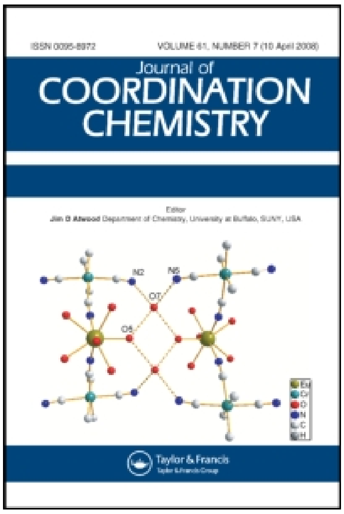

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Synthesis and crystal structure of metal complexes of Schiff bases derived from Glycylglycine and Salicylaldehyde $[Ni(H_2O)_6(Ml)_2]\cdot nH_2O$ (M = Cu, Ni; L = $C_{11}H_9N_2O_4$)

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SYNTHESIS AND CRYSTAL STRUCTURE OF METAL COMPLEXES OF SCHIFF BASES DERIVED FROM GLYCYLGLYCINE AND SALICYLALDEHYDE $[Ni(H_2O)_6(Ml)_2] \cdot nH_2O$ (M = Cu, Ni; L = $C_{11}H_9N_2O_4$)

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Complexes $[Ni(H_2O)_6(ML)_2] \cdot nH_2O$ (M = Cu, Ni; L = Schiff base derived from glycylglycine and salicylaldehyde, $C_{11}H_9N_2O_4$) were synthesized and characterized. The $[Ni(H_2O)_6(CuL)_2] \cdot 10H_2O$ complex **1** crystallized in the space group $P\bar{1}$, with $a = 7.217(1)$, $b = 11.674(1)$, $c = 12.678(1)$ Å, $\alpha = 66.56(1)$, $\beta = 76.60(1)$, $\gamma = 80.46(1)°$, and $Z = 1$. The $[Ni(H_2O)_6(NiL)_2] \cdot 2H_2O$ complex **2** crystallized in the group $P2(1)/c$, with $a = 10.564(2)$, $b = 20.246(4)$, $c = 6.965(2)$ Å, $\beta = 103.14(1)°$, and $Z = 2$. Hydrogen bonding involving $[ML]^-$, $Ni(H_2O)_6{}^{2+}$ and molecular water forms a three-dimensional (3D) supermolecule. The determination of variable-temperature magnetic susceptibilities indicates an antiferromagnetic interaction between the metallic atoms of **1**, and a corresponding ferromagnetic interaction for **2**.

Keywords: Metal complexes; Schiff base; Dipeptide; Hydrogen-bond network

INTRODUCTION

Metal Schiff-base complexes derived from amino acids (or peptides) play an important role as the key compounds for modeling more complicated PLP-amino acid Schiff bases (PLP = pyridoxal-5′-phosphate), as these are key intermediates in a variety of metabolic reactions involving amino acids, such as decarboxylation, transamination, racemization, and C–C bond cleavage, which are catalyzed by enzymes that require PLP as a cofactor [1–4]. Considerable effort has been devoted to the preparation, structural characterization, appropriate spectroscopy and magnetic studies of Schiff-base complexes derived from salicylaldehyde and amino acids such as Gly, β-Ala, Val, Ser, Thr,

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Met, Glu, Phe, Tyr, Trp [5–14] and reduced salicylidene amino acid [15], but little attention has been given to Schiff bases derived from simple peptides [16], and few structurally characterized complexes have been reported. In this article, we report the synthesis, structure and IR, UV-vis, ESR and magnetic study of Schiff-base complexes, namely $[Ni(H_2O)_6(ML)_2] \cdot nH_2O$ (M = Cu, Ni; L = Schiff bases derived from glycylglycine and salicylaldehyde, $C_{11}H_9N_2O_4$).

