

A Ladder-like Coordination Polymer $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$ Constructed From Metallo-Ligand $\text{Na}[\text{CuL}]$ and $\text{Sr}(\text{NO}_3)_2$: Crystal Structure and ESR Study

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Abstract Ligand L (H_3L = Glycylglycine, *N*-[1-(2-hydroxy,5-bromophenyl)propylidene]) has been prepared which contain flexible dipeptide group and substituted phenol group. The ligand react with $\text{Cu}(\text{NO}_3)_2$ to give the metallo-ligand $[\text{CuL}]^-$, in which L acting as quadridentate ONNO chelate, coordinate to Cu(II) ion. The metallo-ligand $[\text{CuL}]^-$ is rigid and has multifunctional groups. Reaction of metallo-ligand with $\text{Sr}(\text{NO}_3)_2$ leads to the formation of the title complexes $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$ (**1**). This heteronuclear compound has been characterized by elemental analyses, spectroscopic analyses, and single crystal diffraction. Structural analyses reveal that the complex was crystallized in triclinic space group *P*-1 and has intricate 2D net-structure, which contain an infinite 1D $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2]^+$ ladder-like structure. In addition ESR (electron spin resonance) property and thermogravimetric analysis of **1** are discussed in detail.

Keywords Metallo-ligand · ESR · Crystal structure · Dipeptide · Coordination polymer

1 Introduction

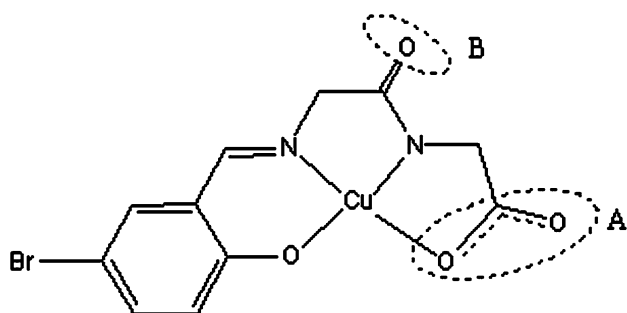
Porous coordination polymers have become of increasing interest in recent years, because of their intriguing variety of architectures, topologies [1–8] and potential applications

in catalysis, [9] gas storage, [10–12] separation, [13] non-linear optics, [14] and drug delivery [15]. For the self-assembly of coordination polymers, the choice of building blocks is of significant at initial stage of preparations [16]. Several strategies are possible for the design of building blocks. The commonly used one is selecting appropriate organic compound as bridging ligands and choosing metal ions with suitable coordination geometries [17–21]. Meanwhile, metal complexes can also be used as building blocks, sometimes called “metallo-ligands”. Up to now, various coordination polymers have been synthesis with metallo-ligand [9, 21–30]. These metallo-ligands contain uncoordinated or/and coordination unsaturated donor atoms which are capable to combine with other metal ions under certain reaction conditions to create extended architectures [31–35].

As a metallo-ligand to assembly coordination polymers, $[\text{CuL}]^-$ (H_3L = Glycylglycine, *N*-[1-(2-hydroxy,5-nitrophenyl)-propylidene]) was considered for the following reasons. (a) Multicoordination ability: It could furnish various coordination modes due to the presence of the multifunctional group. As shown in Scheme 1, $[\text{CuL}]^-$ has two kinds of Lewis-base coordination groups, carboxylate (group A) and carbonyl (group B) moieties. Group A contributes to both chelating of the central Cu(II) ion (formation of the metallo-ligand) and bridging with other metal ions. While group B just contributes to the linkage of $[\text{CuL}]^-$ with other metal ions; (b) Rigidity: Metallo-ligand $[\text{CuL}]^-$ has a rigid planner structure, which is suitable for the contraction of robust coordination polymers [19]; (c) Hydrogen bonding ability: The peptide bond, phenol and carboxylate group in $[\text{CuL}]^-$ has a strong capability of forming hydrogen bonds, which could play an important role in the assembly of supramolecular compounds [36, 37]; (d) Furthermore, metallo-ligand $[\text{CuL}]^-$ is easy to

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Scheme 1 Two kind of coordination groups (A and B) in $[\text{CuL}]^-$

construct heterometallic assembly systems [26]. L coordinate with Cu(II) in a ONNO mode. Non coordinated carboxylate and carbonyl O atoms can act as potential donors for other metal ions, which may lead to the formation of the heterometallic coordination polymers.

