This paper deals with the synthesis and spectral characterization of nine Cu(II) complexes of 2-benzoylpyridine-*N*(4)-phenylsemicarbazone along with the crystal structure of $[Cu_2L_2(OAc)_2]$ (**1a**).

2. Experimental

2.1. Materials

4-Phenylsemicarbazide (Fluka), 2-benzoylpyridine (CDH), potassium thiocyanate (CDH), sodium azide (CDH), copper acetate, copper chloride, copper nitrate, copper bromide, copper perchlorate and copper sulfate (BDH) were used without further purification. All solvents obtained commercially were distilled before use.

2.2. Synthesis of the ligand HL and its metal complexes

The semicarbazone ligand was synthesized by the following method. 4-Phenyl semicarbazide (0.151 g, 1 mmol) dissolved in hot methanol (50 ml) was added to a solution of 2-benzoylpyridine (0.183 g, 1 mmol) in the same solvent. Two drops of glacial acetic

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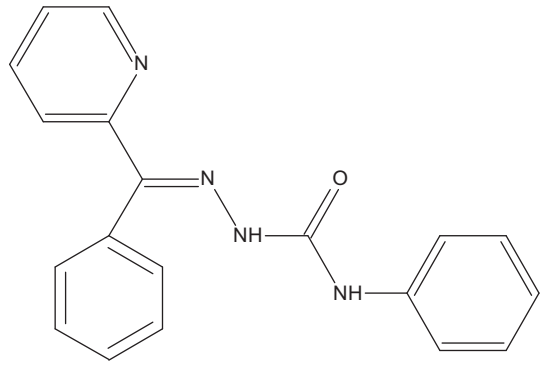

Scheme 1. Structure of 2-benzoylpyridine-*N*(4)-phenylsemicarbazone.

acid were added to the reaction mixture. Then the reaction mixture was refluxed for 6 h on a water bath and cooled to room temperature. The product formed was filtered off and washed with methanol to obtain a pale yellow crystalline compound. The structural formula of the ligand (HL) is represented in Scheme 1.

The complex $[Cu_2L_2(OAc)_2]\cdot H_2O$ was prepared by refluxing a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of $Cu(OAc)_2\cdot H_2O$ (0.398 g, 2 mmol) for 4 h. The complex $[CuLNO_3]\cdot ½H_2O$ was prepared by refluxing a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of $CuNO_3\cdot 3H_2O$ (0.483 g, 2 mmol) for 3 h. The complex $[Cu(HL)Cl_2]\cdot H_2O$ was prepared by stirring a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of $CuCl_2\cdot 2H_2O$ (0.340 g, 2 mmol) for 3 h. The complex $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ was prepared by refluxing a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of $CuSO_4\cdot 5H_2O$ (0.499 g, 2 mmol) for 5 h. The complex $[CuLClO_4]\cdot ½H_2O$ was prepared by stirring a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of copper perchlorate (0.371 g, 2 mmol) for 3 h. The complex $[CuLBr]\cdot 2H_2O$ was synthesized by refluxing a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) with a hot filtered methanolic solution of copper bromide (0.446 g, 2 mmol) for 3 h. These microcrystals obtained were separated and filtered. They were thoroughly washed with water, methanol and then ether and finally dried over P_4O_{10} in vacuo.

The complexes $[CuLNCS]\cdot ½H_2O$ and $[CuLN_3]\cdot CH_3OH$ were synthesized by the following method. A hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) was mixed with a hot filtered methanolic solution of potassium thiocyanate (0.194 g, 2 mmol) or sodium azide (0.130 g, 2 mmol). A hot filtered solution of $Cu(OAc)_2\cdot H_2O$ (0.398 g, 2 mmol) was added with constant stirring. The mixture was then refluxed for 3 h. The complexes separated as microcrystals were filtered and thoroughly washed with water, methanol and ether and finally dried over P_4O_{10} in vacuo.

The complex $CuL_2\cdot H_2O$ was obtained when a hot solution of HL (0.633 g, 2 mmol) in methanol (20 cm^3) was mixed a hot filtered methanolic solution of $Cu(OAc)_2\cdot H_2O$ (0.199 g, 1 mmol) with constant stirring and then the mixture was refluxed for 3 h. The complex obtained as microcrystals was filtered and thoroughly washed with water, methanol and ether and finally dried over P_4O_{10} in vacuo.

Single crystals of $[Cu_2L_2(OAc)_2]$ (**1a**) suitable for X-ray diffraction were obtained from solution of **1** in a mixture of dimethylformamide and methanol (1:1).

2.3. Physical methods

A Vario EL III CHNS analyzer at SAIF, Kochi, India was used for elemental analyses. IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR Spectrophotometer with KBr pellets and ATR technique at SAIF, Kochi, India. A Cary 5000, version 1.09 UV–Vis-NIR Spectrophotometer was used for recording electronic spectra in acetonitrile and DMF as solvents. Magnetic susceptibility measurements were carried out in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 k Oersted field strength. EPR spectra of the complexes in the polycrystalline and solution state at 298 K and in frozen DMF at 77 K were recorded in the X-band frequency, using 100 kHz field modulation on a Varian E-112 X-band EPR spectrometer using TCNE as a standard (g = 2.00277) at SAIF, IIT, Bombay, India.