EXPERIMENTAL

Physical Measurements

IR spectra were recorded on a Bruker Vector22 spectrophotometer from KBr pellets in the range 400–4000 cm^{-1}. The UV spectra were recorded on a UV-3100 spectrophotometer. Elemental analyses (H, C, N) were performed on a Perkin-Elmer 240 instrument. All X-band ESR spectra were recorded using a JES-FEIXG spectrometer. Variable-temperature magnetic susceptibilities were carried out on powder samples with a CAHN-2000 Faraday-type magnetometer in the temperature range 75–300 K. Diamagnetic correction for the constituent atoms was made using Pascal's constants.

Synthesis

All chemicals were of reagent grade and were used as supplied by commercial sources. The Schiff base was prepared by condensing glycylglycine and salicylaldehyde. Glycylglycine (10 mmol) was dissolved in refluxing absolute MeOH (40 cm^3) containing $LiOH \cdot H_2O$ (10 mmol). After cooling to room temperature, a solution of salicylaldehyde (10 mmol) in absolute MeOH was added slowly with stirring for 10 min, then $Cu(ClO_4)_2 \cdot 6H_2O$ (10 mmol) was added to the solution and the pH was adjusted to 9–11 by 1 N NaOH solution. After stirring at room temperature for 30 min, the volume was reduced to *ca.* 5 cm^3 *in vacuo*. Anhydrous EtOH was added to precipitate the product, which was recrystallized from MeOH solution. Anal. Calcd. for $C_{11}H_{13}N_2O_6Cu$ Na(%): C, 37.1; H, 3.6; N, 7.9. Found: C, 37.2; H, 3.6; N, 7.9.

Synthesis of $[Ni(CuL)_2] \cdot 12H_2O$ 1

$Na[CuL] \cdot 2H_2O$ (2 mmol) was dissolved in water (15 cm^3) $\cdot$ $Ni(ClO_4)_2 \cdot 6H_2O$ (2 mmol) was added to the solution with stirring. A violet precipitate was obtained. The filtrate was allowed to evaporate slowly at room temperature. After several days violet-red crystals were obtained. The complex is not stable and tends to lose water in air. Anal. Calcd. for $C_{22}H_{42}N_4O_{20}Cu_2Ni$(%): C, 30.4; H, 4.9; N, 6.5. Found: C, 30.5; H, 4.9; N, 6.5.

Synthesis of $[Ni(NiL)_2] \cdot 8H_2O$ 2

$[Ni(NiL)_2] \cdot 8H_2O$ was obtained in a similar way using $NiCl_2 \cdot 6H_2O$ instead of $Cu(ClO_4)_2 \cdot 6H_2O$. Anal. Calcd. for $C_{22}H_{34}N_4O_{16}Ni_3$(%): C, 33.6; H, 4.4; N, 7.1. Found: C, 33.7; H, 4.3; N, 7.2.

Crystallographic Data Collection and Structure Solution

Since the crystal is not stable in air, we put it in a glass tube sealed with oil. Crystal data for **1** were collected on a Siemens P4 diffractometer and crystal data for **2** were collected on a Siemens SMART-CCD diffractometer. The structure solution by direct methods revealed the metal atom coordinates, and subsequent different Fourier methods yielded the positions of all remaining atoms. All non-H atoms were refined anisotropically by full-matrix least-squares calculations using SHELXTL v. 5.1 [17]. For the two complexes all the hydrogen atoms were found in different Fourier maps, assigned a fixed isotropic displacement parameter 1.2 times the equivalent isotropic U value of the attached atoms and allowed to ride on their respective parent atoms. A summary of the data collection and structure refinement is listed in Table I.

RESULTS AND DISCUSSION

Crystal Structure of 1

Selected bond lengths and angles are summarized in Table II. An ORTEP drawing of complex **1** with labeling of the atoms is shown in Fig. 1. The unit contents consist of one $Ni(H_2O)_6^{2+}$, two $[CuL]^-$ and ten water molecules. The coordination environment of the

