

## Syntheses of Two New 1D and 3D Networks of Cu(II) and Co(II) Using Malonate and Urotropine as Bridging Ligands: Crystal Structures and Magnetic Studies

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Received September 11, 2002

Two new metal–organic based polymeric complexes,  $[\text{Cu}_4(\text{O}_2\text{CCH}_2\text{CO}_2)_4(\text{L})]\cdot 7\text{H}_2\text{O}$  (**1**) and  $[\text{Co}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2(\text{L})\cdot 2\text{H}_2\text{O}$  (**2**) [L = hexamethylenetetramine (urotropine)], have been synthesized and characterized by X-ray crystal structure determination and magnetic studies. Complex **1** is a 1D coordination polymer comprising a carboxylate bridged  $\text{Cu}_4$  moiety linked by a tetradentate bridging urotropine. Complex **2** is a 3D coordination polymer made of pseudo-two-dimensional layers of Co(II) ions linked by malonate anions in *syn-anti* conformation which are bridged by bidentate urotropine in *trans* fashion. Complex **1** crystallizes in the orthorhombic system, space group *Pmmn*, with  $a = 14.80(2)$  Å,  $b = 14.54(2)$  Å,  $c = 7.325(10)$  Å,  $\beta = 90^\circ$ , and  $Z = 4$ . Complex **2** crystallizes in the orthorhombic system, space group *Imm2*,  $a = 7.584(11)$  Å,  $b = 15.80(2)$  Å,  $c = 6.939(13)$  Å,  $\beta = 90.10^\circ(1)$ , and  $Z = 4$ . Variable temperature (300–2 K) magnetic behavior reveals the existence of ferro- and antiferromagnetic interactions in **1** and only antiferromagnetic interactions in **2**. The best fitted parameters for complex **1** are  $J = 13.5$  cm<sup>-1</sup>,  $J' = -18.1$  cm<sup>-1</sup>, and  $g = 2.14$  considering only intra- $\text{Cu}_4$  interactions through carboxylate and urotropine pathways. In case of complex **2**, the fit of the magnetic data considering intralayer interaction through carboxylate pathway as well as interlayer interaction via urotropine pathway gave no satisfactory result at this moment using any model known due to considerable orbital contribution of Co(II) ions to the magnetic moment and its complicated structure. Assuming isolated Co(II) ions (without any coupling,  $J = 0$ ) the shape of the  $\chi_{\text{M}}T$  curve fits well with experimental data except at very low temperatures.

### Introduction

There has been an increasing interest in metal–organic hybrid materials containing paramagnetic metal ions exhibiting extended open structures due to their wide application in separation technology as well as in the field of molecular magnetism.<sup>1–4</sup> The most commonly used strategy to obtain these extended structures is to employ appropriate bridging ligands that are capable of binding to several metal centers through direct bond formation. Much of the current effort on such extended hybrid metal–organic complexes is

directed toward synthesizing interesting frameworks using polycarboxylates<sup>5–7</sup> due to greater thermal stability. These

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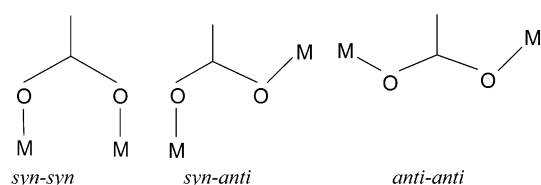
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Scheme 1



polycarboxylates may exhibit versatile coupling to mediate magnetic interactions owing to their different coordination modes, i.e., *syn-syn*,<sup>7g,h</sup> *syn-anti*,<sup>7j</sup> *anti-anti*,<sup>7g</sup> etc. (Scheme 1), accomplishing the transmission of magnetic coupling to different degrees.<sup>7</sup>

Recently, several groups as well as our group have reported the syntheses, X-ray crystal structure analyses, and SQUID measurements of multidimensional complexes of transition metals using dicarboxylate and nitrogen donor bridging ligands.<sup>8,9</sup> In this present contribution, we have extended our work using a flexible dicarboxylate, the malonate, and a nitrogen donor bridging ligand, the urotropine.

In this paper, we report the synthesis, single crystal X-ray diffraction analysis, and variable temperature (300–2 K) magnetic behavior of two 1D and 3D polymeric networks of Cu(II) and Co(II), respectively, using malonate and urotropine as bridging ligands. The first complex, having empirical formula  $[\text{Cu}_4(\text{O}_2\text{CCH}_2\text{CO}_2)_4(\text{L})] \cdot 7\text{H}_2\text{O}$  (**1**) [ $\text{L}$  = hexamethylenetetramine (urotropine)], is an one-dimensional coordination polymer formed by  $\text{Cu}_4$  entities linked by the urotropine bridging ligand. The latter one,  $[\text{Co}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2(\text{L})] \cdot 2\text{H}_2\text{O}$  (**2**), is formed by Co(II) ions linked by malonate ligands in *syn-anti* conformation forming a pseudo-2D layer which is bridged by another similar layer via urotropine resulting in a 3D network which is completely different from its Cu(II) analogue.

Temperature dependent magnetic studies down to 2 K reveal the existence of antiferromagnetic and ferromagnetic interactions in **1** and weak antiferromagnetic interactions in **2**. Susceptibility data of **1** were fitted considering only

intratetramer interactions (within the  $\text{Cu}_4$  entities) via carboxylate and urotropine pathways. In the case of complex **2**, owing to its complicated structure with both intra- and interlayer interactions, and the spin-orbit coupling of Co(II) ion, full modeling of the magnetic data was not attempted. Comparison with the magnetism assuming hypothetical isolated Co(II) ions indicates that the possible coupling is very weak and antiferromagnetic.