2.4. X-ray crystallography

Single crystals of compound $[Cu_2L_2(OAc)_2]$ suitable for X-ray diffraction studies were grown from its solution in a mixture of dimethylformamide and methanol (1:1 v/v). A green crystal of approximate dimensions $0.20 \times 0.14 \times 0.06$ mm^3 was selected and mounted on a BRUKER SMART CCD diffractometer, equipped with a graphite crystal, incident-beam monochromator, and a fine focus sealed tube, Mo Kα (λ = 0.71073 Å) X-ray source. The crystallographic data along with details of structure solution refinements are given in Table 1. The unit cell dimensions were measured and the data collection was performed at 273 K. Bruker SMART software was used for data acquisition and Bruker SAINT Software for data integration [9]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [10]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-*PLUS* software package (version 5.1) [11]. The non-hydrogen atoms were made

Table 1
Crystal refinement parameters of $[Cu_2L_2(OAc)_2]$.

Empirical formula	$C_{42}H_{38}Cu_2N_{10}O_6$
Formula weight	875.86
Color	Green
T (K)	273(2)
λ (Mo Kα) (Å)	0.7107
Crystal system	monoclinic
Space group	$P2_1/n$
Lattice constants	
a (Å)	8.6851(7)
b (Å)	16.5515(14)
c (Å)	13.6252(12)
α (°)	90
β (°)	91.680(2)
γ (°)	90
V ($Å^3$)	1957.8(3)
Z	4
$D_{Calc.}$ (ρ) (Mg m^{-3})	1.496
Absorption coefficient, μ (mm^{-1})	1.151
F(0 0 0)	900
Crystal size (mm^3)	$0.20 \times 0.14 \times 0.06$
θ Range for data collection	1.94–28.28
Limiting indices	$-9 \leqslant h \leqslant 11$, $-21 \leqslant k \leqslant 21$, $-17 \leqslant l \leqslant 15$
Reflections collected	7862
Unique reflections (R_{int})	3556 [$R_{(int)}$ = 0.087]
Completeness to 2θ	28.28 70.8 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3556/0/266
Goodness-of-fit on F^2	0.859
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0741, wR_2 = 0.1575
R indices (all data)	R_1 = 0.1128, wR_2 = 0.1695
Largest difference peak and hole (e $Å^{-3}$)	0.826 and −0.421

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

anisotropic. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they are attached. The hydrogen atom attached to nitrogen atoms were located from difference Fourier maps and refined with isotropic displacement parameters. The molecular graphics employed was DIAMOND version 3.2d [12].

3. Results and discussion

The semicarbazone ligand (HL) was synthesized by the direct condensation of 2-benzoylpyridine with *N*(4)-phenylsemicarbazide. Semicarbazone can exist in two tautomeric forms, keto and enol or an equilibrium mixture of the two since it has an amide –NH–C=(O) function. However, the IR spectrum of HL indicates that it remains in keto form in solid state. However, the IR spectra of complexes except two complexes do not show any intense absorption band at 1698 cm^{-1}, due to the carbonyl stretching of the semicarbazone moiety. This shows that it tautomerises to the enol form and coordinates to the metal in the enolate form in solution.

The complexes $[CuLNCS]\cdot\frac{1}{2}H_2O$ and $[CuLN_3]\cdot CH_3OH$ were readily formed by the reaction of the ligand and heterocyclic base, potassium thiocyanate or sodium azide with copper acetate. The complexes $[Cu_2L_2(OAc)_2]\cdot H_2O$, $[CuLNO_3]\cdot\frac{1}{2}H_2O$, $[Cu(HL)Cl_2]\cdot H_2O$, $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$, $[CuLClO_4]\cdot\frac{1}{2}H_2O$, $[CuLBr]\cdot 2H_2O$, were formed by the reaction of the ligand with corresponding copper salts. The complex $CuL_2\cdot H_2O$ was obtained when a hot solution of HL was reacted with a hot filtered methanolic solution of $Cu(OAc)_2\cdot H_2O$. The ligand HL undergoes deprotonation to L^- and chelates in enolate form as evidenced by the IR spectra. The elemental analyses suggest the general formula as $(CuLX)\cdot xH_2O$ for complexes **1**–**8** but for the complex **9**, CH_3OH takes the place of water. The complexes are appreciably soluble in alcohol and DMF.

The colors, elemental analyses, stoichiometries of HL and its complexes are presented in Table 2. The conductivity measurements were made in DMF solutions and the values were found to be less than 20 Ω^{-1} mol^{-1} cm^2. This shows that all complexes are found to be non-electrolytes [13], which indicates that the anion and the ligand are coordinated to the copper(II).

The magnetic susceptibilities of the complexes at room temperature in the polycrystalline state except complexes **1** and **5** fall in the range of 1.60–2.00 B.M., which are very close to the spin-only value of 1.73 B.M. for a typical copper(II) system. The low value of complexes **1** and **5** is an evidence for their behavior as dimers.

3.1. Crystal structure of $[Cu_2L_2(OAc)_2]$

The single crystal X-ray diffraction study of the compound $[Cu_2L_2(OAc)_2]$ shows that the compound exists as an oxygen bridged dimer. The molecular structure of the compound along with atom numbering scheme is given in Fig. 1. The asymmetric unit is formed by one half of the molecule and the other half is related by a centre of inversion. The lattice nature is monoclinic with space group $P2_1/n$. The structure contains two copper centers where each centre is pentacoordinated with azomethine nitrogen (N2), pyridyl nitrogen (N1) and enolate oxygen (O1) of semicarbazone moiety and oxygens (O2, O2A) from acetato group. The compound exhibits a distorted square pyramidal geometry with the basal plane occupied by semicarbazone ligand and the acetate oxygen (O2). The relevant bond lengths and angles are presented in Table 3. The oxygen (O2A) from acetato group of the adjacent monomer plugs in to the axial position resulting in a dimer with a Cu···Cu separation of approximately 3.422 Å. The comparison of bond distances Cu(1)–O(2) (1.945(3) Å), Cu(1)–O(2A) (2.344(4) Å), Cu(1A)–O(2) (2.346 Å) and Cu(1A)–O(2A) (1.944 Å) confirms the possibility of a bridging dinuclear structure. The Cu–N and Cu–O bond lengths are smaller ~1.936 and 2.009 Å indicating the domination of semicarbazone moiety in the bonding. It is found that copper atom is closer to semicarbazone moiety than the acetato group. The Cu–$N_{pyridyl}$ bonds are 0.09 Å larger than Cu–N_{imine} bonds show the

