

# Hydrothermal syntheses, crystal structures and magnetic properties of two copper(II) complexes involved *in situ* ligand synthesis†‡§

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The hydrothermal reaction of  $\text{Cu}(\text{NO}_3)_2$ , isophthalate (ip) and 2,2'-bipyridine (2,2'-bpy) without or with  $\text{K}_2\text{Cr}_2\text{O}_7$  affords different complexes, whose structures are controlled only by the addition of the  $\text{K}_2\text{Cr}_2\text{O}_7$ . The reaction of  $\text{Cu}(\text{NO}_3)_2$ , isophthalate and 2,2'-bipyridine yields a novel one-dimensional double-chain coordination polymer  $[\text{Cu}_3(\text{ip})_2(\text{Hip})_2(\text{bpy})_2]_n$  (**1**). However, with the addition of  $\text{K}_2\text{Cr}_2\text{O}_7$  in the above reaction at the same hydrothermal conditions, a discrete hexanuclear Cu(II) complex  $[\text{Cu}_6(\text{ipO})_4(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (**2**) (ipOH = 2-hydroxyisophthalate) was isolated. It is interesting to find that the *in situ* reaction of isophthalate (ip) oxidized to 2-hydroxyisophthalate (ipOH) occurs.  $\text{K}_2\text{Cr}_2\text{O}_7$  acts as an oxidant. The magnetic properties of **1** and **2** have been investigated by variable-temperature magnetic susceptibility and magnetization measurements, and the results reveal that intramolecular ferromagnetic interactions exist with weak intermolecular antiferromagnetic interactions at very low temperature in **1** and weak antiferromagnetic interactions admixture with strong ferromagnetic interactions in **2**.

## Introduction

The design and construction of coordination polymers has attracted much attention owing to their intriguing topologies and potential applications as functional materials.<sup>1–3</sup> The hydro(solvo)thermal method has been a promising technique in synthesizing novel metal–organic frameworks.<sup>4</sup> It has been found that *in situ* ligand reactions,<sup>5</sup> such as ligand oxidative coupling, hydrolysis, cleavage of C–S or C–C bonds, decarboxylation and hydroxylation of aromatic groups and cycloaddition of organonitriles with ammonia, can occur under the hydro(solvo)thermal conditions. In the previous work,<sup>5a,b</sup> Chen *et al.* reported the *in situ* ligand synthesis of 2-hydroxyisophthalate (ipOH) from the reaction of isophthalate (ip) or 1,2,3-benzenetricarboxylic acid, 4,4'-bipyridine and copper nitrates under hydrothermal conditions. In this paper, we report the syntheses, crystal structures and magnetic properties of  $[\text{Cu}_3(\text{ip})_2(\text{Hip})_2(2,2'\text{-bpy})_2]_n$  (**1**) and  $[\text{Cu}_6(\text{ipO})_4(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (**2**). It is surprising to find that *in situ* hydroxylation of isophthalate into 2-hydroxyisophthalate(ipOH) was observed in **2**.

## Experimental

### Materials and methods

All reagents and solvents employed were commercially available and used without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400  $\text{cm}^{-1}$  on a Nicolet 5DX spectrometer. X-Ray powder diffraction (XPRD) data were recorded with a Rigaku D/max 2200 vpc diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range of 2–300 K with an applied field of 10 KG.

### Hydrothermal syntheses

#### $[\text{Cu}_3(\text{ip})_2(\text{Hip})_2(2,2'\text{-bpy})_2]_n$ (**1**)

A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.120 g, 0.5 mmol), 2,2'-bpy (0.056 g, 0.5 mmol),  $\text{H}_2\text{ip}$  (0.041 g, 0.5 mmol), NaOH (0.02 g, 0.5 mmol), and  $\text{H}_2\text{O}$  (10 ml) in a 23-ml Teflon reactor, was heated at 160 °C for five days and then cooled to room temperature at a rate of 5 K  $\text{h}^{-1}$ . Green block crystals (0.107 g) of **1** were obtained in 55% yield after washing with water and drying in air. Anal. calcd. for  $\text{C}_{52}\text{H}_{34}\text{Cu}_3\text{N}_4\text{O}_{16}$ : C, 53.77; H, 2.95; N, 4.82. Found: C, 53.65; H, 3.01; N, 4.92. IR (KBr,  $\text{cm}^{-1}$ ): 3436 s, 3036 w, 2712 w, 1683 s, 1613 s, 1529 s, 1497 m, 1315 w, 1269 s, 1159 m, 742 s, 454 m.