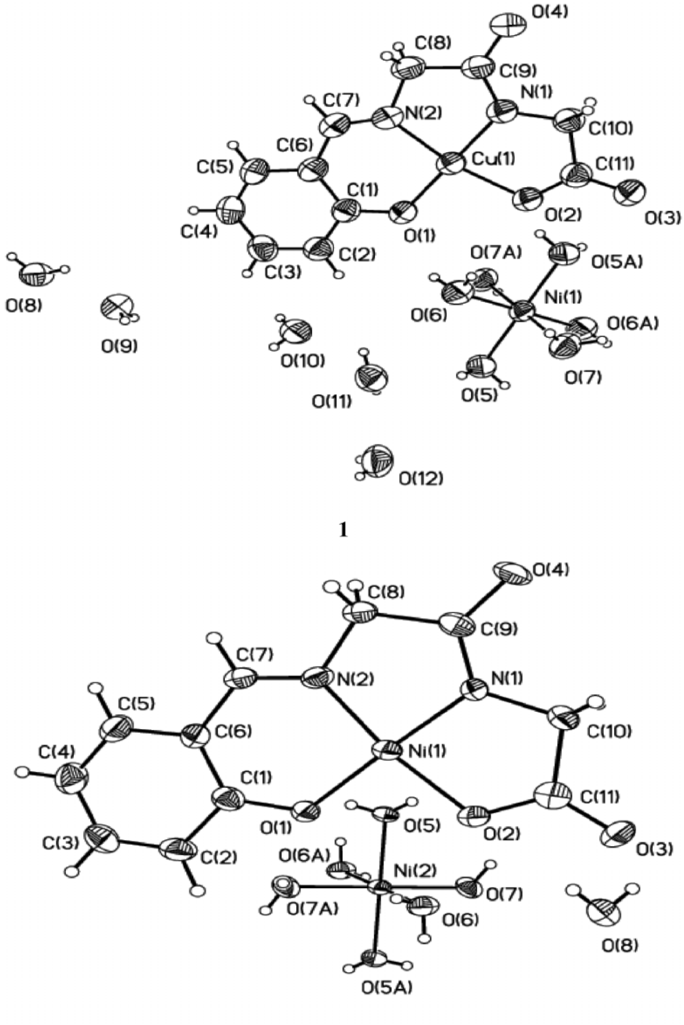
TABLE I Crystal data and structure refinement

Formula	$[Ni(H_2O)_6(CuL)_2]\cdot 10H_2O$ (**1**)	$[Ni(H_2O)_6(NiL)_2]\cdot 2H_2O$ (**2**)
Empirical formula	$C_{22}H_{50}N_4O_{24}Cu_2Ni$	$C_{22}H_{34}N_4O_{16}Ni_3$
Formula weight	940.45	786.60
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	7.217(1)	10.564(2)
b (Å)	11.674(1)	20.246(4)
c (Å)	12.678(1)	6.965(2)
α (°)	66.56(1)	90.00
β (°)	76.60(1)	103.14(1)
γ (°)	80.46(1)	90.00
V (Å)^3	950.1(2)	1450.7(7)
Z	1	2
D_{calc} (g cm^{-3})	1.644	1.801
μ (Mo Kα) (cm^{-1})	1.692	2.010
λ (Mo Kα) (Å)	0.71073	0.71073
T (K)	293(2)	293(2)
F(000)	488	812
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.15$	$0.25 \times 0.20 \times 0.15$
θ range for data collection	1.78–25.04	2.01–27.09
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 13$, $-15 \le l \le 14$	$-13 \le h \le 12$, $-24 \le k \le 25$, $-8 \le l \le 8$
Reflections collected	4935	8352
Independent reflections	3305	3164
Observed reflections	2915	1979
R(int)	0.028	0.076
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3305/0/241	3164/0/217
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0498$, $wR2 = 0.1403$	$R1 = 0.0386$, $wR2 = 0.0640$
R indices (all data)	$R1 = 0.0552$, $wR2 = 0.1471$	$R1 = 0.0712$, $wR2 = 0.0675$
Goodness-of-fit on F^2	1.062	1.001