Table 2
Colors, elemental analyses and magnetic susceptibilities of 2-benzoylpyridine-*N*(4)-phenyl semicarbazone and its copper(II) complexes.

Compound	Colour	Found (Calc.) %			μ (B.M.)
		C	H	N	
HL	Pale yellow	72.47(72.13)	5.20(5.10)	18.14(17.71)	–
$[Cu_2L_2(OAc)_2]\cdot H_2O$ (**1**)	Green	56.20(56.43)	4.08(4.28)	12.67(12.54)	1.06
$[CuLNCS]\cdot\frac{1}{2}H_2O$ (**2**)	Green	53.72(54.97)	3.12(3.62)	15.31(15.70)	1.75
$[CuLNO_3]\cdot\frac{1}{2}H_2O$ (**3**)	Pale green	50.97(50.72)	3.64(3.58)	15.72(15.57)	1.87
$[Cu(HL)Cl_2]\cdot H_2O$ (**4**)	Dark green	49.25(48.68)	3.84(3.87)	11.94(11.95)	1.93
$[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ (**5**)	Pale green	44.11(44.66)	4.42(3.75)	10.86(10.96)	1.15
$[CuLClO_4]\cdot\frac{1}{2}H_2O$ (**6**)	Green	46.65(46.83)	2.96(3.31)	11.35(11.50)	1.71
$[CuLBr]\cdot 2H_2O$ (**7**)	Pale green	46.12(45.83)	3.38(3.87)	10.97(11.32)	1.76
$[CuL_2]\cdot H_2O$ (**8**)	Green	63.71(64.08)	4.02(4.53)	15.28(15.73)	1.89
$[CuLN_3]\cdot CH_3OH$ (**9**)	Dark green	52.71(53.03)	4.07(4.23)	21.85(21.65)	1.83

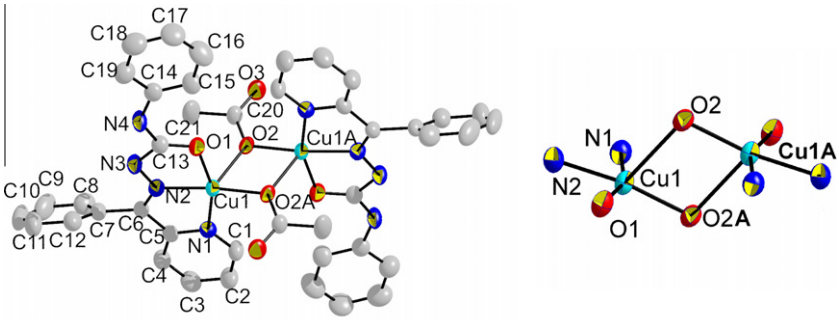

Fig. 1. The molecular structure of $[Cu_2L_2(OAc)_2]$ (**1a**) along with the atom numbering scheme. Symmetry code: 1 − *x*, −*y*, 1 − *z*. The hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) of $[Cu_2L_2(OAc)_2]$.

Cu(1)–N(1)	2.024(4)
Cu(1)–N(2)	1.938(4)
Cu(1)–O(1)	2.010(4)
Cu(1)–O(2)	1.945(3)
Cu(1)–O(2A)	2.344(4)
C(13)–O(1)	1.261(7)
C(6)–N(2)	1.306(6)
C(13)–N(3)	1.363(6)
Cu1···Cu1A	3.422
N(1)–Cu(1)–N(2)	80.86(18)
N(2)–Cu(1)–O(1)	79.05(16)
N(1)–Cu(1)–O(1)	159.91(17)
N(1)–Cu(1)–O(2)	99.82(17)
N(1)–Cu(1)–O(2A)	92.03(16)
N(2)–Cu(1)–O(2)	171.06(17)

strength of azomethine nitrogen coordination. The four coplanar base atoms show a significant distortion from a square geometry as indicated by the N1–Cu1–O1 bond angle of 159.91(17)°. 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 N(2)–Cu1–O(2), 171.06(17)° and N1–Cu1–O2, 99.82(17)°. Most of the angles involving the central copper atoms are widely different from 90° and 180°, indicating significant distortion from the square pyramidal geometry.

The unit cell-packing diagram of the compound **1** viewed along the *a*-axis is given in Fig. 2. It can be observed that the molecules are packed in a two-dimensional manner with the parallel arrangement of the rings. The adjacent units are interconnected through H-bonding interactions involving the oxygen atom of the acetate group and *N*(4) hydrogen of the phenyl group (Fig. 2). The H-bonding, C–H···π and ring metal interactions are shown in Table 4. The H-bonding interaction is observed with donor-acceptor distance of 2.852 Å. The aromatic π–π stacking interactions between pyridine rings with Cg–Cg distance of 3.6755 Å (Sym. code: $2 - x$, $-y$, $1 - z$) reinforces crystal structure cohesion in molecular packing in the crystal lattice.