Herein, we describe the synthesis, structure, and spectra properties of the molecule ladder $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$, which is synthesized bases on the rigid metallo-ligand $[\text{CuL}]^-$.

2 Experimental

2.1 Materials and Measurements

All chemicals were of reagent grade and were used as supplied by commercial sources. FT-IR spectra were measured from KBr pellets using a Nicolet FT-IR 400 system in the range of $4,000\text{--}400\text{ cm}^{-1}$. The UV spectra were recorded by a Perkin Elmer Lambda 900 spectrophotometer. Elemental microanalyses (EA) were performed on a Perkin-Elmer CHN-2400 analyzer.

2.2 Synthesis of $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$, **1**

Glycylglycine (10 mmol), 5-bromosalicylaldehyde (10 mmol) and LiOH (20 mmol) were dissolved and refluxed in MeOH/ H_2O (v:v = 1:1). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10 mmol) was then added to the solution and the resulting solution was adjusted to the pH 9–11. At last, $\text{Sr}(\text{NO}_3)_2$ (5 mmol) was added. After stirring for 2 h, the violet precipitate was filtered off. The filtrate was allowed to evaporate slowly at room temperature. After several days, violet red crystals suitable for X-ray diffraction were obtained. We failed to obtain the single crystals of the complex by a “one-pot” method, although we tried several times. Therefore, the stepwise method may be necessary to obtain single crystals of the title complex. $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$ **1**. Calcd. for $\text{C}_{22}\text{H}_{28.5}\text{Br}_2\text{Cu}_2\text{N}_4\text{O}_{14.25}\text{Sr}$: C, 27.8%; H, 3.0%; N, 5.9%. Found: C, 27.9%; H, 2.9%; N, 5.9%. IR (KBr, cm^{-1}): 3423(m),

1653(s), 1607 (s), 1554(s), 1514(m), 1406 (m), 1349(w), 1180(s), 947(w), 857(m), 719(m), 626(m).

2.3 X-ray Structure Determination

A suitable white block crystal with dimensions of $0.20\text{ mm} \times 0.10\text{ mm} \times 0.10\text{ mm}$ was mounted on a glass fiber and the data were collected on a Bruker Smart 1000 CCD diffractometer with a $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 293(2) K by using an ω scan mode in the range of $2.10 < \theta < 26.0^\circ$. For the title complex, a total of 8,215 reflections were collected, of which 5,876 were unique with $R_{\text{int}} = 0.069$. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques for 4,030 observed reflections with $I > 2\sigma(I)$ to the final $R = 0.0711$, $wR = 0.1875$ ($w = 1/\sigma^2(F_o)^2 + (0.1239P)^2$), where $P = (F_o^2 + 2F_c^2)/3$, $S = 0.98$ and $(\Delta/\sigma)_{\text{max}} = 0.000$. The highest and lowest residual peaks in the final difference Fourier map are 1.88 and $-1.90\text{ e/\AA}^3$, respectively. All calculations were performed by the SHELXTL 97 program [38]. The selected bond lengths and bond angles are listed in Table 1.