#### $[\text{Cu}_6(\text{ipO})_4(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ (**2**)

A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.120 g, 0.5 mmol), 2,2'-bpy (0.056 g, 0.5 mmol),  $\text{H}_2\text{ip}$  (0.041 g, 0.5 mmol), NaOH (0.02 g, 0.5 mmol),  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.01 g, 0.03 mmol) and  $\text{H}_2\text{O}$  (10 ml) in a 23-ml Teflon reactor, was heated at 160 °C for six days and then

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† The HTML version of this article has been enhanced with colour images.

‡ CCDC reference numbers 605846 for **1** and 605847 for **2**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704327a

§ Electronic supplementary information (ESI) available: The simulated and experimental X-ray powder diffraction patterns for **1–2**. See DOI: 10.1039/b704327a

cooled to room temperature at a rate of 5 K h<sup>-1</sup>. Green block crystals of **2** (0.091 g) were isolated in 25% yield after washing with water and drying in air. Anal. calcd. for C<sub>52</sub>H<sub>44</sub>Cu<sub>6</sub>N<sub>4</sub>O<sub>28</sub>: C, 40.19; H, 2.85; N, 3.60. Found: C, 40.35; H, 2.65; N, 3.48. IR (KBr, cm<sup>-1</sup>): 3443 w, 1614 m, 1568 s, 1385 s, 1270 s, 776 s, 742 m, 715 s.

### X-Ray crystallography§

Single-crystal X-ray diffraction measurements were carried out on a Bruker P4 diffractometer at room temperature. The data collections were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell dimensions were obtained with least squares refinements, and all structures were solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$ .<sup>6</sup> The water H atoms were located and refined, with distance restraints of O–H = 0.85(1) and H...H = 1.39(1) Å. Crystallographic data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

## Results and discussion

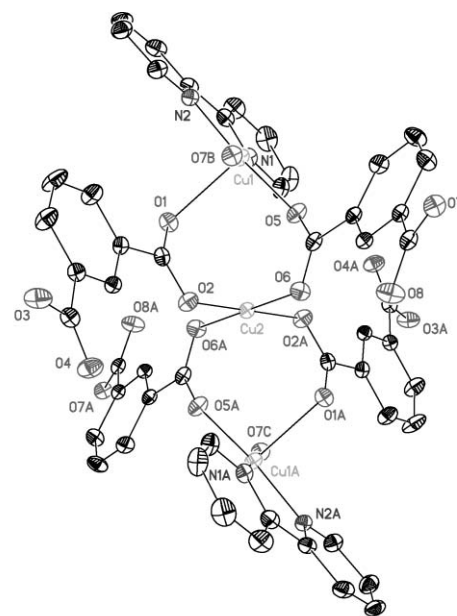
### Structures of [Cu<sub>3</sub>(ip)<sub>2</sub>(Hip)<sub>2</sub>(2,2'-bpy)<sub>2</sub>]<sub>n</sub> (**1**) and [Cu<sub>6</sub>(ipO)<sub>4</sub>(2,2'-bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·6H<sub>2</sub>O (**2**)

Compound **1** exhibits a one-dimensional double-chain structure in which the asymmetric unit contains one and a half Cu(II) ions, one ip, one Hip and one 2,2'-bpy ligand. Fig. 1a shows a fragment of the chain in the structure of **1**. Each Cu(1) atom in **1** is coordinated by three oxygen atoms from two ip ligands and one Hip ligand in mono-bidentate and bidentate coordination modes (Cu1–O1 2.386(3) Å, Cu1–O5 1.953(3) Å, Cu1–O7A 1.958(3) Å) and two nitrogen atoms from a chelate 2,2'-bpy ligand (Cu1–N1 2.006(4) Å, Cu1–N2 1.993(4) Å) to furnish a distorted square pyramidal geometry. However, each Cu2 atom is four-coordinated with

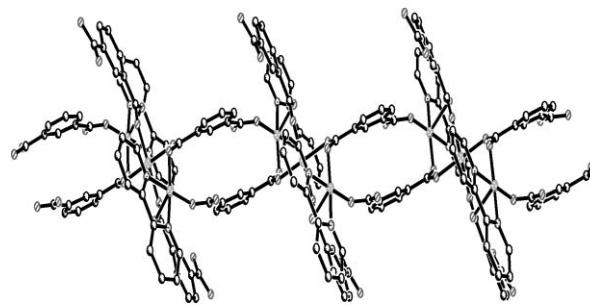
**Table 1** Crystallographic data and structural refinement summary for **1** and **2**