## Experimental Section

**Materials.** High purity hexamethylenetetramine (urotropine) was purchased from E. Marck (India) Ltd. Chemical Company and used as received. All the other chemicals were of A.R. grade.

**Physical Measurements.** Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer elemental analyzer. IR spectra (4000–600  $\text{cm}^{-1}$ ) were taken in KBr pellets using a Jasco FT-IR (model 300E) instrument. The magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS SQUID magnetometer (applied field 1000 Oe) working in the temperature range 300–2 K. Diamagnetic corrections were estimated from Pascal's tables.<sup>10</sup>

**Synthesis of  $[\text{Cu}_4(\text{O}_2\text{CCH}_2\text{CO}_2)_4(\text{L})] \cdot 7\text{H}_2\text{O}$  (**1**).** An aqueous solution (5 mL) of urotropine (1 mmol) was added dropwise to an aqueous solution (5 mL) of copper(II) perchlorate hexahydrate (1 mmol) with constant stirring for 5 min until the solution turned to curdy light blue. To this resulting mixture was added an aqueous solution (5 mL) of disodium malonate (1 mmol) dropwise yielding a blue transparent solution which was filtered, and the filtrate was kept in a  $\text{CaCl}_2$  desiccator. After a few days, deep blue crystals suitable for X-ray analysis were obtained. Yield: 70%. Anal. Found (%): C, 23.17; H, 3.30; N, 5.86. Calcd for  $\text{C}_{18}\text{H}_{34}\text{N}_4\text{Cu}_4\text{O}_{23}$  (%): C, 23.27; H, 3.66; N, 6.03. The infrared spectra exhibited the following absorptions: 3480–3025(s, v br), 1639(vs), 1547(vs), 1458(m), 1364(m), 1025(m), 991(m), 746(w) 704(w), 565(vw)  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{Co}_2(\text{O}_2\text{CCH}_2\text{CO}_2)_2(\text{L})] \cdot 2\text{H}_2\text{O}$  (**2**).** To a methanolic solution (5 mL) of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) was added an aqueous solution (5 mL) of urotropine dropwise with constant stirring. To this solution was added an aqueous solution (5 mL) of disodium malonate (1 mmol) yielding a deep pink compound. The single crystals suitable for X-ray analysis were obtained by diffusing the methanolic solution (10 mL) of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  on an aqueous layer of disodium malonate and urotropine (1:1 mixture) (10 mL) in a tube. The deep pink crystals were found at the junction of the two solutions after three weeks. Yield: 60%. Anal. Found (%): C, 28.65; H, 3.87; N, 11.11. Calcd for  $\text{C}_6\text{H}_{10}\text{CoN}_2\text{O}_5$  (%): C, 28.92; H, 4.01; N, 11.24. The infrared spectra exhibited the following absorptions: 3436–3190(s, v br), 2992(vw), 1571(vs), 1383(vs), 1247(w), 1031(w), 995(m), 710(w), 579(vw)  $\text{cm}^{-1}$ .

**Crystallographic Data Collection and Refinement.** Suitable single crystals of complexes **1** and **2** were positioned 70 mm from the image plate. A total of 100 frames were measured at  $2^\circ$  intervals with a counting time of 2 min. For **1** and **2**, 4728, 1278 reflections were collected with Mo  $\text{K}\alpha$  radiation using the MAR research image plate system. Data analysis was carried out with the XDS program<sup>11</sup> to provide 1625, 705 independent reflection ( $R_{\text{int}} = 0.087, 0.029$ ). The structures were solved using direct methods via the SHELX-86 program.<sup>12</sup> In **1**, the non-hydrogen atoms were refined

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**Table 1.** Crystal Data and Structure Refinement for Complexes **1** and **2**

	<b>1</b>	<b>2</b>
formula	C <sub>18</sub> H <sub>34</sub> N <sub>4</sub> O <sub>23</sub> Cu <sub>4</sub>	C <sub>6</sub> H <sub>10</sub> CoN <sub>2</sub> O <sub>5</sub>
fw	928.58	249.07
temp (K)	293	293
space group	<i>Pmmm</i> (No. 59)	<i>Imm2</i> (No. 6)
wavelength (Å)	0.71073	0.71073
<i>a</i> /Å	14.80(2)	7.584(11)
<i>b</i> /Å	14.54(2)	15.80(2)
<i>c</i> /Å	7.325(10)	6.939(13)
cryst syst	orthorhombic	orthorhombic
$\beta$ /deg	90	90.10(1)
<i>V</i> (Å <sup>3</sup> )	1576(4)	831(2)
<i>Z</i>	4	4
<i>D</i> <sub>calcd</sub> gm/cm <sup>3</sup>	1.944	1.957
$\mu$ mm <sup>-1</sup>	2.768	2.061
<i>F</i> (000)	896	500
$\theta_{\min}$ – $\theta_{\max}$ /deg	2.8–26.0	2.6–25.9
<i>R</i> indices <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	R1 = 0.0852 wR2 = 0.2231	R1 = 0.0372 wR2 = 0.1077

