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# Synthesis, Structure, and Magnetic Properties of Cobalt(II) Coordination Polymers from a New Tripodal Carboxylate Ligand: Weak Ferromagnetism and Metamagnetism

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**ABSTRACT:** A new tripodal carboxylic ligand, 5-(4-carboxy-phenoxy)-isophthalic acid, readily ( $\text{cpiaH}_3$ ) reacts with Co(II) salts in the presence of pyridine-based coligands under solvothermal conditions to afford four different coordination polymers,  $\{\text{Co}_2(\text{cpia})(\text{OH})(\text{bipy})_{0.5}\}_n$  (**1**),  $\{[\text{Co}_2(\text{cpia})(\text{OH})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**2**),  $\{\text{Co}_{1.5}(\text{cpia})(\text{bipyethane})\}_n$  (**3**), and  $\{\text{Co}_{1.5}(\text{cpia})(\text{pyridine})_2\}_n$  (**4**). All these coordination polymers have been characterized by single crystal X-ray diffraction, IR spectroscopy, thermogravimetry and elemental analysis. The structures of **1** and **2** can be described as a repetition of a tetranuclear core with subtle differences — two tetranuclear cores are shared by an O atom in **2**, while no such bridging is present in **1**. The structures of **3** and **4**, on the other hand, consist of a trinuclear core extending to three-dimensional networks. Variable temperature magnetic susceptibility measurements indicate that **1** exhibits ferromagnetic behavior below 13 K, while **2** shows metamagnetic behavior. These interesting magnetic features are associated with the mixed hydroxyl/carboxylate-bridged polynuclear Co(II) clusters as subunits.

## Introduction

Coordination polymers have attracted considerable attention in recent years because of their potential applications as functional materials as well as the intriguing nature of molecular connectivities and topologies.<sup>1</sup> The study of molecule-based magnetic materials has evoked considerable interest among researchers during the past decades and has gradually become one of the most active fields in inorganic and materials chemistry.<sup>2</sup> Inorganic moieties such as clusters,<sup>3</sup> chains,<sup>4</sup> or layers<sup>5</sup> may be formed and linked by multidentate organic bridging ligands to form hybrid organic–inorganic structures. Bulk magnetic properties of hybrid organic–inorganic materials (particularly coordination polymers) are excellent candidates to study some of the fundamental magnetic phenomenon, such as spin canting,<sup>6</sup> metamagnetism,<sup>7</sup> single chain magnets,<sup>8</sup> etc. One of the main challenges in this field is the design of molecular-based metal complexes exhibiting spontaneous magnetization. To achieve such magnetic entities, a reasonable choice of bridging ligands is of great importance because they can determine the magnetic strength and nature of the magnetic coupling between metal centers.<sup>9</sup> Carboxylates have been widely used as bridging ligands to construct molecular magnetic materials, due to their wide range of binding modes that provide superexchange pathways for magnetic coupling among paramagnetic metal centers.<sup>10</sup>

To design homometallic coordination polymers showing interesting magnetic behavior, we have chosen the Co(II) ion with large magnetic anisotropy, that forms tetranuclear or trinuclear cobalt clusters as the secondary building unit (SBUs) and the new ligand, 5-(4-carboxy-phenoxy)-isophthalic acid ( $\text{cpiaH}_3$ ) (Scheme 1) as the bridging ligand. Metal carboxylate systems with high dimensionality are important because of the possibility of enhancement of the bulk magnetic interactions.<sup>11</sup> Use of a second bridging ligand to extend the

metal carboxylate systems is one of the common ways to obtain higher dimensional networks. In the majority of the cases, pyridyl donors as neutral ligands have been used for this purpose. Herein we report the synthesis and crystal structural studies of four coordination polymers of Co(II) having the formulas  $\{\text{Co}_2(\text{cpia})(\text{OH})(\text{bipy})_{0.5}\}_n$  (**1**),  $\{[\text{Co}_2(\text{cpia})(\text{OH})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**2**),  $\{\text{Co}_{1.5}(\text{cpia})(\text{bipyethane})\}_n$  (**3**), and  $\{\text{Co}_{1.5}(\text{cpia})(\text{pyridine})_2\}_n$  (**4**), where  $\text{bipy}$  = 4,4'-bipyridyl and  $\text{bipyethane}$  = 4,4'-bipyridylethane. Magnetic studies show that **1** displays weak ferromagnetism below 13 K while **2** displays metamagnetic behavior.