TABLE II Selected bond length (Å) and angles (°) for **1**

Cu(1)–N(1)	1.878(3)	Cu(1)–O(1)	1.879(3)
Cu(1)–N(2)	1.916(3)	Cu(1)–O(2)	1.977(3)
Ni(1)–O(5) #	2.049(3)	Ni(1)–O(5)	2.049(3)
Ni(1)–O(6)	2.050(3)	Ni(1)–O(6)#	2.050(3)
Ni(1)–O(7)	2.060(3)	Ni(1)–O(7)	2.060(3)
C(7)–N(2)	1.278(5)	C(8)–N(2)	1.480(5)
N(1)–Cu(1)–O(1)	179.26(13)	N(1)–Cu(1)–N(2)	84.04(14)
O(1)–Cu1–N(2)	96.08(13)	N(1)–Cu(1)–O(2)	83.44(13)
O(1)–Cu1–O(2)	96.44(11)	N(2)–Cu(1)–O(2)	167.46(13)
O(5)–Ni1–O(5)#	180.000(1)	O(5)–Ni(1)–O(6)	90.74(12)
O(5)–Ni1–O(7)	87.89(12)	O(6)–Ni(1)–O(6)#	180.000(1)
O(6)–Ni1–O(7)	89.96(13)	O(7)–Ni(1)–O(7)#	180.00(15)

Symmetry transformations used to generate equivalent atoms: #(1−*x*, −*y*, 2−*z*).



1

2

FIGURE 1 ORTEP views of **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level.

copper(II) centers is approximately square planar. The Schiff-base ligand is deprotonated, thus acting as a triple negatively charged quadridentate ONNO chelate, coordinated to the copper(II) atom via one phenolic oxygen [Cu(1)–O(1) = 1.879(3) Å], one deprotonated amide nitrogen atom [Cu(1)–N(1) = 1.878(3) Å], one imino nitrogen atom [Cu(1)–N(2) = 1.916(3) Å] and one carboxylate oxygen atom [Cu(1)–O(2) = 1.977(3) Å]. The bond to the deprotonated amide nitrogen atom is shorter than the bond to the imino nitrogen atom and the bond to the phenolic oxygen is shorter than the bond to the carboxylate oxygen. The values 1.480(5) Å for the C(8)–N(2) bond, shorter than the usual C–N single bond, and 1.278(5) Å for the double bond C(7)–N(2) agree well with the values for type I Schiff bases [18]. A slight distortion in the square planar geometry of Cu(II) is present (observed bond angles vary from 83.44(13) to 96.44(11)°). The best-fit least-squares plane through the four basal and Cu atoms shows these atoms to be nearly coplanar. The O(1)–Cu(1)–N(1) angle of 179.26(13)° is nearly linear. The phenyl ring [C(1)–C(6)] and the C(1), C(6), C(7), N(2), O(1), Cu(1) chelate ring are almost coplanar with a small dihedral angle of 3.0°, suggesting a large π-electron delocalization. The nickel(II) center is almost octahedral, coordinated with six aqua ligands. The six Ni–O bonds in the structure are in the range 2.049–2.060 Å.

The crystal lattice shows an interesting H-bond network (possible H-bonds are given in Table III). In the packing scheme of compound **1** the intermolecular and intramolecular hydrogen bonds play a very important role. The hydrogen atoms of water are involved in both intra- and intermolecular hydrogen bonds with the carbonylic, carboxylic and phenolic oxygens of the Schiff-base ligand (see Fig. 2). The intermolecular bonds have H···O distances ranging from 1.94 to 2.615 Å. These intermolecular bond distances obviously indicate that the interaction between the hydroxyl hydrogen and the carbonyl is very strong when compared to that of the hydroxyl hydrogen with phenolic oxygen and carboxylic oxygen. The molecules are linked by the extensive hydrogen bonding to form a three-dimensional network in the solid state.