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

**Table 2.** Dimensions in the Metal Coordination Spheres: Distances (Å) and Angles (deg) for Complex **1**<sup>a</sup>

Cu(1)–O(11)	1.965(8)	Cu(1)–O(200)	2.257(9)
Cu(1)–O(100)	2.003(9)	Cu(1)–N(151)	2.109(10)
Cu(1)–O(21)	1.970(8)	Cu(2)–O(13)	1.966(8)
Cu(2)–O(16)	1.946(6)	Cu(2)–O(26)	1.957(8)
Cu(2)–O(23)	1.942(8)	Cu(2)–N(155)	2.354(10)
O(11)–Cu(1)–O(21)\$1	169.9(4)	O(11)–Cu(1)–O(100)	85.2(2)
O(11)–Cu(1)–N(151)	94.5(3)	O(200)–Cu(1)–N(21)	172.5(4)
O(11)–Cu(1)–O(200)	92.0(2)	O(200)–Cu(1)–O(100)	93.3(3)
N(151)–Cu(1)–O(200)	94.4(4)		
O(16)–Cu(2)–O(26)	168.9(3)	O(13)–Cu(2)–O(23)	87.1(8)
O(16)–Cu(2)–O(13)	91.1(3)	O(23)–Cu(2)–O(26)	91.3(3)
O(26)–Cu(2)–N(155)	111.6(3)	O(13)–Cu(2)–N(155)	89.2(3)

$$^a \text{Symmetry elements: } \$1, 1.5 - x, y, z; \$2, x, 0.5 - y, z.$$

with anisotropic thermal parameters. However the crystal of **2** was twinned (*hkl, hk-l*) with a refined factor of 0.51(1). The metal atom was refined anisotropically, and the remaining atoms, isotropically. In both structures, the hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms bonded to the water oxygen atoms could not be located. Empirical absorption corrections were carried out using the DIFABS program.<sup>13</sup> The structures were refined on *F*<sup>2</sup> using SHELXL.<sup>14</sup> All crystallographic data are summarized in Table 1. The crystals of **1** provided poor data due to misshapen spots in the diffraction pattern resulting high R1 value. Selected bond lengths and bond angles are given in Tables 2 and 3 for complexes **1** and **2**, respectively.

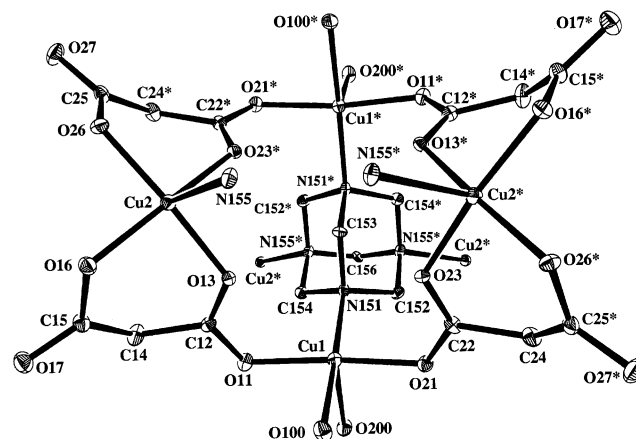
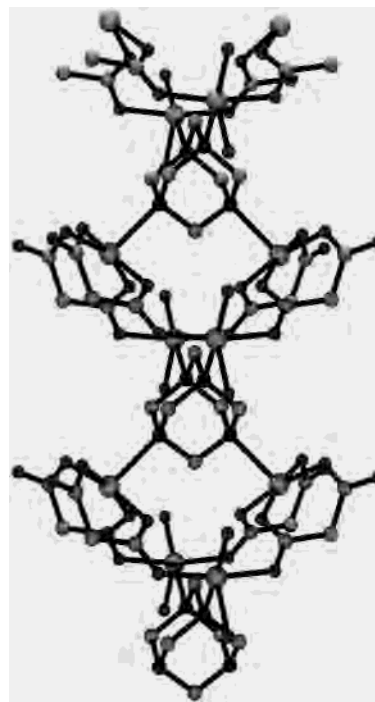
## Results and Discussion

**Structure Description of Complex 1.** Complex **1** is a one-dimensional polymer made by Cu<sub>4</sub> entities linked by urotropine bridges. The coordination mode of the malonate and urotropine with the atom numbering scheme is shown in Figure 1. There are two independent copper atoms, Cu(1) and Cu(2), in the asymmetric unit, both occupying a site with *m* symmetry. The view of a chain is shown in Figure

**Table 3.** Dimensions in the Metal Coordination Spheres: Distances (Å) and Angles (deg) for Complex **2**<sup>a</sup>

Co(1)–O(11)	2.107(5)	Co(1)–O(12)\$1	2.073(5)
Co(1)–O(100)	2.150(8)	Co(1)–N(31)	2.218(7)
O(11)–Co(1)–O(12)\$1	86.3(3)	O(11)–Co(1)–O(11)\$2	101.5(3)
O(11)–Co(1)–O(100)	89.8(2)	O(11)–Co(1)–N(31)	84.8(3)
O(11)–Co(1)–O(12)\$3	172.2(2)	O(12)\$1–Co(1)–O(12)\$3	85.9(3)
O(12)\$1–Co(1)–O(100)	90.7(3)	O(12)\$1–Co(1)–N(31)	95.5(2)
O(100)–Co(1)–N(31)	171.5(2)		

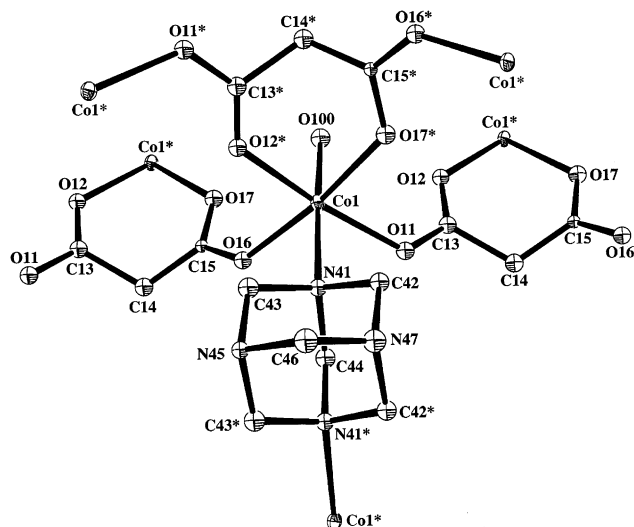
$$^a \text{Symmetry elements: } \$1, 0.5 - x, 0.5 - y, -0.5 + z; \$2, 1 - x, y, z; \$3, -0.5 + x, 0.5 - y, -0.5 + z.$$