	<b>1</b>	
Chem. formula	C <sub>52</sub> H <sub>34</sub> Cu <sub>3</sub> N <sub>4</sub> O <sub>16</sub>	C <sub>52</sub> H <sub>44</sub> Cu <sub>6</sub> N <sub>4</sub> O <sub>28</sub>
Formula wt	1161.45	1554.15
Cryst syst.	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	10.317(2)	8.469(2)
<i>b</i> /Å	10.801(2)	12.639(2)
<i>c</i> /Å	11.578(2)	13.067(1)
$\alpha$ /°	83.15(1)	95.44(9)
$\beta$ /°	84.60(1)	108.13(1)
$\gamma$ /°	66.18(1)	91.52(1)
<i>V</i> /Å <sup>3</sup>	1170.5(3)	1321.0(1)
<i>T</i> /K	293	293
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.648	1.954
<i>Z</i>	1	1
$\mu$ (Mo-K)/mm <sup>-1</sup>	1.432	2.475
No. unique data ( <i>R</i> <sub>int</sub> )	4495 (0.0177)	5196 (0.0324)
No. total reffs	6358	6307
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>b</sup>	0.0323/0.0824	0.0391/0.1049

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



(a)



(b)

**Fig. 1** A trinuclear [Cu<sub>3</sub>(ip)<sub>2</sub>(Hip)<sub>2</sub>(bpy)<sub>2</sub>] subunit with thermal ellipsoids at 30% probability. Symmetry transformations used to generate equivalent atoms: A:  $-x + 1, -y, -z + 1$  B:  $-x + 1, -y, -z$  C:  $x, y, z + 1$  (a) and a double chain fragment (b) in **1**.

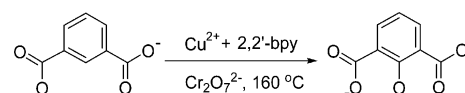
four oxygen atoms (Cu1–O2 1.912(3), Cu1–O2A 1.912(3), Cu1–O6 2.011(2), Cu1–O6A 2.011(2) Å), forming a slightly distorted square geometry. The carboxylate oxygen atoms *via* the *syn-anti* O,O'-bridges bridge three copper atoms (Cu1, Cu2 and Cu1A) to form a trinuclear [Cu<sub>3</sub>(ip)<sub>2</sub>(Hip)<sub>2</sub>(bpy)<sub>2</sub>] subunit (Fig. 1a), which are interconnected through the bridging ip groups to form an infinite one-dimensional double chain with the Cu...Cu distance of 3.802(3) and 9.888(3) Å (Fig. 1b). The lateral 2,2'-bpy ligands from adjacent double-chains are paired to furnish moderately strong  $\pi$ - $\pi$  stacking interactions (face-face distance *ca.* 3.45 Å),<sup>7</sup> which extend the double-chains into two-dimensional wavelike layers parallel to the *ab* plane in the lattice. These layers are further linked *via* strong hydrogen bonds between uncoordinated carboxylate oxygen atoms of ip ligands (O3...O8 ( $-x + 2, -y, -z$ ) 2.528(1) Å), forming a three-dimensional supramolecular network. The hydrogen bonding and  $\pi$ - $\pi$  stacking interactions enhance the stability of the complex.

**2** exhibits a discrete hexanuclear Cu(II) complex (Fig. 2a). There are three crystallographically independent Cu(II) centers in the asymmetric unit. Cu(1) and Cu(2) are four-coordinated and primarily coordinated by four oxygen atoms in a distorted square geometry, of which two belong to phenoxo groups (Cu(1)–O(3) 1.923(3) Å; Cu(1)–O(8) 1.930(3) Å; Cu(2)–O(3) 1.924(3) Å; Cu(2)–O(8) 1.943(3) Å;) and the other two to carboxylate groups of the ipO ligands (Cu(1)–O(4) 1.879(4) Å; Cu(1)–O(6) 1.888(4) Å; Cu(2)–O(1) 1.922(4) Å; Cu(2)–O(9) 1.892(3) Å). The metal atom (Cu1) is deviated from the plane (0.09 Å), and the metal atom (Cu2) is deviated from the plane (0.14 Å). Cu(1), Cu(2) and two ipO ligands form a  $[\text{Cu}_2(\text{ipO})_2]^{2-}$  subunit. Unlike Cu(1) and Cu(2), each Cu(3) atom is five-coordinated and is coordinated by two nitrogen atoms from 2,2'-bpy (Cu(3)–N(1) 2.002(3) Å; Cu(3)–N(2) 2.023(3) Å), two oxygen atoms from two different ipO ligands (Cu(3)–O(2) 1.949(3) Å; Cu(3)–O(7) 2.243(3) Å) and an aqua ligand (Cu(3)–O1W 1.956(3) Å), therefore Cu(3) has a square-pyramidal coordination geometry.