TABLE III Selected H-bond distances (Å) and angles (°) for **1**

D–H	*d(D–H)*	*d(H···A)*	< *DHA*	*d(D···A)*	*A*
O(5)–H(5C)	0.850	2.242	124.59	2.813	O(2) $[-x+1, -y, -z+1]$
O(5)–H(5D)	0.850	2.216	120.03	2.742	O(11)
O(6)–H(6A)	0.850	2.344	110.90	2.764	O(1) $[x, y, z+1]$
O(6)–H(6B)	0.850	2.615	148.40	3.369	O(2) $[x, y, z+1]$
O(7)–H(7B)	0.850	2.225	120.96	2.761	O(8) $[x-1, y-1, z+1]$
O(8)–H(8D)	0.850	2.057	133.00	2.709	O(9)
O(8)–H(8C)	0.850	2.281	116.51	2.767	O(3) $[x+1, y+1, z]$
O(9)–H(9C)	0.850	2.233	114.30	2.696	O(11) $[-x+1, -y+1, -z+1]$
O(9)–H(9B)	0.850	1.940	155.21	2.735	O(4) $[x+1, y, z]$
O(10)–H(10C)	0.850	2.256	121.88	2.800	O(4) $[x+1, y, z]$
O(10)–H(10D)	0.850	2.266	129.09	2.879	O(4) $[-x+1, -y+1, -z+1]$
O(11)–H(11A)	0.850	2.121	125.43	2.704	O(10)
O(11)–H(11B)	0.850	2.215	120.20	2.743	O(12)
O(12)–H(12B)	0.850	2.564	128.99	3.169	O(12) $[-x+1, -y, -z+1]$
O(12)–H(12A)	0.850	2.067	142.48	2.789	O(3) $[x+1, y, z]$

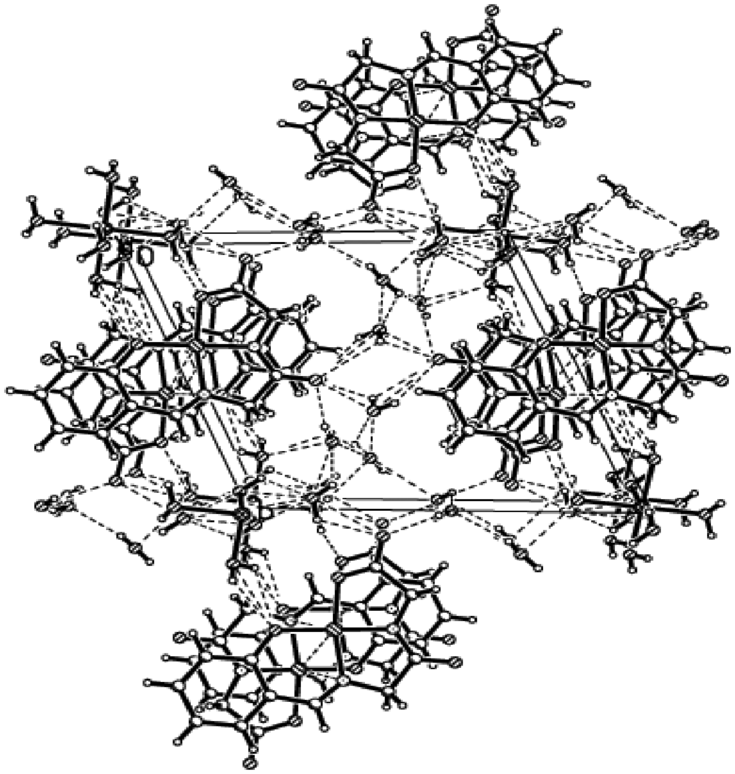


FIGURE 2 The packing diagram of a unit cell of **1** along the *a* axis.

TABLE IV Selected bond length (Å) and angles (°) for **2**

Ni(1)-N(1)	1.819(3)	Ni(1)–N(2)	1.822(3)
Ni(1)–O(1)	1.839(2)	Ni(1)–O(2)	1.886(2)
Ni(2)–O(5)	2.002(3)	Ni(2)–O(5)#	2.002(3)
Ni(2)–O(6)	2.066(3)	Ni(2)–O(6)#	2.066(3)
Ni(2)–O(7)#	2.072(3)	Ni(2)–O(7)	2.072(3)
C(7)–N(2)	1.281(4)	C(8)–N(2)	1.468(4)
N(1)–Ni(1)–N(2)	85.65(13)	N(1)–Ni(1)–O(1)	177.70(12)
N(2)–Ni(1)–O(1)	96.65(11)	N(1)–Ni(1)–O(2)	85.33(12)
N(2)–Ni(1)–O(2)	170.97(12)	O(1)–Ni(1)–O(2)	92.38(10)
O(5)–Ni(2)–O(5)#	180.0	O(5)–Ni(2)–O(6)	88.21(12)
O(5)–Ni(2)–O(7)	93.12(11)	O(6)–Ni(2)–O(6)#	180.0
O(6)–Ni(2)–O(7)	89.06(12)	O(7)–Ni(2)–O(7)#	180.0

Symmetry transformations used to generate equivalent atoms: #($-x+1$, $-y$, $-z+2$).