**Figure 1.** Local coordination environment of Cu(II) in complex **1** with atom numbering scheme, atoms are drawn at the 30% thermal ellipsoids.**Figure 2.** View of the polymeric chain of complex **1** along the crystallographic *b* axis.

2, and from Figure 1, it is clear that each urotropine ligand is bonded through its four tetrahedrally orientated nitrogen atoms to four different copper atoms, two Cu(1), and two Cu(2). Both copper atoms are five-coordinated with square pyramidal geometry. Cu(1) is bonded in a monodentate fashion to two oxygen atoms [O(11) and O(21)] from two

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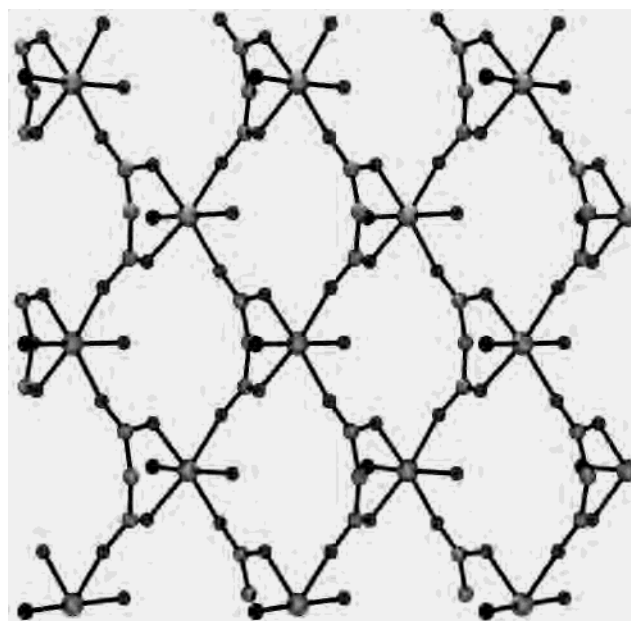
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**Figure 3.** Local coordination environment of Co(II) in complex **2** with atom numbering scheme, atoms are drawn at the 30% thermal ellipsoids.

different malonate dianions at 1.965(8) and 1.970(8) Å: one water molecule by the O(100) atom at 2.003(9) Å, one nitrogen atom, N(151), at 2.109(10) Å in the equatorial basal plane, and one further water molecule through the O(200) atom at 2.257(9) Å in the apical position. By contrast, Cu(2) is bonded to four oxygen atoms from two malonate groups, forming two chelating six-membered rings with distances Cu(2)–O(16) = 1.946(6) Å, Cu(2)–O(13) = 1.966(8) Å, Cu(2)–O(26) = 1.957(8) Å, and Cu(2)–O(23) = 1.942(8) Å, respectively, (basal plane) together with a nitrogen atom, N(155), in the axial position at 2.354(10) Å. It will be noted that this Cu(2)–N bond in an axial site is significantly longer than the Cu(1)–N bond to an equatorial site. As is apparent from Figure 1, each malonate ion is bonded to two metal atoms, bidentate to Cu(2), and monodentate to Cu(1). The oxygen atom, O(17), of the malonate anion, remains unbonded, but it forms hydrogen bonds to the two water molecules bonded to Cu(1), e.g., O(100) at 3.07 Å and O(200) at 2.69 Å. The urotropine ligand links the Cu(2) ions of one entity through N(155) (apical position) to the Cu(1) atoms of the adjacent entity via N(151) (basal position) giving the one-dimensional system (Figure 2).

**Structure Description of Complex 2.** Though the composition of metal to ligand is almost the same as in **1**, the structure of **2** is totally different from the Cu(II) analogue. It is a three-dimensional coordination polymer where the environment around each Co(II) is octahedral, as shown in Figure 3 with the atom numbering scheme. The cobalt atom is six-coordinated with a distorted octahedral environment surrounded by a nitrogen atom of the urotropine, N(41), [2.217(7) Å] a water molecule, O(100) [2.150(8) Å] in mutually *trans* positions together with four oxygen atoms from three different bridging malonates as shown in the Figure 3. One malonate ion acts as a bidentate ligand via a six-membered chelating ring with distances of 2.091(14) Å for O(12) and 2.064(14) Å for O(17) and two other bonds in a monodentate fashion at 2.097(15) Å for O(16) and 2.124(17) Å for O(11). Thus, each malonate binds to three different