The trigonality index τ is calculated using the equation $\tau = (\beta - \alpha)/60$ [14] (for perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity, respectively). The value of τ for molecule is 0.185, which shows distorted square pyramidal geometry.

3.2. Electronic and IR spectra

The electronic spectral bands of the ligand and the complexes recorded in acetonitrile and DMF solution are presented in Table 5.

The electronic spectrum of HL consists of a broad band at 32 890 cm^{-1} which is due to $n \rightarrow \pi^*$ band of the pyridine ring. An absorption band observed at 37 410 cm^{-1} in the spectrum of the ligand may be due to $\pi \rightarrow \pi^*$ transition. The electronic spectra of Cu(II) complexes consist of bands in the region 27 000–33 000 cm^{-1} which are assigned to $n \rightarrow \pi^*$ band of the pyridine ring. The semicarbazone and copper(II) complexes have two bands; one centered around 37 000 cm^{-1} and another around 32 000 cm^{-1}. These bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of phenyl rings and semicarbazide moiety, respectively [15]. The charge transfer bands were observed in the 23 000–25 000 cm^{-1} range, and its broadness can be explained as due to the combination of O → Cu and N → Cu LMCT transitions [16]. For Cu(II) complexes, there are three spin allowed transitions, $A_{1g} \leftarrow B_{1g}$, $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$. But it is very difficult to resolve them into separate bands due to the very low energy difference between these bands. All the complexes gave d–d bands in the 14 000–17 500 cm^{-1} range [17–21].

The IR spectral bands of HL and its copper(II) complexes and its tentative assignments for determining the ligand's mode of coordination are presented in Table 6. The ν(C=N) band of the semicarbazone at 1600 cm^{-1} undergoes a negative shift of wavenumber in the complexes indicating coordination via azomethine nitrogen. This has been confirmed by the bands in the 410–440 cm^{-1} range and it is assignable to the ν(Cu–N) band [22,23]. A strong band found at 1132 cm^{-1} is assigned to the ν(N–N) band of the semicarbazone.

The positive shift of the frequency assigned to ν(N–N) band in the spectra of complexes is owing to the increase in double bond character, counterbalancing the loss of electron density via donation to the metal. This confirms the coordination of the ligand to the metal via the azomethine nitrogen. The presence of bands in the 1510–1560 cm^{-1} range in complexes except in complexes **4** and **5** due to asymmetric stretching vibration of the newly formed C=N bond demonstrates the enolization of the ligand. A band at 1698 cm^{-1} in the ligand has significant contribution from C=O stretching vibration and absence of such a band in all the complexes except **4** and **5** supports the enolate form of the ligand in these complexes [24]. For the **4** and **5** this band is shifted to 1641 and 1627 cm^{-1}, respectively showing the coordination in the keto form [25].

The ν(N–H) band of semicarbazone disappears in complexes except in $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ and $[Cu(HL)Cl_2]\cdot H_2O$ also adding more evidences for the enolization and deprotonation of HL followed by coordination to Cu and it is supported to a great extent by the appearance of a new peak in the 500–540 cm^{-1} range due to ν(Cu–O) stretching frequency. Based on the above spectral evidences, it is confirmed that the ligand HL is tridentate, coordinating to copper(II) via the azomethine nitrogen, the pyridyl nitrogen and keto or enolate oxygen.

In the thiocyanato complex, a very strong band at 2119, a medium band at 902 and a strong band at 453 cm^{-1} are assigned to ν(CN), ν(CS) and δ(NCS) modes of the NCS group, respectively. The intensity and position of these bands indicate the unidentate coordination of the thiocyanate group through the nitrogen [26,27]. In the nitrato complex, the three bands observed at 1448, 1354 and 1130 cm^{-1} indicate the ν_4, ν_1 and ν_2 modes of the nitrato group. The fact that the nitrato group is terminally bonded is understood from the separation of 94 cm^{-1} between its two highest frequency bands mentioned above [28].

In the azido complex, the strong band observed at 2054 cm^{-1} is assigned to the azido group indicative of azide coordination [29]. The perchlorate complex showed single broad bands at 1121 and 1033 cm^{-1}, a strong band at 623 cm^{-1} and a weak band at 923 cm^{-1} indicating the presence of coordinated perchlorate [23]. The coordination is confirmed by a ν(Cu–O) band at 534 cm^{-1}. The bands at 1121 and 623 cm^{-1} are assignable to $\nu_3(ClO_4)$ and $\nu_4(ClO_4)$, respectively. For the sulfato complex, strong bands at 1142 and 1055 cm^{-1} are assignable to ν_3 of the monocoordinated sulfato group. Medium bands at 976 cm^{-1} (ν_1) and 650 cm^{-1} (ν_4) confirm the unidentate behaviour of sulfato group [23].

Thus it is seen that the semicarbazone (HL) acts as a monoanionic tridentate ligand in complexes $[Cu_2L_2(OAc)_2]\cdot H_2O$, $[CuLNCS]\cdot ½H_2O$, $[CuLNO_3]\cdot ½H_2O$, $[CuLClO_4]\cdot ½H_2O$, $[CuLBr]\cdot 2H_2O$, $[CuL_2]\cdot H_2O$ and $[CuLN_3]\cdot CH_3OH$ and neutral one in complexes $[Cu(HL)Cl_2]\cdot H_2O$ and $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$.