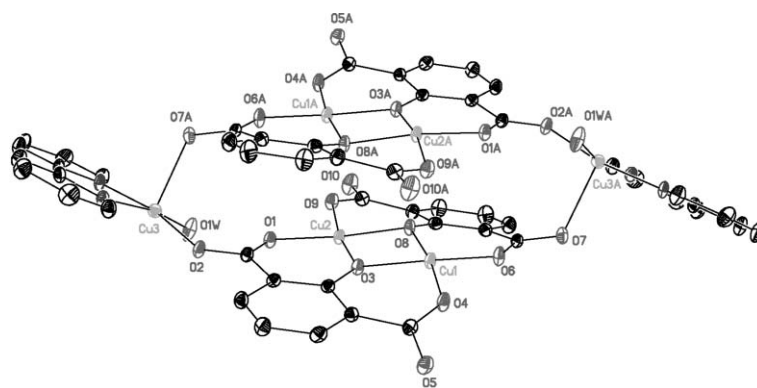
The most striking feature of **2** is the connection of two  $[\text{Cu}_2(\text{ipO})_2]^{2-}$  subunits and two  $[\text{Cu}(2,2'\text{-bpy})(\text{H}_2\text{O})]^{2+}$  to form a discrete hexanuclear Cu(II) complex. Adjacent discrete hexanuclear Cu(II) units are interconnected by the weak Cu–carboxylate interactions to form a one-dimensional chain. These chains are further extended into a two-dimensional layer through intercalation

between the lateral 2,2'-bpy ligands from adjacent chains in a zipper-like, offset fashion with an interplanar distance of *ca.* 3.35 Å (Fig. 2b), indicating strong aromatic stacking interactions.<sup>8</sup> Furthermore, the adjacent layers are connected together through hydrogen bonding interactions among the lattice water molecules, ipO oxygen atoms and the aqua ligands. The typical hydrogen bonds are O1W...O3W (*x*, *y*–1, *z*) 2.602(2) Å, O1W...O1 2.772(2) Å, O1W...O4W (*x*, *y*–1, *z*) 2.948(2) Å, O2W...O6 2.900 Å, O2W...O4W (–*x*, –*y*+1, –*z*+1) 2.836(4) Å, O4W...O5(–*x*, –*y*+1, –*z*+1) 2.837(3) Å, O3W...O10 (–*x*+1, –*y*, –*z*+1) 2.719(2) Å and O3W...O2W 2.928(2) Å.<sup>9</sup>

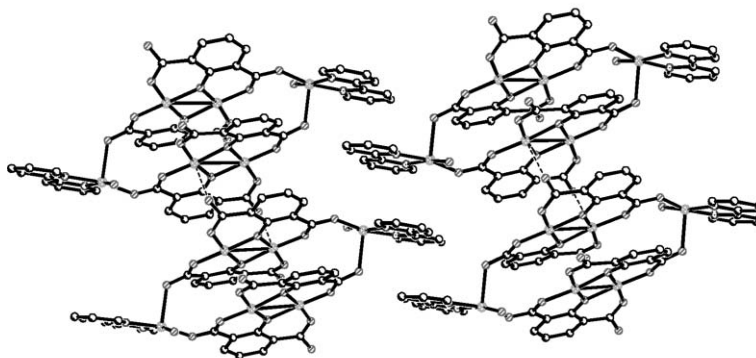
It is interesting to found that the *in situ* hydroxylation of isophthalate into 2-hydroxyisophthalate was observed (Scheme 1). To date, there are two examples of the *in situ* ligand synthesis of ipOH under hydrothermal conditions. One is the *in situ* hydroxylation of isophthalate similar to **2**,  $[\text{Cu}_2(\text{ipO})(4,4'\text{-bpy})]_n$ ,<sup>5a</sup> which was synthesized by isophthalate, 4,4'-bpy and copper nitrates. The other example,  $[\text{Cu}_3(\text{ipO})_2(4,4'\text{-bpy})_{0.5}(\text{H}_2\text{O})_2]_n$ ,<sup>5b</sup> was synthesized by the