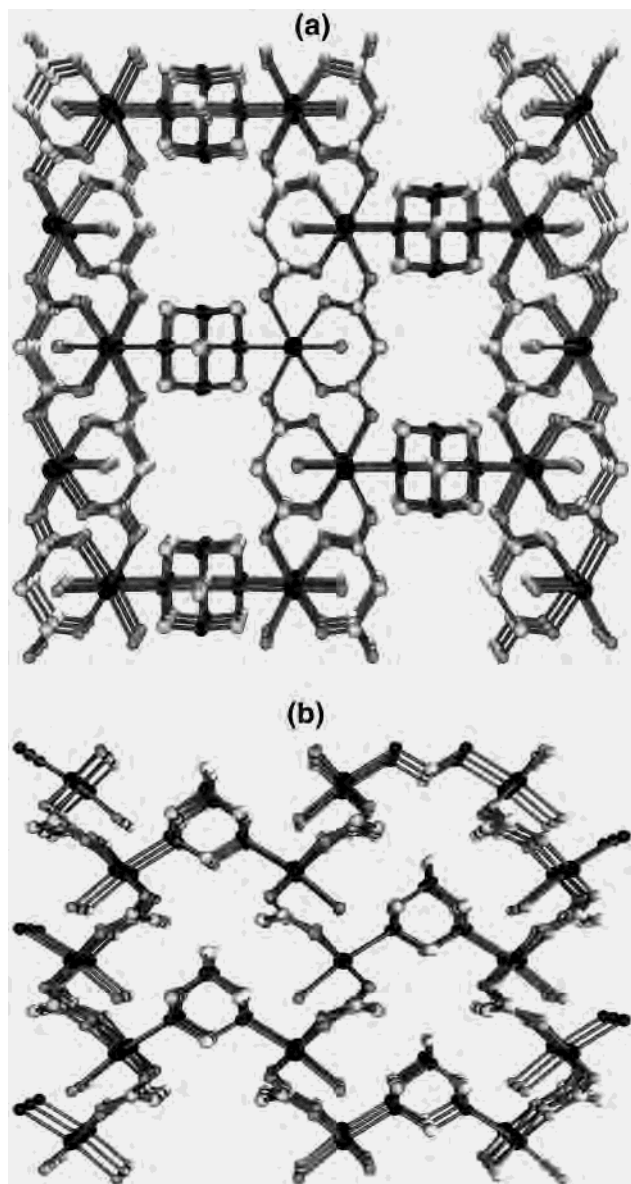


**Figure 4.** View of the Co(carboxylate) plane in complex **2** down the crystallographic axis *b*. For urotropine, only the coordinated nitrogens are indicated.

cobalt atoms. By contrast with the structure of **1**, the urotropine ligand is only bonded to two metal atoms by the N(41) atoms, and the remaining two nitrogen atoms (N(45) and N(47)) remain unbonded. Coordination through malonate in a *syn-anti* conformation produces a pseudo-two-dimensional layer (Figure 4) which is again linked by a urotropine to a neighboring layer in *trans* fashion to produce a 3D coordination polymeric network, the view of which is shown in Figure 5a,b.

**Magnetic Properties. Complex 1.** The magnetic properties of complex **1** in the form of  $\chi_M T$  and  $\chi_M$  (insert) versus *T* plots ( $\chi_M$  is the molar magnetic susceptibility for 4 Cu(II) ions, as indicated below for the model of fit) are shown in Figure 6a. The value of  $\chi_M T = 1.731 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 300 K for four magnetically quasi-isolated spin doublets [or  $0.43 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  per Cu(II) for  $g = 2.14$ ] is as expected. The  $\chi_M T$  values smoothly increase from room temperature to 20 K ( $1.945 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ) and, then, quickly decrease to  $0.96 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K. The global feature is characteristic of the coexistence of ferromagnetic (increasing  $\chi_M T$  zone) and antiferromagnetic (decreasing  $\chi_M T$  zone) interactions. The  $\chi_M$  curve [inset of Figure 6a] is less indicative: it starts at  $0.00577 \text{ cm}^3 \text{ mol}^{-1}$  at room temperature and increases in a uniform way to  $0.481 \text{ cm}^3 \text{ mol}^{-1}$  at 2 K. The reduced molar magnetization ( $M/N\beta$ ) per Cu<sub>4</sub> entity tends to 3.5 electrons [Figure 6b]. This value is less than that expected for four Cu(II) ions if not coupled ( $>4$ ). This feature agrees with the global antiferromagnetic coupling within the four copper(II) ions.

As shown in the crystallographic part, complex **1** is formed by Cu<sub>4</sub> entities linked by the urotropine bridges giving the one-dimensional system. Thus, two kinds of coupling parameters must be considered to interpret the magnetic properties of complex **1**: intratetramer interactions (inside

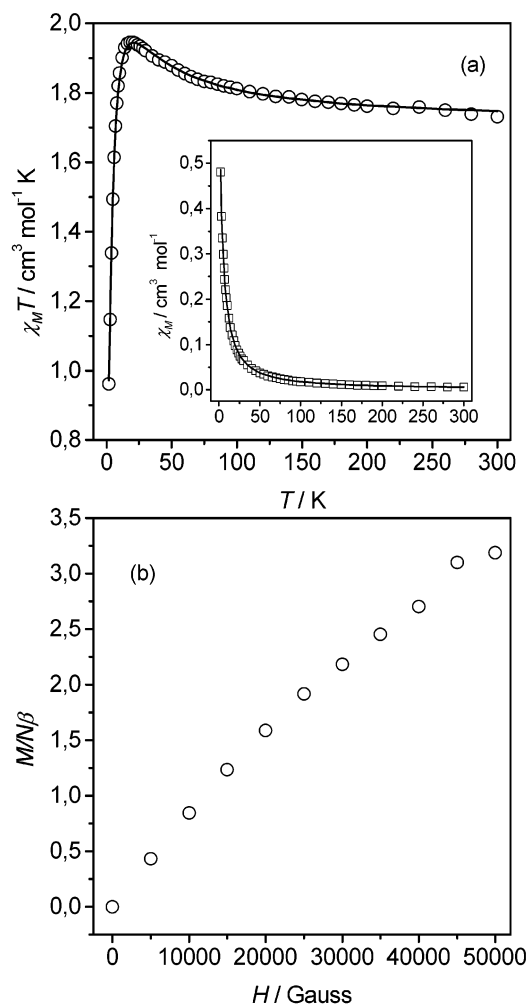


**Figure 5.** (a) View of the molecular packing diagram of complex **2** down the crystallographic axis *a*. (b) View of the molecular packing diagram of complex **2** down the crystallographic axis *c*.

each Cu<sub>4</sub> moiety) and intertetramer interactions among these Cu<sub>4</sub> entities via urotropine.