Crystal Structure of 2

The structure of **2** is similar to that of **1**, with one $Ni(H_2O)_6{}^{2+}$, two $[NiL]^-$ and two water molecules. Selected bond distances and angles for **2** are listed in Table IV. The coordination environment of the nickel(II) center of $[NiL]^-$ is approximately square planar. The Ni–N bond distances are 1.819 and 1.822 Å and the Ni–O bond lengths are 1.839 and 1.886 Å. The phenyl ring [C(1)–C(6)] and the C(1), C(6), C(7), N(2), O(1), Ni(1) chelate ring are almost coplanar with a small dihedral angle of

TABLE V Selected H-bond distances (Å) and angles (°) for **2**

D–H	*d(D-H)*	*d(H···A)*	*<DHA*	*d(D···A)*	*A*
O(5)–H(5B)	0.820	2.071	128.73	2.662	O(1) $[x, y, z+1]$
O(6)–H(6A)	0.820	2.031	152.07	2.782	O(4) $[-x+1, y-1/2, -z+1/2]$
O(7)–H(7B)	0.820	1.886	172.61	2.701	O(8) $[x, y, z+1]$
O(8)–H(8F)	0.850	2.260	126.65	2.851	O(3)
O(8)–H(8F)	0.850	2.599	179.61	3.449	O(2)
O(8)–H(8E)	0.850	2.364	115.65	2.838	O(3) $[x, -y+1/2, z+1/2]$
O(6)–H(6B)	0.691	2.077	174.05	2.765	O(4) $[x, -y+1/2, z+1/2]$
O(5)–H(5C)	0.699	2.043	146.03	2.652	O(2) $[x, y, z+1]$
O(7)–H(7C)	0.767	2.103	157.23	2.826	O(4) $[-x+1, y-1/2, -z+3/2]$

2.3°, suggesting a large π-electron delocalization. The nickel(II) center of $Ni(H_2O)_6{}^{2+}$ is almost octahedral, coordinated with six aqua ligands. The Ni–O bond lengths range from 2.002 to 2.072 Å. The geometrical data for hydrogen bonds of **2** are listed in Table V. Similar to **1**, in **2** the molecules are linked by extensive hydrogen bonding to form a three-dimensional network in the solid state.

Spectroscopic Properties

In the Schiff base, $\nu_{C=N}$ occurrs at 1655 cm^{-1}. After complexation with M(II), $\nu_{C=N}$ shifts to lower frequencies of 1646–1635 cm^{-1} indicating coordination of the imine nitrogen to M(II). The Schiff base has a medium intensity band at *ca.* 1526 cm^{-1}, attributed to the exocyclic C=C stretch [19], which shifts to around 1542–1533 cm^{-1} after coordination to M(II). The $\nu(CO_2)_{as}$ shifts from 1602 to 1613–1604 cm^{-1} after coordination to M(II). The π–π^* transitions of benzene are observed at 212 nm for the ligand, 218 nm for **1** and 223 nm for **2**. There is a peak for both the ligand and the complexes at approximately 199–202 nm, which may be attributed to the $n \rightarrow \pi^*$ transition of the phenols. The peaks at approximately 326 nm in the spectra of the ligand and 349–356 nm in those of the complexes are assigned to the imine $n \rightarrow \pi^*$ transitions. The weak asymmetric broad band at 580 nm, observed only for complex **1**, was assigned to a d–d transition.