3.3. Magnetic and EPR studies

Variable temperature magnetic susceptibility measurements of complexes $[Cu_2L_2(OAc)_2]\cdot H_2O$ and $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ were carried out in the temperature range 80–298 K. The magnetic moment μ_{eff} of $Cu_2L_2(OAc)_2]\cdot H_2O$ decreases from a value 1.06 at 298 K to 0.54 μ_B at 80 K indicating a moderate antiferromagnetic exchange

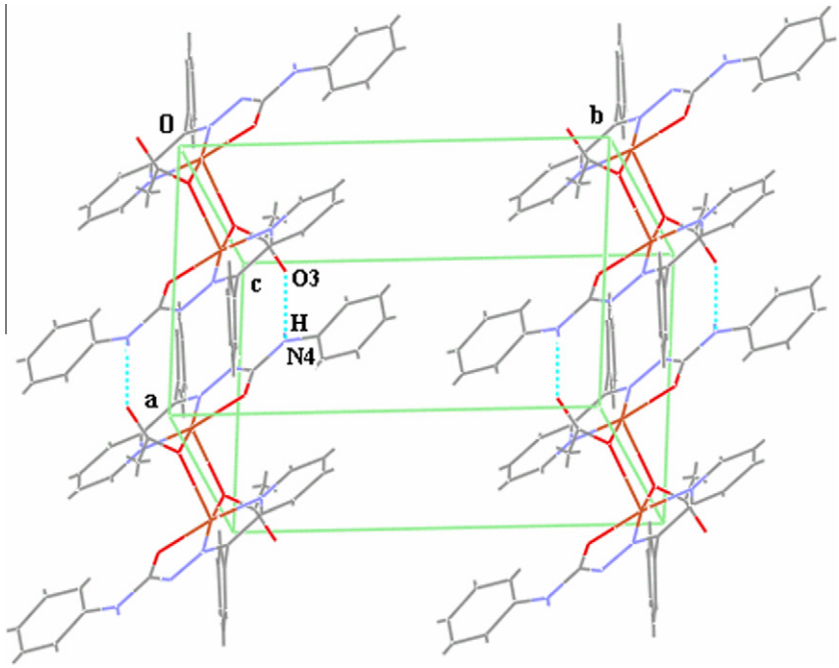

Fig. 2. Packing diagram of compound **1a** showing H bonding.

Table 4
Hydrogen bonding.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
N(4)–H4···O(3)[a]	0.76(6)	2.10(6)	2.852(7)	169(6)
Equivalent position code: $a = 2 - x, -y, 1 - z$.				
[π···π interactions]				
Cg(I)···Cg(J)	Cg–Cg (Å)	α (°)	β (°)	γ (°)
Cg(2)···Cg(2)[b]	3.6755(25)	0.02	18.68	18.68
Equivalent position code: $b = 2 - x, -y, 1 - z$.				
Cg (1) = Cu(1), O(2), Cu(1)A, O(2)A				
Cg (2) = Cu(1), O(1), C(13), N(3), N(2)				
C–H···π interactions				
X–H(I)···Cg(J)	H···Cg (Å)		X···Cg (Å)	∠X–H–Cg (°)
C(21)–H(21B)···Cg(2)[c]	2.69		4.17	138

Equivalent position code: $c = 1 - x, -y, 1 - z$.
D, donor; A, acceptor; Cg, centroid; α, dihedral angles between planes I and J; β, angle between Cg···Cg and Cg(J) perp.; γ, angle between Cg···Cg and Cg(I) perp.

Table 5
Electronic spectral assignments, λ (cm^{-1}) for HL and its copper(II) complexes.

Compound	State	d → d	LMCT	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
HL	Acetonitrile	–	–	32 890	37 410
$[Cu_2L_2OAc_2]\cdot H_2O$ ((**1**)	Acetonitrile	14 330	23 970	31 750	37 590
	DMF	16 040	23 970	31 610	37 450
$[CuLNCS]\cdot ½H_2O$((**2**)	Acetonitrile	14 390	23 870	31 850	37 590
	DMF	14 850	23 970	31 860	37 450
$[CuLNO_3]\cdot ½H_2O$(**3**)	Acetonitrile	17 210	23 950	32 000	37 170
	DMF	17 410	23 830	32 110	37 450
$[Cu(HL)Cl_2]\cdot H_2O$ (**4**)	Acetonitrile	17 430	24 700	31 060	36 630
	DMF	17 370	24 700	31 130	36 770
$[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$(**5**)	Acetonitrile	14 440	24 040	32 000	37 340
	DMF	16 210	23 900	32 070	35 070
$[CuLClO_4]\cdot ½H_2O$ (**6**)	Acetonitrile	15 580	23 870	31 750	37 340
	DMF	15 580	23 910	31 680	37 540
$[CuLBr]\cdot 2H_2O$ (**7**)	Acetonitrile	16 130	23 980	31 970	34 480
	DMF	16 130	23 890	32 070	36 080
$[CuL_2]\cdot H_2O$ (**8**)	Acetonitrile	15 690	23 910	30 860	35 740
	DMF	15 690	23 910	31 040	35 740
$[CuLN_3]\cdot CH_3OH$ (**9**)	Acetonitrile	16 060	23 920	31 350	37 590
	DMF	16 400	23 830	31 370	37 450

interaction between the two Cu(II) ions in one molecule, namely, parallel arrangement with a total spin $S = 1$ and the ground state $S = 0$ [30]. A similar trend is shown by $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ in which μ_{eff} value decreases from 1.15 at 298 K to 0.43 μ_B at 80 K. The antiferromagnetic behavior of the binuclear complexes is attributed to spin–spin interaction via the super exchange pathway provided by the bridging groups rather than a direct metal–metal interaction [31]. The copper–copper distance in complex **1** is observed to be 3.422 Å from X-ray diffraction studies. This separation generally rules out any significant amount of direct copper–copper interaction. The magnetic moment values for other complexes were calculated at room temperature and found to be very close to the spin only value 1.73 μ_B, expected for the mononuclear copper(II) systems.