3 Results and Discussion

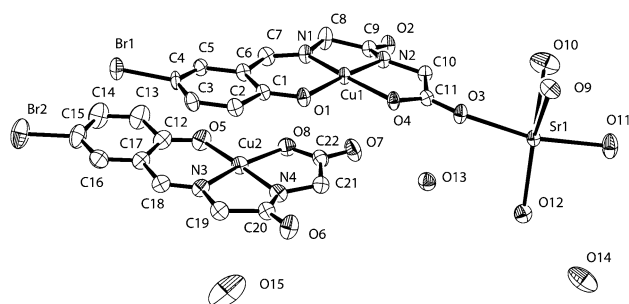
3.1 Crystal Structure of **1**

The independent unit of the crystal structure is shown in Fig. 1. The coordination environment of the Cu(II) center is approximately square-planar. The ligand deprotonated, acting as a triple negatively charged quadridentate ONNO chelate, coordinated to the Cu(1) atom via one phenolic oxygen(O(1)), one deprotonated amide nitrogen atom (N(2)), one imino nitrogen atom(N(1)) and one carboxylate oxygen atom (O(4)). The values $1.467\text{ \AA}$ for C(8)–N(1) bond shorter than the usual C–N single bond and the double bond C(7)–N(1) length of $1.284\text{ \AA}$ agree well with the values of Schiff Base type I [39]. 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(2) angle of $174.68(18)^\circ$ is nearly linear. The phenyl ring [C(1)–C(6)] and the ring of C(1), C(6), C(7), N(2), O(1), Cu(1) chelate ring are almost coplanar with a small dihedral angle of 5.2° (Table 2).

The coordination environment of Cu(2) is similar to that of Cu(1). Sr(II) is 8-coordinated by four water molecules (O(9)–O(12)), one carbonyl oxygen atoms (O(2) i; symmetry

Table 1 Crystal data and structure refinement parameters for 1

Empirical formula	C ₂₂ H _{28.5} N ₄ O _{14.25} Br ₂ Cu ₂ Sr
Formula weight	951.51
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	7.004 (2)
<i>b</i> (Å)	9.706 (3)
<i>c</i> (Å)	23.114 (7)
α (°)	100.77 (1)
β (°)	91.47 (1)
γ (°)	92.99 (1)
<i>V</i> [Å ³]	1540.5 (8)
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ^{−3})	2.051
θ range for data collection (°)	2.1–26.0
$\mu_{\text{MoK}\alpha}$ (mm ^{−1})	5.761
<i>F</i> (000)	937
Crystal size (mm ³)	0.10 × 0.10 × 0.20
Index ranges	−8 ≤ <i>h</i> ≤ 7; −11 ≤ <i>k</i> ≤ 11; −28 ≤ <i>l</i> ≤ 28
Reflections collected	8215
Independent reflections	5876 (<i>R</i> _{int} = 0.069)
Observed reflections	4030
Goodness-of-fit on <i>F</i> ²	0.98
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0711, 0.1875

**Fig. 1** Perspective views of the coordination environments of the Cu and Sr ions for 1. The thermal Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity

code i: $-x, -y, -z + 1$) and three carboxylic oxygen atoms (O(3), O(3) ii, O(4) ii; symmetry code ii: $-x, -y + 1, -z + 1$). The Sr–O (water) distances ranging from 2.517 to 2.605 Å. The Sr–O (carboxylic and carbonyl oxygen) distances range from 2.514 to 2.753 Å. There are two crystallographically unique [CuL][−] anions in the structure. One of the [CuL][−] containing O(2) O(3) and O(4) coordinate to strontium ions as tridentate unit. The other one [CuL][−] do not coordinate to Strontium atom and act as counter anion. The nearest Cu–Cu distance (Cu(1)–Cu(2)) is 3.536 Å. The distances between Cu and the N atom of the nearby [CuL][−] are