Magnetic Properties and ESR Spectra

Magnetic susceptibility measurements at different temperatures have been successfully fitted to the Curie–Weiss law $(1/x_m = (T-\theta)/C)$ [**1**, $C = 2.214$ emu K mol^{-1}, $\theta = -61.471$ K; **2**, $C = 2.672$ emu K mol^{-1}, $\theta = 6.367$ K]. The variation of the inverse of the magnetic susceptibility (x_m^{-1}) and x_m of **1** and **2** are shown in Fig. 3. The θ values of the complexes indicate antiferromagnetic interactions between the metallic atoms of **1**, and ferromagnetic interactions in **2**.

ESR spectra of **1** at 110 K in DMSO are shown in Fig. 4. The spectra show axial character with $g_{zz} = g_{\perp}(2.215) > g_{\zeta}(2.05) = g_{xx} = g_{yy} > g_e(2.0023)$ and $A_{zz} = A_{11}$ (198G) $> A_{xx} = A_{yy} = A_{\perp}$(28G), typical for square-planar (or tetragonal symmetry) coordination of the copper(II) ion and indicate that the unpaired electron occupies predominantly the $d_{x^2-y^2}$ orbital having $^2B_{1g}$ as the ground state term [20]. Kivelson and Neiman have shown that g_{11} is a moderately sensitive function for

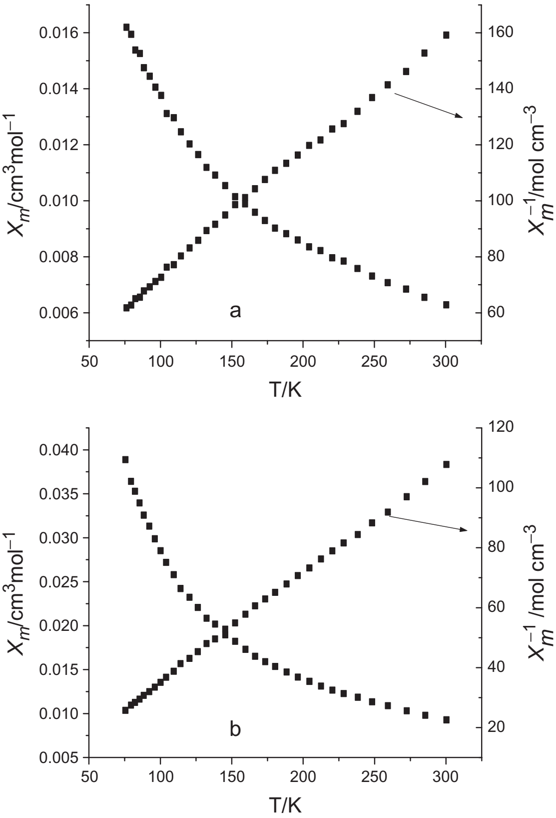


FIGURE 3 Thermal variation of x_{m} and x_{m}^{-1} for **1** (a) and **2** (b).

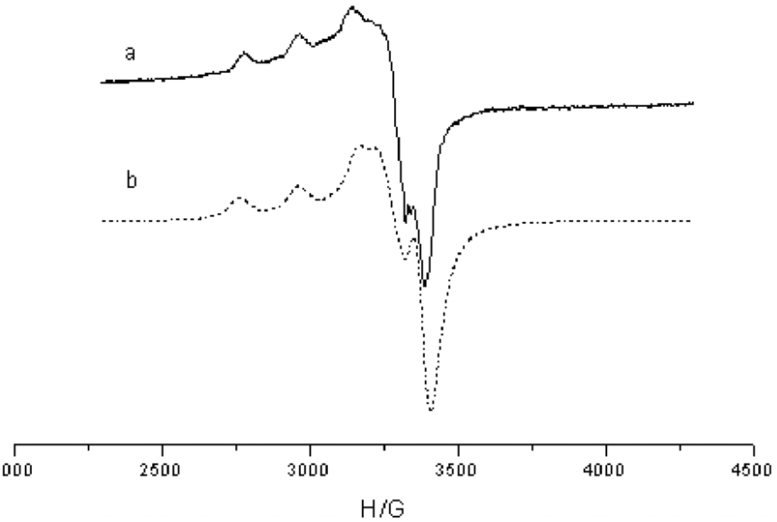


FIGURE 4 Experimental ESR spectra of **1** taken in DMSO at 110K (a), together with the calculated curve (b).

indicating covalence. Relatively speaking $g_{11} > 2.3$ is characteristic of an ionic environment and $g_{11} < 2.3$ of a covalent environment in M–L bonding [21]. In our complexes g_2 indicates a fair degree of covalent character in the Cu–L bonding.