The EPR parameters of the copper(II) complexes are presented in Table 7. The EPR spectra of the complexes recorded in polycrystalline state at room temperature provide information about the coordination environment around copper(II) in these complexes.

The EPR spectra of $[CuLNCS]\cdot ½H_2O$, $[CuLNO_3]\cdot ½H_2O$ and $[CuLClO_4]\cdot ½H_2O$ in the polycrystalline state at 298 K showed only one

Table 6
Infrared spectroscopic assignments (cm^{-1}) for the 2-benzoylpyridine-*N*(4)-phenylsemicarbazone and its copper(II) complexes.

Compound	ν(C=N)	ν(N–N)	ν(C=O)	ν(Cu–N)	ν(C=N)	ν(NH)	ν(Cu–O)
HL	1600	1132	1698	–	–	3375	–
$[Cu_2L_2OAc_2]\cdot H_2O$ (**1**)	1568	1145	–	416	1520	–	508
$[CuLNCS]\cdot ½H_2O$ (**2**)	1595	1158	–	420	1554	–	510
$[CuLNO_3]\cdot ½H_2O$ (**3**)	1599	1213	–	418	1546	–	529
$[Cu(HL)Cl_2]\cdot H_2O$ (**4**)	1597	1213	1641	415	1568	3068	503
$[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ (**5**)	1595	1213	1627	415	1575	3199	507
$[CuLClO_4]\cdot ½H_2O$ (**6**)	1599	1212	–	410	1538	–	534
$[CuLBr]\cdot 2H_2O$ (**7**)	1598	1211	–	436	1536	–	508
$[CuL_2]\cdot H_2O$ (**8**)	1568	1146	–	412	1516	–	510
$[CuLN_3]\cdot CH_3OH$ (**9**)	1568	1213	–	420	1517	–	506

Table 7
Spin Hamiltonian and bonding parameters of copper(II) complexes of 2-benzoylpyridine-*N*(4)-phenylsemicarbazone.

	1	2	3	4	5	6	7	8	9
Polycrystalline (298 K)									
$g_{\|\|}$	2.206			2.204	2.216		2.262	2.134	2.165
$g_{\perp}$	2.084			2.074	2.062		2.084	2.047	2.045
g_{iso}/g_{av}	2.124	2.141	2.076	2.116	2.064	2.120	2.148	2.076	2.085
G	2.452			2.702	2.625		3.256	3.110	3.672
DMF (77 K)									
$g_{\|\|}$	2.224	2.248	2.285	2.273	2.212	2.289	2.287	2.298	2.257
$g_{\perp}$	2.062	2.054	2.005(g_1)	2.051	2.074 (g_1)	2.055	2.016 (g_1)	2.058	2.057
			2.087(g_2)		2.084 (g_2)		2.097 (g_2)		
g_{av}	2.116	2.118	2.113	2.125	2.075	2.133	2.133	2.138	2.123
$A_{\|\|}$	199.35	194.67	170.68	167.0	193.3	161.0	157.0	148.0	172.0
$A_{\perp}$							1.91		
α^2	0.9926	0.9796	0.9335	0.9188	0.8077	0.9301	0.9200	0.9120	0.9346
β^2	0.7373	0.7568	0.9225	0.9161	0.8815	0.8821	0.9042	0.9168	0.8488
γ^2	0.7630	0.6919	0.7221	0.7740	0.9263	0.7535	0.7828	0.7930	0.7840
$K_{\|\|}$	0.7319	0.7414	0.8612	0.8418	0.7128	0.8205	0.8319	0.8362	0.7933
$K_{\perp}$	0.7574	0.6777	0.6741	0.7112	0.7485	0.7009	0.7200	0.7233	0.7328

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

broad signal at g_{iso} = 2.076, 2.141 and 2.012, respectively. Such isotropic spectra, consisting of only one broad signal and hence only one *g* value is due to dipolar broadening and enhanced spin lattice relaxation. These types of spectra unfortunately give no information on the electronic ground state of the Cu(II) ion present in the complexes. However, the consistency of these g_{iso} values with the g_{av} values of the spectra in frozen solution show the existence of the same geometry in both states. The spectra of other compounds are typically axial with well defined $g_{||}$ and $g_{\perp}$ values. The spectra are often broad because of the fast spin lattice relaxation and exchange coupling. All complexes having $g_{||}$ values less than 2.3 indicate a fair degree of covalent character in Cu–L bonding [28]. The geometric parameter *G* is the measure of the exchange interaction between the copper centres in polycrystalline state and this could be calculated using the equation: $G = (g_{||} - 2.0023)/(g_{\perp} - 2.0023)$ for axial spectra and for rhombic spectra, $g_{\perp} = (g_1 + g_2)/2$ [32]. The value of *G* is less than 4 indicates considerable exchange interaction in the crystalline compound and if $G > 4$, the exchange interaction is negligible [30]. Calculated *G* valued of the complexes **1** and **5** are found to be less than 4 and reveals with considerable exchange interaction. In all the polycrystalline complexes, $g_{||} > g_{\perp} > 2.0023$ which is consistent with a $d_{x^2-y^2}$ ground state in a square planar or square pyramidal geometry [32,33]. Although the compounds **3**, **5** and **7** show axial nature in polycrystalline state, they show rhombic symmetry in the solution at 77 K.