**(1) Intratetramer Interactions.** There are two such interactions (Scheme 1).

**(1a) Syn–Anti Carboxylate Interactions.** According to the structure of **1**, the copper(II) atoms are linked by carboxylate groups in a *syn–anti* conformation: Cu(1)–O(11)–C(12)–O(13)–Cu(2) and Cu(1)–O(21)–C(22)–O(23)–Cu(2). This pathway is schematized in Scheme 2 as *J* coupling. Cu(1) and Cu(2) are almost in perfectly square pyramidal geometry with the four short distances close to 2 Å (1.942–2.105 Å). For copper(II) complexes, the *syn–syn* conformation mediates large antiferromagnetic interactions (singlet–triplet energy gap  $\approx -300$  cm<sup>-1</sup>).<sup>9d,7g–i</sup> Weak antiferro- or ferromagnetic interactions are observed in these carboxylato bridged copper(II) complexes in which the carboxylate adopts the *syn–anti* conformation.<sup>15–25</sup> The small

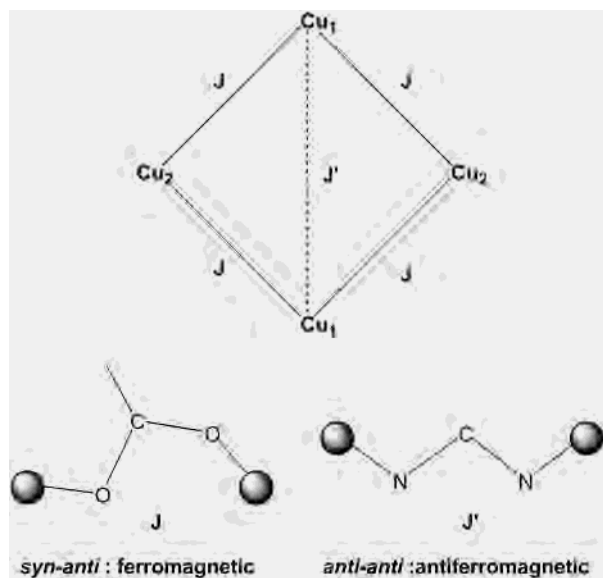


**Figure 6.** (a) Plots of the temperature dependence (from 300 to 2 K) of  $\chi_M$  (inset) and  $\chi_M T$  in **1**. Solid lines ( $\chi_M$  and  $\chi_M T$ ) represents the best theoretical fit (see text for models and parameters). (b) Magnetization curve of complex **1** at 2 K.

overlap between the magnetic orbitals of the copper atom through the *anti–syn* carboxylate bridge, for a Cu–O–C–O–Cu skeleton that is planar, accounts for the weak coupling

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Scheme 2



observed. This overlap is significantly reduced for cases in which the Cu–O–C–O–Cu skeleton deviates from the planarity (out-of-phase exchange pathway), thus reducing the antiferromagnetic contribution, and the ferromagnetic term becomes dominant.<sup>7j,24,25</sup> The magnetic orbital at each copper atom is defined by the short equatorial bonds, and it is of the  $d_{x^2-y^2}$  type with possibly some mixture of the  $d_z^2$  character in the axial position. In the case of **1**, the conformation is not planar enhancing, thus, the ferromagnetic coupling. Theoretical DFT calculations also corroborate this weak ferromagnetic coupling for *syn-anti* conformation.<sup>9a</sup> In the *anti-anti* carboxylate bridge, the coupling is always small antiferromagnetic.<sup>9a</sup>

**(1b) Anti–Anti N–C–N Interaction.** The two Cu(1) ions are linked by the urotropine bridge, but from magnetic point of view, only pathway Cu(1)–N(151)–C(153)–N(151)–Cu(1) is operative (Figure 1, Scheme 1, coupling parameter =  $J'$ ). Though this bridge is similar to an *anti-anti* carboxylate complex from a structural point, substituting the oxygen atoms from the carboxylate by nitrogen atoms, electronically they are not identical due to delocalized nature of carboxylate. As already indicated, in the *anti-anti* carboxylate bridge the coupling is always weak antiferromagnetic.<sup>9a</sup> We can expect a weak antiferromagnetic coupling through this N–C–N bridge, similar to that created by an *anti-anti* carboxylate group. The lower electronegativity of the nitrogen atom in comparison to the oxygen could give strong antiferromagnetic coupling. The unpaired electrons in these Cu(II) ions are mainly in the magnetic orbital  $d_{x^2-y^2}$ ; thus, the participation in the  $d_z^2$  will be minimal.