Table 2 Selected bond lengths [Å] and angles [°] for 1

Bond	Distance
Cu(1)–O(1)	1.879 (3)
Cu(1)–O(4)	1.976 (3)
Cu(2)–N(3)	1.925 (4)
Sr(1)–O(11)	2.517 (4)
Sr(1)–O(12)	2.605 (4)
Sr(1)–O(4) ^b	2.753 (3)
Cu(1)–N(2)	1.891 (4)
Cu(2)–N(4)	1.872 (5)
Cu(2)–O(8)	1.950 (4)
Sr(1)–O(9)	2.533 (4)
Sr(1)–O(2) ^a	2.661 (3)
Cu(1)–N(1)	1.918 (4)
Cu(2)–O(5)	1.880 (4)
Sr(1)–O(3)	2.514 (4)
Sr(1)–O(10)	2.599 (5)
Sr(1)–O(3) ^b	2.710 (3)
Angle	(°)
O(1)–Cu(1)–N(2)	174.68 (18)
O(1)–Cu(1)–O(4)	96.11 (14)
N(4)–Cu(2)–O(5)	177.7 (2)
N(4)–Cu(2)–O(8)	84.24 (18)
O(3)–Sr(1)–O(11)	167.73 (15)
O(3)–Sr(1)–O(10)	85.44 (16)
O(3)–Sr(1)–O(12)	104.11 (13)
O(10)–Sr(1)–O(12)	141.20 (14)
O(9)–Sr(1)–O(2) ^a	143.61 (13)
O(3)–Sr(1)–O(3) ^b	70.15 (12)
O(10)–Sr(1)–O(3) ^b	138.13 (15)
O(3)–Sr(1)–O(4) ^b	117.09 (10)
O(10)–Sr(1)–O(4) ^b	135.15 (14)
O(3) ^b –Sr(1)–O(4) ^b	47.31 (10)
O(1)–Cu(1)–N(1)	95.52 (16)
N(2)–Cu(1)–O(4)	83.81 (16)
N(4)–Cu(2)–N(3)	83.4 (2)
O(5)–Cu(2)–O(8)	96.51 (18)
O(3)–Sr(1)–O(9)	79.79 (13)
O(11)–Sr(1)–O(10)	83.23 (17)
O(11)–Sr(1)–O(12)	87.73 (15)
O(3)–Sr(1)–O(2) ^a	80.15 (11)
O(10)–Sr(1)–O(2) ^a	77.64 (14)
O(11)–Sr(1)–O(3) ^b	116.11 (12)
O(12)–Sr(1)–O(3) ^b	79.22 (12)
O(11)–Sr(1)–O(4) ^b	68.90 (11)
O(12)–Sr(1)–O(4) ^b	73.90 (11)
N(2)–Cu(1)–N(1)	83.96 (18)
N(1)–Cu(1)–O(4)	166.39 (16)
O(5)–Cu(2)–N(3)	95.94 (19)

Table 2 continued

Angle	(°)
N(3)–Cu(2)–O(8)	167.39 (19)
O(11)–Sr(1)–O(9)	92.00 (15)
O(9)–Sr(1)–O(10)	70.77 (14)
O(9)–Sr(1)–O(12)	147.46 (12)
O(11)–Sr(1)–O(2) ^a	101.92 (12)
O(12)–Sr(1)–O(2) ^a	67.47 (12)
O(2) ^a –Sr(1)–O(3) ^b	71.74 (12)
O(9)–Sr(1)–O(3) ^b	127.80 (11)
O(9)–Sr(1)–O(4) ^b	75.69 (12)
O(2) ^a –Sr(1)–O(4) ^b	140.69 (12)

Symmetry transformation (a) $-x, -y, -z + 1$; (b) $-x, -y + 1, -z + 1$

Cu(1)–N(4) 3.033 Å; Cu(2)–N(1) 3.276 Å. The Cu(1), Cu(2), N(1), N(4) are almost coplanar, and the mean deviation from the plane is 0.0571 Å.

Figure 2a shows the assembly of an infinite ladder framework (1-D chain) from $[\text{CuL}]^-$ unit and node $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$. The carboxylic oxygen atom (O(3)) of the tridentate $[\text{CuL}]^-$ unit bridge the adjacent $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$ (Sr(1), Sr(1) ii; symmetry code ii: $-x, -y + 1, -z + 1$) together to form the rungs of the ladder. The nearest Sr–Sr distance is 4.277 Å. The rails of the ladder are made of 7-atoms unit O(2)–C(9)–N(2)–C(10)–C(11)–O(4)–Sr(1) in which carbonyl oxygen (O(2)) of the tridentate $[\text{CuL}]^-$ unit link with $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$ along *b* axis.