All the EPR spectra of the samples in DMF solution at 77 K were simulated using EasySpin package [34]. Four well resolved hyperfine lines corresponding to coupling of the electron spin with the nuclear spin ($^{63,65}Cu$, $I = 3/2$) are obtained in the parallel region. The EPR spectra of complexes $[CuLBr]\cdot 2H_2O$ (Fig. 3), $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ and $[CuLNO_3]\cdot ½H_2O$ showed five nitrogen superhyperfine lines in the perpendicular region, which arise from the coupling of the electron spin with the nuclear spin of the two coordinating nitrogen atoms while the EPR spectra of the complexes $[CuLNCS]\cdot ½H_2O$ $[Cu(HL)Cl_2]\cdot H_2O$ and $[CuLN_3]\cdot CH_3OH$ (Fig. 4) showed four hyperfine splitting only in the parallel region without any superhyperfine splitting.

The complex $[Cu_2(HL)_2(SO_4)_2]\cdot 4H_2O$ gave a rhombic spectrum in DMF solution at 77 K. The appearance of four line pattern in solution may be due to the decomposition of the dimer into monomers or due to slight loss of magnetic coupling between the two copper ions. In addition it exhibited a half field signal ($g = 4.162$) with well resolved seven line hyperfine structure with an average hyperfine splitting of $A = 83.3$ G. The half field signal was retained, but not well resolved, when it is recorded in DMSO at 77 K and again confirms the existence of binuclear geometry. It also shows antiferromagnetic interaction ($\mu_{eff} = 1.15$ μ_B at 298 K) between the two copper nuclei. This situation could arise when two equivalent copper(II) ions are coupled via an exchange interaction, in a binuclear complex.

The solution EPR spectrum of $[Cu_2L_2(OAc)_2]\cdot H_2O$ at 77 K is axially symmetric ($g_{||} = 2.224$ and $g_{\perp} = 2.062$) having a quartet hyperfine structure (Fig. 5) on the parallel component arising from the interaction of an unpaired electron with a single copper nucleus. This signal is typical of copper mononuclear complex. Apart from this, a weak signal observed at lower field (near half of the resonance field) suggests a dimeric structure for the complex. This half field signal arises from the coupling of the two copper ions and corresponds to the forbidden transition $\Delta M_s = \pm 2$. However, a seven

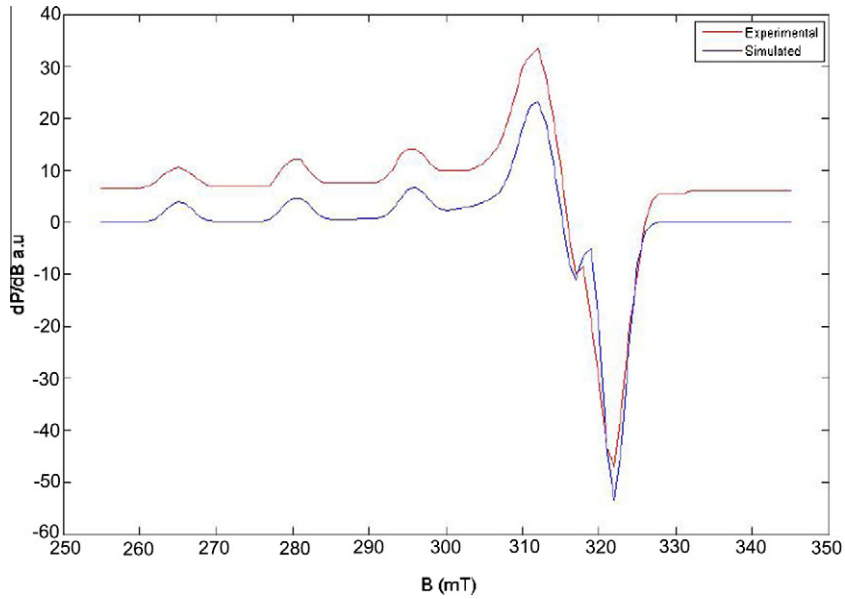

Fig. 3. EPR spectrum of $[CuLBr]\cdot 2H_2O$ in DMF at 77 K.

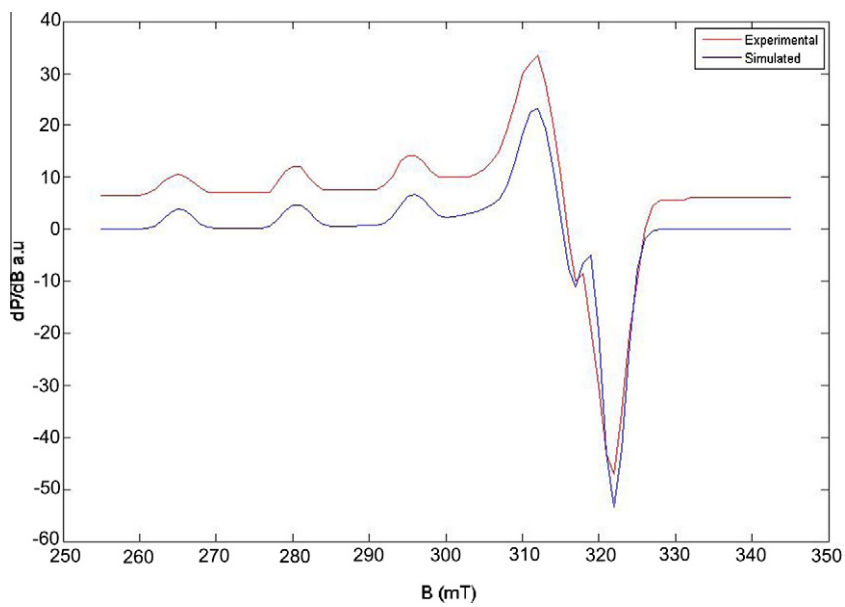

Fig. 4. EPR spectrum of $[CuLN_3]\cdot CH_3OH$ in DMF at 77 K.