Scheme 1



(a)



(b)

**Fig. 2** Perspective drawings of **2** showing the local coordination environment with thermal ellipsoids at 30% probability. Symmetry transformations used to generate equivalent atoms: A:  $-x + 1, -y, -z + 1$  (a) and the two-dimensional network (b) showing strong aromatic  $\pi$ – $\pi$  stacking interactions viewed along the *c*-axis in which the lattice water molecules and all hydrogen atoms are omitted for clarity.

reaction of 1,2,3-benzenetricarboxylic acid, 4,4'-bpy and copper nitrates at high pH values, in which the 2-carboxylate unit of 1,2,3-benzenetricarboxylic acid was replaced by a hydroxyl group.  $\text{Cu}^{2+}$  acts as an essential oxidant. In this paper, the hydrothermal reaction of  $\text{Cu}(\text{NO}_3)_2$ , isophthalate and 2,2'-bipyridine without or with  $\text{K}_2\text{Cr}_2\text{O}_7$  affords different complexes,  $[\text{Cu}_3(\text{ip})_2(\text{Hipa})_2(\text{bpy})_2]_n$  (**1**) and  $[\text{Cu}_6(\text{ipO})_4(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  (**2**), and their structures are controlled only by the addition of  $\text{K}_2\text{Cr}_2\text{O}_7$ . In **2**, the *in situ* hydroxylation of isophthalate occurs,  $\text{K}_2\text{Cr}_2\text{O}_7$  acts as the oxidant. With these results, it is much clearer that the reaction conditions and oxidant are critical for the formation of 2-hydroxyisophthalate.

The valence sum calculations<sup>10</sup> give the value of 2.17 for the Cu(1), 2.09 for Cu(2) and 1.787 for Cu(3) atom, indicating that all Cu centers in **2** are in the +2 oxidation state. The coordinated water O1W in **2** and uncoordinated O(3) atoms of the ip ligands in **1** have bond valence sums of 0.408 and 1.238, respectively. These values suggest that O1W is a coordinated water molecule while O(2) is a protonated oxygen atom of the carboxylate group.<sup>11</sup> These results are consistent with the charge balance considerations.

### IR spectra and XRPD patterns

The presence of a strong peak at  $1678\text{ cm}^{-1}$  in **1** reveals that protonated carboxylic groups exist. However, the absence of strong peaks around  $1700\text{ cm}^{-1}$  in **2** indicates that all carboxylic groups are deprotonated,<sup>12</sup> which is consistent with the results of the valence sum calculations. The simulated and experimental XRPD patterns of **1** and **2** are shown in Fig. S1.† Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.<sup>13</sup>

### Magnetic properties

The magnetic properties of complex **1** as  $\lambda_M T$  vs.  $T$  plot ( $\lambda_M$  is the molar magnetic susceptibility for three Cu(II) ions) is shown in Fig. 3. The value of  $\lambda_M T$  at 300 K is close to  $1.40\text{ cm}^3\text{ mol}^{-1}\text{ K}$  which is as expected for three magnetically quasi-isolated spin doublets ( $g > 2.00$ ). Starting from room temperature  $\lambda_M T$  values increase to  $1.95\text{ cm}^3\text{ mol}^{-1}\text{ K}$  at 3 K, decreasing slightly to 2 K. This feature

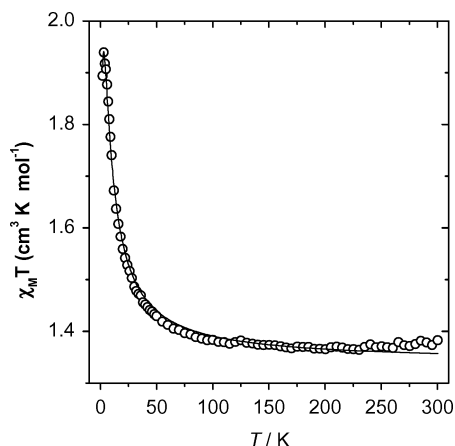


Fig. 3 Plots of  $\lambda_M T$  versus  $T$  for the polycrystalline samples of **1** (o) with solid lines showing the theoretical fit to the experimental data.

is characteristic of noticeable intramolecular ferromagnetic interactions with weak intermolecular antiferromagnetic interactions at very low temperature.