**(2) Intertetramer Interactions.** There are four equivalent interactions ( $J_{\text{inter}}$ ): two Cu(2)–N(155)–C(154)–N(151)–Cu(1) and two Cu(2)–N(155)–C(152)–N(151)–Cu(1). As indicated in the structural description, Cu(2)–N(155) = 2.354(10) Å, and Cu(1)–N(151) = 2.109(10) Å; the unpaired electron is mainly in the  $d_{x^2-y^2}$  orbitals, directed through Cu(1)–N(151) but not through Cu(2)–N(155), which is the apical position for Cu(2). This apical–equatorial bond gives

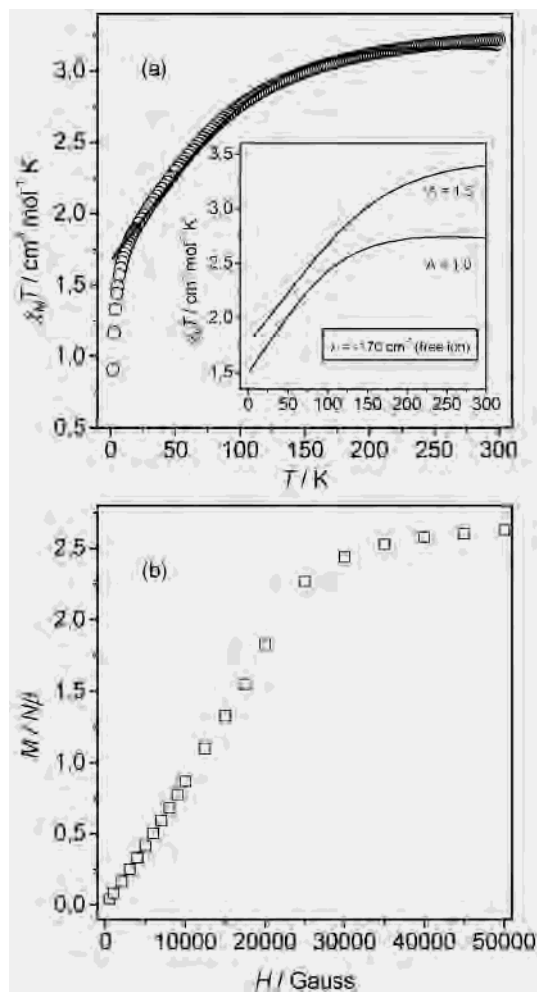
orthogonality of the magnetic orbitals; thus, the coupling must be zero or weak ferromagnetic. The bridge is triatomic, N(155)–C(154)(or C(152))–N(151), which reduces the possibility of ferromagnetic coupling, even if the magnetic orbitals are orthogonal. Thus, we can conclude that this coupling must be negligible.

With these considerations, several attempts to fit the  $\chi_{\text{M}}T$  data with  $J$ ,  $J'$ ,  $J_{\text{inter}}$ ,  $g$ , and TIP by using the irreducible tensor operator (ITO) formalism through the CLUMAG program,<sup>26</sup> with the Hamiltonian  $H = -J\sum_i S_i S_j$ , were made. According to the theoretical considerations already given, in all cases,  $J_{\text{inter}}$  was close to 0  $\text{cm}^{-1}$ . Thus, in order not to overparametrize the calculation, a simply Cu<sub>4</sub> entity was taken introducing  $J$  (*syn-anti* carboxylate),  $J'$  (*anti-anti* pseudo-carboxylate),  $g$ , and TIP parameters, using the same CLUMAG program.<sup>26</sup> The best-fit parameters are  $J = 13.5 \text{ cm}^{-1}$ ,  $J' = -18.1 \text{ cm}^{-1}$ ,  $g = 2.14$ , TIP =  $1.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$  (very typical for four Cu(II) ions), and  $R = 2.04 \times 10^{-5}$  ( $R$  is the agreement factor defined as  $\sum_i [(\chi_{\text{M}}T)_{\text{obs}} - (\chi_{\text{M}}T)_{\text{calc}}]^2 / \sum_i [(\chi_{\text{M}}T)_{\text{obs}}]^2$ ). This  $J$  value indicates that the coupling between the Cu(II) centers through the *syn-anti* carboxylate bridge is weakly ferromagnetic and of the same order as those found in the literature for similar planar *syn-anti* carboxylate systems.<sup>20</sup> The  $J'$  value is weakly antiferromagnetic, as deduced from the structure (similar to *anti-anti* carboxylate systems).<sup>9a</sup>

**Complex 2.** The magnetic properties of complex **2** in the form of the  $\chi_{\text{M}}T$  versus  $T$  plot ( $\chi_{\text{M}}$  is the molar magnetic susceptibility for the Co(II) ion) are shown in Figure 7a. The value of  $\chi_{\text{M}}T$  at 300 K is  $3.222 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  which is larger than that expected for the spin-only case ( $\chi_{\text{M}}T = 1.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $S = 3/2$ ), which indicates that an important orbital contribution is involved. The  $\chi_{\text{M}}T$  values continuously decrease from room temperature to  $0.91 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 1.96 K. The global feature is characteristic of weak antiferromagnetic interactions. The  $\chi_{\text{M}}$  curve is less indicative: it starts at  $0.011 \text{ cm}^3 \text{ mol}^{-1}$  at room temperature and increases in a uniform way to  $0.463 \text{ cm}^3 \text{ mol}^{-1}$  at 2 K. The absence of a maximum in this  $\chi_{\text{M}}$  curve may indicate that the possible antiferromagnetic coupling is very weak. The reduced molar magnetization ( $M/N\beta$ ) per Co(II) attends to 2.6 electrons (Figure 7b). This value is less than that expected for an isolated Co(II) ion if not coupled ( $3N\beta$ ). This feature agrees to the weak antiferromagnetic coupling within the Co(II) ions. The shape of the curve at low fields (sigmoid shape) is also indicative that this antiferromagnetic coupling occurs.