As anticipated, classical hydrogen bonds between water and carboxylate (or carbonyl) were observed with the O...O distances varying from 2.662 to 2.905 Å. As a consequence, these hydrogen-bonding interactions further extend the 1D arrangement to generate a 2D framework (Table 3; Fig. 2b). As shown in Fig. 2c uncoordinated counter anion and solvent water were located in the framework.

3.2 Spectroscopic Analyses and Thermogravimetric Analysis (TGA)

π – π^* transitions of benzene ring are observed at 212 nm for the ligand and 217 nm for the complex **1**. There is a peak for both the ligand and for the complexes at approximately 202–205 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 355 nm in that of the complex are assigned to the imine n – π^* transitions. The weak asymmetric broad band at 580 nm, observed only for the complexes, was assigned to a d – d transition.

Thermogravimetric experiment was performed to explore thermal stability (Fig. 3). The first weight-loss is 8.26% (Calcd.: 8.34%) 40–130 °C and corresponds to the

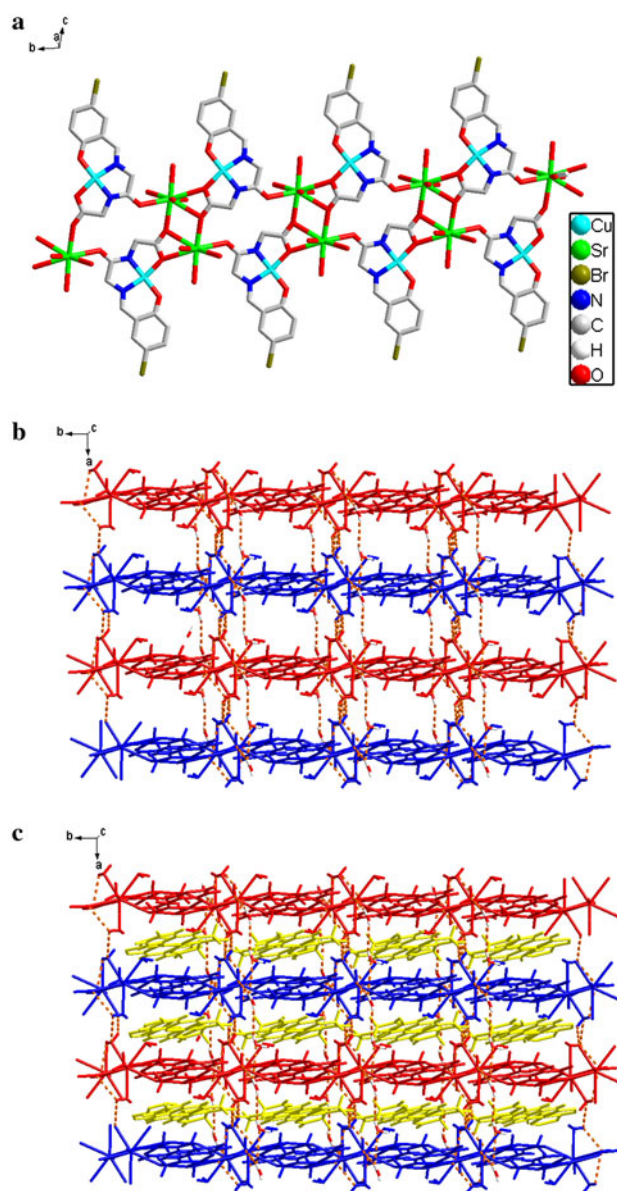


Fig. 2 a View of the assembly of an infinite ladder structure from the $[\text{CuL}]^-$ unit and $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$ node. b 1D ladders were linked to form 2D framework by hydrogen bonds indicated by dashed lines. c $[\text{CuL}]^-$ counter anion located in the cavities of the 2D framework

loss of four water molecules per formula unit. A plateau is observed from 135 to 225 °C indicating no further weight loss. Above 225 °C the framework starts to decompose rapidly.