Complex **1** is, actually, a double chain, but from a magnetic viewpoint it can be considered as trinuclear copper(II) entities, linked by the long carboxylates bridging ligands. The fit of the susceptibility data has been carried out using the Hamiltonian,  $H = -J(S_1 S_2 + S_2 S_3)$ , applying the formula for a linear trinuclear Cu(II) system, given by Kahn in his book,<sup>14</sup> modulated with a  $J'$  value (intermolecular interactions) applying the molecular field approximation, indicated by the same author. The best-fit parameters obtained are  $J = 8.5 \pm 0.15\text{ cm}^{-1}$ ,  $J' = -0.16 \pm 0.01$ ,  $g = 2.18 \pm 0.01$  and  $R = 3.2 \times 10^{-4}$ .

The positive  $J$  value can be interpreted as a consequence of the coordination mode of the carboxylate within the trinuclear entity: *syn-anti* in short-short and short-long (short indicating equatorial and long apical in the external distorted square-pyramidal copper ions). The *syn-anti* coordination mode gives antiferromagnetic or ferromagnetic coupling, the planarity or torsion angle between the carboxylate groups is one of the most important factors.<sup>15</sup> In complex **1** the torsion angle Cu1–O5–O6–Cu2 is close to  $75^\circ$ , being undoubtedly the main factor of the ferromagnetic coupling. The small  $J$  value is due to the intermolecular interactions among the trinuclear entities, in which the magnetic pathway is the long carboxylate ligand (the shortest Cu–Cu distance is  $9.5\text{ \AA}$ ).

The thermal variation of  $\chi_M T$  of **2** is displayed in Fig. 4. The  $\chi_M T$  vs.  $T$  plot has a value of  $2.35\text{ cm}^3\text{ mol}^{-1}\text{ K}$  at 300 K, and decreases continuously on cooling to a value of  $1.81\text{ cm}^3\text{ mol}^{-1}\text{ K}$  at 150 K. Then increases continuously to a maximum of  $2.73\text{ cm}^3\text{ mol}^{-1}\text{ K}$  at ca. 5 K before decreasing again. This magnetic behavior, similar to that of  $[\text{Cu}_2(\text{ipO})(4,4'\text{-bpy})_n]_n$ ,<sup>5a</sup> is very interesting. The results reveal that there exists a weak antiferromagnetic interaction at higher temperature (150–300 K) and a strong ferromagnetic interaction at lower temperature (2–150 K).

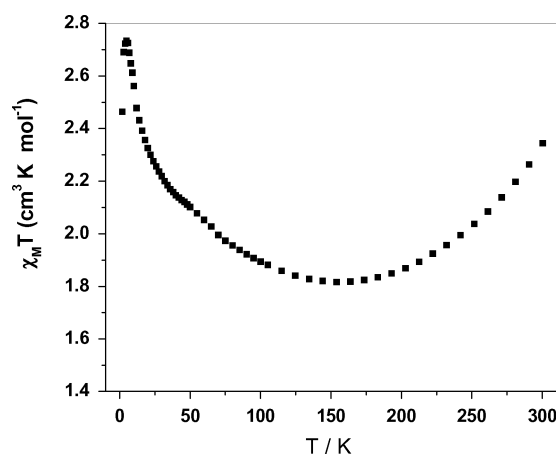


Fig. 4 Plot of  $\lambda_M T$  versus  $T$  for the polycrystalline samples of **2**.

### Conclusions

In this paper, the successful synthesis of complexes of **1** and **2** not only proves the capability of hydrothermal reactions in preparing



novel complexes but also further confirms that the strong oxidant  $K_2Cr_2O_7$  may result in the occurrence of *in situ* ligand oxidative reaction of the dicarbonylates. The magnetic properties of **1** reveal that there exist intramolecular ferromagnetic interactions with weak intermolecular antiferromagnetic interactions at very low temperature. The magnetic properties of **2** show weak antiferromagnetic interactions admixture with strong ferromagnetic interactions.

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