line hyperfine structure is absent in this half field region. A half field signal was found in DMSO in frozen state and it strengthens the existence of binuclear geometry of the complex. It has been known that if the separation between the two metal centers is more than 3.5 Å, an interaction is not expected. From the X-ray structural analysis, the distance between two copper ions is 3.422 Å in $Cu_2L_2(OAc)_2]\cdot H_2O$. Therefore, only a small interaction is expected and the seven line hyperfine splitting is not observed. In addition, the dihedral angle between the two copper atoms and the connecting ligand atoms also plays an important role in deciding the extent of interaction.

The $g_{||}$ values are nearly the same for all the complexes indicating that the bonding is dominated by the semicarbazone moiety. The $g_{||} > g_{\perp}$ values accounts to the distorted square pyramidal structure and rules out the possibility of a trigonal bipyramidal structure which would be expected to have $g_{\perp} > g_{||}$ [35,36].

The EPR parameters $g_{||}$, $g_{\perp}$, $A_{||}$ (Cu) and the energies of d–d transitions were used to evaluate the bonding parameters α^2, β^2 and γ^2 which may be regarded as measures of the covalency in the in-plane σ-bonds, in-plane π-bonds and out-of-plane π-bonds. The value of in-plane σ-bonding parameter α^2 estimated from the expression [36],

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

The following simplified parameters were used to evaluate the bonding parameters [37],

$$K_{||}^2 = (g_{||} - 2.00277)E_{d-d}/8\lambda_o$$

$$K_{\perp}^2 = (g_{\perp} - 2.00277)E_{d-d}/2\lambda_o$$

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

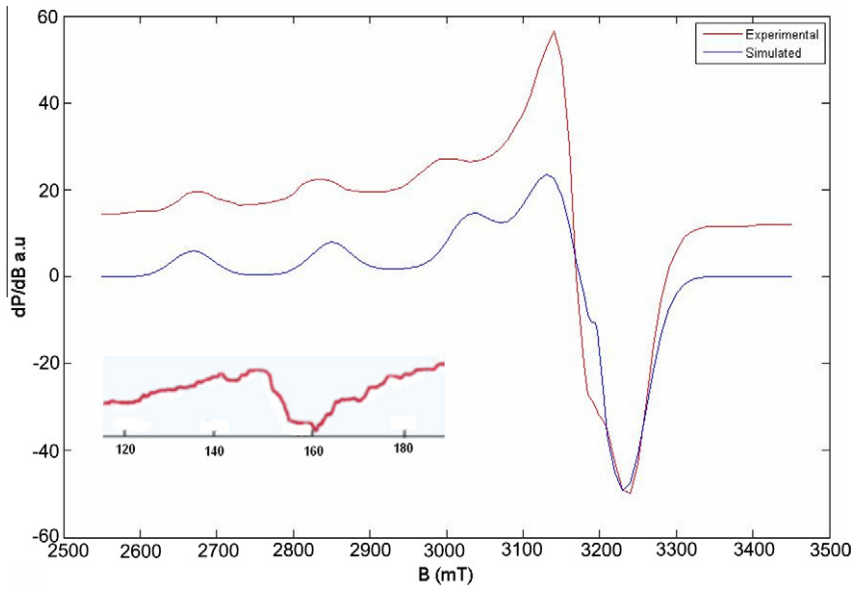

Fig. 5. EPR spectrum of $[Cu_2L_2OAc_2]\cdot H_2O$ in DMF at 77 K (the half field signal is also given at the bottom left corner).

Hathaway [38] has pointed out that, for pure sigma bonding, $K_{||} \approx K_{\perp} \approx 0.77$, and for in plane π-bonding, $K_{||} < K_{\perp}$, while for out-of-plane π-bonding $K_{\perp} < K_{||}$. In all complexes, except the compounds **1** and **5**, it is observed that $K_{||} > K_{\perp}$ which indicates the presence of significant out-of-plane π bonding while the compounds **1** and **5** shows in-plane π bonding. Moreover α^2, β^2 and γ^2 values of all compounds are found to be less than 1.0 and they indicate covalent character of the bonds.

4. Conclusion

In all complexes, $g_{||} > g_{\perp} > 2.0023$ substantiates the existence of unpaired electron in $d_{x^2-y^2}$ orbital. The X-ray single crystal data and the EPR spectra show that the compounds **1** and **5** have distorted square pyramidal arrangement whereas the compounds **2**, **3**, **4**, **6**, **7** and **9** reflect a square planar environment around the metal atom and the EPR spectra of the compounds **3** and **7** further suggest an extensive distortion from its regularity. Lastly, the typical tetragonal EPR spectrum of the compound **8** demonstrates a tetragonally distorted atmosphere around the central metal atom by the two ligands.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center CCDC reference number is 667699 for $[Cu_2L_2(OAc)_2]$. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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