In order to obtain a qualitative picture of the metal–ligand bonding nature in the two complexes, the following simplified expressions were used for the evaluation of bonding coefficients [22]:

$$\alpha^2 = (-A_{11}/P) + (g_{11} - g_e) + 3/7(g_\perp - g_e) + 0.04$$
$$\alpha^2\beta^2 = (g_{11} - g_e)\Delta/8\lambda_0$$

where λ_0 is the spin-orbit coupling constant ($-828\,\mathrm{cm}^{-1}$) for the free copper(II) ion,

$$P = g_e\beta_e g_N\beta_N < d_{x^2-y^2} \mid r^{-3} \mid d_{x^2-y^2}$$

$P = 0.036\,\mathrm{cm}^{-1}$. Δ represent the d-electronic transitions between the ground state and the excited state. For compound **1** the value is $17\,240\,\mathrm{cm}^{-1}$. The values of α^2 and β^2 coefficients are given in Table VI. From the α^2 value, it can be seen that the complex possesses more covalent characteristics. The α^2 and β^2 values are consistent with both strong in-plane σ bonds and in-plane π-bonds in the complex.

ESR spectra of complex **1** at room temperature in DMSO are shown in Fig. 5. The experimental spectra have been evaluated simultaneously by the WINEPR

TABLE VI ESR parameters for **1** in DMSO and bonding parameters.

Compound	g_o	g_2	g_ζ	A_o^{Cu} *(G)*	A_{11} *(G)*	$A_\perp$ *(G)*	α^2	β^2	*a, b, c*	a_o^N *(G)*
$[Ni(CuL)_2]\cdot16H_2O$ (**1**)	2.116	2.215	2.05	80	198	28	0.82	0.68	36, 18, 4.7	17

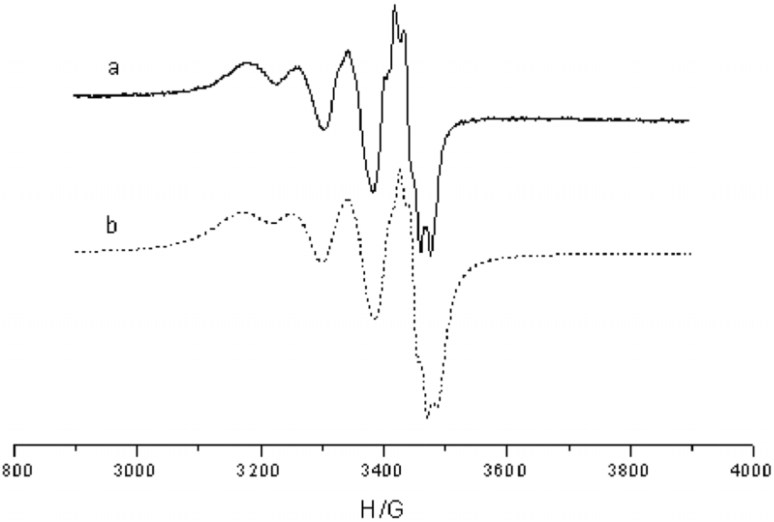


FIGURE 5 Experimental ESR spectra of **1** taken in DMSO at room temperature (a), together with the calculated curve (b).

SimFonia program. The different widths of copper hyperfine lines H_{MI} were taken into consideration by fitting the relaxation parameters *a*, *b*, *c* where $H_{MI} = a + bM_I + cM_I^2$. Table VI summarizes the ESR parameters. The spectra exhibit a line-shape with five nitrogen superhyperfine (shf) structure indicating ligation of two nitrogen atoms to the metal ion.

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Supplementary Data

Crystallographic data in CIF format are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition numbers CCDC 201913 for **1** and CCDC 201914 for **2**.

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