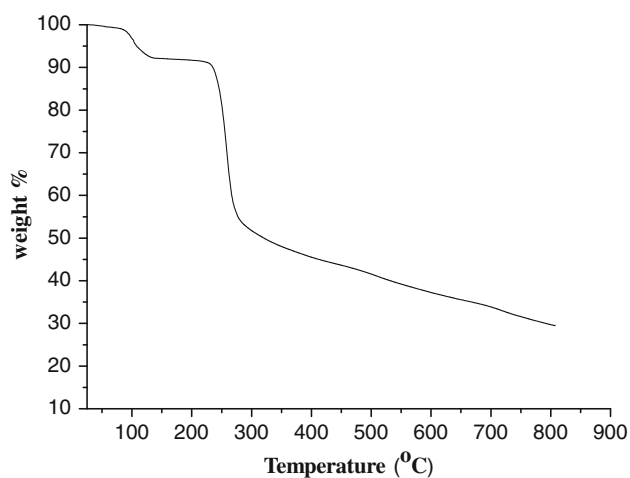
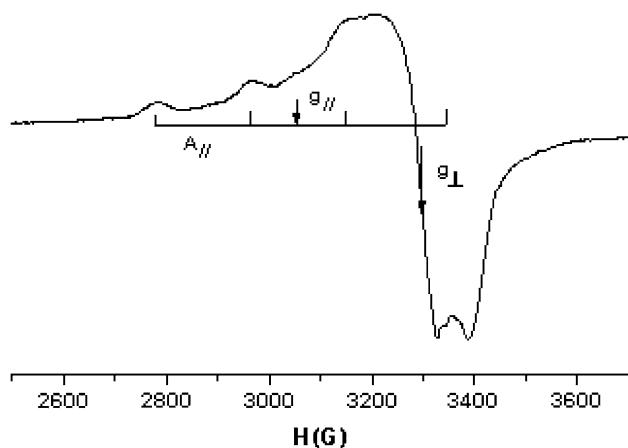
3.3 ESR Spectra

ESR spectrum of **1** at 110 K in DMSO is shown in Fig. 4. The trend $g_{\parallel}(2.211) > g_{\perp}(2.065) > g_c(2.0023)$ observed for **1** indicates a $d(x^2-y^2)$ ground state. It has been shown that $g_{\parallel}$ is a moderately sensitive function for indicating

Table 3 Distances [Å] and angles [°] of selected hydrogen bonding for complex **1**

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
O(9)–H(9A)...O(12) ^a	0.85	2.28	2.905 (6)	130
O(9)–H(9B)...O(13) ^b	0.85	2.24	2.821 (6)	125
O(10)–H(10E)...O(7) ^c	0.85	2.43	2.741 (6)	102
O(11)–H(11A)...O(14) ^a	0.96	2.13	2.739 (8)	120
O(11)–H(11C)...O(1) ^b	0.96	2.00	2.887 (5)	153
O(12)–H(12C)...O(6) ^d	0.85	2.07	2.662 (6)	126
O(13)–H(13A)...O(10) ^e	0.85	2.33	2.861 (7)	121
O(13)–H(13D)...O(7)	0.85	2.27	2.740 (6)	115
O(13)–H(13D)...O(9) ^b	0.85	2.48	2.821 (6)	105
O(14)–H(14C)...O(5) ^f	0.85	2.49	2.872 (7)	108
O(14)–H(14D)...O(6) ^d	0.85	2.10	2.752 (7)	133

Symmetry codes (a) $x-1, y, z$; (b) $-x, -y+1, -z+1$; (c) $-x, -y, -z+1$; (d) $-x+1, -y+1, -z+1$; (e) $x+1, y, z$; (f) $-x+1, -y, -z+1$