As shown in the crystallographic part, complex **2** is made by Co(II) ions linked by the carboxylate ligands in a *syn-anti* conformation giving a pseudolayer, and this layer is linked in a three-dimensional mode by urotropine. This situation is completely different than that of Cu(II) analogue **1**. Three kinds of coupling parameters must be considered to interpret the magnetic properties of complex **2**: inside each Co–carboxylate layer (two interactions through the carboxylate pathways) and the interlayer interaction through the urotropine.

(26) CLUMAG program: Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.



**Figure 7.** (a) Plots of the temperature dependence (from 300 to 2 K) of  $\chi_M T$  (inset shows plots assuming two different interelectronic repulsion parameters  $A$ ) in **2**. Solid lines represent the best theoretical fit (see text for the parameters). (b) Magnetization curve of complex **2** at 2 K.

With these considerations about the three-dimensional structure and the addition of the spin-orbit coupling in the Co(II) ions, any attempts to fit the  $\chi_M T$  data will be unsuccessful. The degeneracy of the  $^4T_{1g}$  ground state of the octahedral Co(II) ion avoids any possible fit, except in the low temperature region.<sup>10</sup> The overall effect of low-symmetry crystal-field components and spin-orbit coupling produces up to six Kramers doublets and results in a doublet ground state.<sup>10</sup> Thus, only for simple systems, it is possible to obtain the fit at low temperatures with special computational programs. For example, very recently, Gatteschi et al. have reported a complete analysis of the  $J$  values for a cobalt(II)-radical systems.<sup>27</sup> Very exact  $J$  parameters have been reported for some tri- and tetranuclear Co(II) complexes by Andres et al., by means of magnetic data and, mainly, by inelastic neutron scattering.<sup>28</sup>

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Assuming that all the antiferromagnetic couplings are very weak (as carboxylate is in *syn-anti* or *anti-anti* conformation), an attempt has been made to fit the  $\chi_M T$  results with the magnetic formula for a mononuclear Co(II) complex, calculating the  $\lambda$  value (spin-orbit coupling parameter) and the  $A$  parameter, which gives a measure of the crystal field strength to the interelectronic repulsions, being equal to 1.5 for a weak crystal field and 1.0 for a strong field.<sup>29</sup> The formula used is

$$\chi_M T = \left\{ \left[ \frac{7(3-A)^2 x}{5} + \frac{12(A+2)^2}{25A} + \left( \frac{2(11-2A)^2 x}{45} + \frac{176(A+2)^2 x}{675A} \right) \exp(-5Ax/2) + \left( \frac{(A+5)^2 x}{9} + \frac{20(A+2)^2}{27A} \right) \exp(-4Ax) \right] \right\} \left\{ \frac{8x}{3} [3 + 2 \exp(-5Ax/2) + \exp(-4Ax)] \right\}$$

where  $x = \lambda/kT$ . The possible  $J$  parameters are assumed to be  $0 \text{ cm}^{-1}$ . With this hypothesis, the best fit is given in Figure 7a with  $\lambda = -136 \text{ cm}^{-1}$ , very close to the  $\lambda$  value reported for free-ion Co(II) complexes ( $\lambda = -170 \text{ cm}^{-1}$ )<sup>2</sup> and  $A = 1.32$ . Taking into account that  $\lambda = \kappa \lambda_{\text{free ion}}$ ,  $\kappa$  (reduction of the spin-orbit coupling due to the covalency) would be equal to 0.8. Obviously, the fit is not very good at very low temperatures, which indicates that the antiferromagnetic coupling exists but it is very weak. The theoretical  $\chi_M T$  values should tend to  $1.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K, but the experimental ones tend to be less than  $1.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K (Figure 7a).

## Conclusion

In the present paper, we have discussed the syntheses, crystal structures, and magnetic behavior in the temperature range 2–300 K of two metal-organic based 1D and 3D polymers of Cu(II) and Co(II), respectively. Using similar bridging ligands, Cu(II) produces a 1D chain (complex **1**) whereas the Co(II) analogue is a 3D coordination polymer (complex **2**). In complex **1**, urotropine behaves as a bidentate bridging ligand whereas in **2** this acts as a tetradentate bridging ligand. Variable temperature magnetic study shows the existence of dominant antiferromagnetic interaction in both the complexes. The magnetic data of **1** are fitted using both intratetramer ( $J = 13.5 \text{ cm}^{-1}$ ,  $J' = -18.1 \text{ cm}^{-1}$ ,  $g = 2.14$ ) as well as intertetramer ( $J_{\text{inter}} = 0$ ) interactions, and the values derived corroborate with the previous results. In the case of the data for **2**, using similar consideration no satisfactory fitting is obtained at this moment due to considerable orbital contribution to the magnetic moment. An attempt has been made to fit the  $\chi_M T$  results with the magnetic formula for a mononuclear Co(II) complex, using the  $\lambda$  value (spin-orbit coupling parameter) and the  $A$

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parameter, which gives a measure of the crystal field strength to the interelectronic repulsions.

**Acknowledgment.** Funding for the work described here provided by the CSIR (New Delhi) Grant Scheme (granted to N.R.C.) is gratefully acknowledged. M.G.B.D. thanks EPSRC and the University of Reading for funds for the image plate system. J.R. also acknowledges the financial support from the Spanish Government (Grant BQU2000/0791). Authors are also grateful to Dr. Golam Mostafa, Prof.

Ennio Zangrando, and Prof. L. K Thompson for scientific discussion.

**Supporting Information Available:** X-ray crystallographic data, in CIF format, and tables giving crystal data and details of the structure determination, bond lengths and angles, atomic and hydrogen coordinates, isotropic displacement parameters, and anisotropic parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC020549U