**Fig. 3** TG curve of compound **1****Fig. 4** Experimental ESR spectra of the complex **1** taken in DMSO at 110 K

covalency. Relatively speaking $g_{\parallel} > 2.3$ is characteristic of an ionic environment and $g_{\parallel} < 2.3$ of a covalent environment in M–L bonding [40]. In complex **1** $g_{\parallel}$ 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 complex **1**, the following simplified express were used for the evaluation of bonding coefficients [41]:

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

$$\alpha^2\beta^2 = (g_{\parallel} - g_e)\Delta/8\lambda_0$$

where λ_0 is the spin–orbit coupling constant (-828 cm^{-1}) for the free Cu^{II} ion,

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

$P = 0.036 \text{ cm}^{-1}$. Δ represent the d-electronic transitions between the ground state and the excited state. For compounds studied, the value is 17240 cm^{-1} (**1**). The values of α^2 and β^2 coefficients given in Table 4.

ESR spectrum of the complex **1** at room temperature in DMSO is shown in Fig. 5. The experimental spectrum has been evaluated simultaneously by the WINEPR SimFonia program. The different widths of copper hyperfine lines ΔH_{MI} were taken into consideration by fitting the relaxation parameters a, b, c where $\Delta H_{\text{MI}} = a + bM_I + cM_I^2$. The spectrum exhibits a clear five-line nitrogen superhyperfine (shf) structure indicating ligation of two nitrogen atoms to the metal ion.

4 Conclusions

In conclusion, we have prepared a ladder coordination polymer $[\text{Sr}(\text{H}_2\text{O})_4(\text{CuL})_2] \cdot (\text{CuL}) \cdot 2.25\text{H}_2\text{O}$ in which rigid $[\text{CuL}]^-$ anion link with $[\text{Sr}(\text{H}_2\text{O})_4]^{2+}$ forming rails and rungs of the ladder. Hydrogen-bond result in the formation of a two-dimensional framework with counter anion $[\text{CuL}]^-$ stay in the cavity. Further study on coordination structures assembly from the rigid “metallo-ligand” $[\text{CuL}]^-$ (or $[\text{NiL}]^-$) and metal ions are in progress.

5 Supplementary Materials

Supporting information: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 791879. This

Table 4 ESR parameters for complex **1** in DMSO

Complex	G_o	$g_{\parallel}$	$g_{\perp}$	$A_{\text{Cu}}^{\text{Cu}}$	$A_{\parallel}$	$A_{\perp}$	α^2	β^2	a, b, c,	a_N^N
1	2.114	2.211	2.065	80	188	26	0.77	0.72	36, 18, 4.7	17

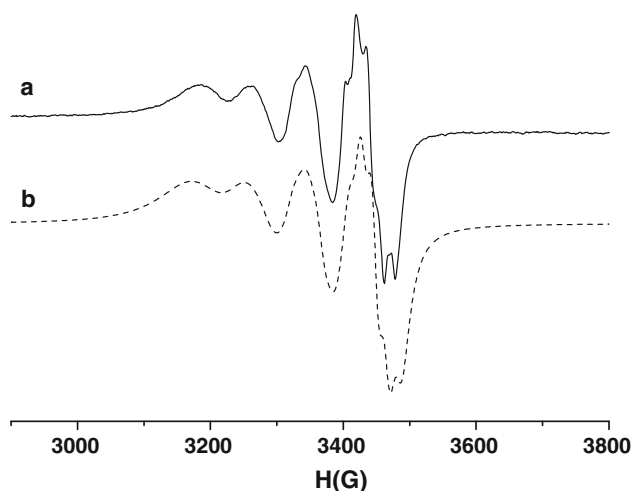


Fig. 5 Experimental ESR spectra of the complex 1, taken in DMSO at room temperature (a), together with the simulated curve (b)

data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (+44)1223336-033; e-mail: deposit@ccdc.cam.ac.uk].

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