## Experimental Section

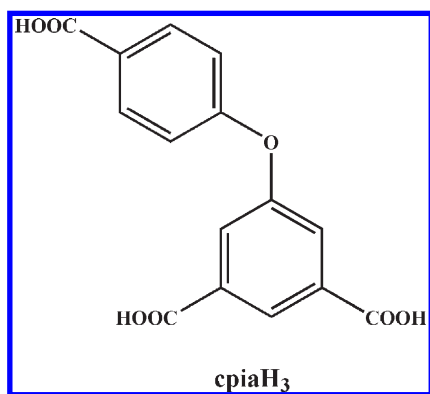
**Materials and Methods.** 4-Fluorobenzonitrile, 5-hydroxyisophthalic acid, 4,4'-bipyridylethane, 4,4'-bipyridyl and Co(II) salts were acquired from Aldrich and used as received. All solvents, pyridine, and  $\text{K}_2\text{CO}_3$  were procured from S. D. Fine Chemicals, India. All solvents were purified prior to use.

Infrared spectra were obtained (KBr disk, 400–4000  $\text{cm}^{-1}$ ) on a Perkin-Elmer model 1320 spectrometer;  $^1\text{H}$  NMR spectra were recorded on a JEOL JNM-LA400 FT (500 MHz) spectrometer in  $\text{DMSO}-d_6$  with  $\text{Me}_4\text{Si}$  as the internal standard; ESI mass spectra were recorded on a WATERS Q-TOF Premier mass spectrometer; X-ray powder patterns ( $\text{Cu K}\alpha$  radiation at a scan rate of  $3^\circ/\text{min}$ , 293 K) were acquired on a Siefert ISODEBYEFLEX-2002 spectrometer. Solid state UV–vis spectra were recorded on double UV–vis-NIR spectrophotometer (Varian Cary 5000). Thermogravimetric analyses (TGA) were recorded on Mettler Toledo (heating rate of  $5^\circ\text{C}/\text{min}$ ). Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.).

**Magnetic Measurements.** Magnetic data were collected at the Unitat de Mesures Magnètiques at the Universitat de Barcelona using crushed crystals of the sample on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants and an experimental correction for the sample holder was applied.

**Synthesis.** **Synthesis of Diethyl 5-(4-Cyanophenoxy)-isophthalate (dcpi).** 5-Hydroxy-isophthalic acid diethyl ester<sup>12</sup> (2 g, 8.4 mmol), dry  $\text{K}_2\text{CO}_3$  (1.7 g, 12.6 mmol) was mixed in a 50 mL round-bottom

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Scheme 1. Schematic Representation of Ligand cpiaH<sub>3</sub>

flask under an inert atmosphere and then 10 mL of dry DMF was added to it. The mixture was stirred for a while at 80 °C followed by addition of 4-fluoro-benzonitrile (1.2 g, 9.2 mmol) and the resulting mixture was stirred for 24 h in an oil-bath at 80 °C. The resulting solution was poured into ice-cold water (100 mL) whereupon a white solid precipitated that was collected by filtration and dried in air. Yield: 2.7 g (95%). Melting point 76 °C; IR: sharp peaks at 2224 and 1731 cm<sup>-1</sup> corresponding to  $\nu_{\text{CN}}$  and  $\nu_{\text{CO}}$  (str) respectively; <sup>1</sup>H NMR,  $\delta$  (ppm): 1.28 (dd,  $J_1 = 7.3$ ,  $J_2 = 6.9$  Hz, 6H); 4.31 (q,  $J = 6.9$  Hz, 4H); 7.19 (d,  $J = 8.8$  Hz, 2H); 7.81 (s, 2H); 7.86 (d,  $J = 8.4$  Hz, 2H); 8.27 (s, 1H); elemental analysis: Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>5</sub> (339.11): C, 67.25; H, 5.05; N, 4.13; Found: C, 67.38; H, 5.0; N, 4.19. ESI-MS:  $m/z$  (100%) 339.1104 [M]<sup>+</sup>.

**Synthesis of 5-(4-Carboxy-phenoxy)-isophthalic acid (cpiaH<sub>3</sub>).** Diethyl 5-(4-cyanophenoxy)-isophthalate (2 g, 5.9 mmol) was hydrolyzed by refluxing it with 6(N) NaOH solution (50 mL). Finally, the resulting solution was acidified with 6(N) HCl solution to obtain a white precipitate. After keeping it overnight in the freeze, it was collected by filtration and dried at 80 °C. Yield: 1.5 g (85%). This compound did not melt up to 300 °C. IR: broad peak (s) at 3555 and 3100 cm<sup>-1</sup> corresponding to  $\nu_{\text{O-H}}$  (str); sharp peak at 1722 cm<sup>-1</sup> corresponding to  $\nu_{\text{CO}}$  (str); <sup>1</sup>H NMR,  $\delta$  (ppm): 7.12 (d,  $J = 6.8$  Hz, 2H); 7.70 (s, 2H); 7.95 (d,  $J = 6.8$  Hz, 2H); 8.24 (s, 1H); elemental analysis: Calcd for C<sub>15</sub>H<sub>10</sub>O<sub>7</sub> (302.04): C, 59.61; H, 3.33; Found: C, 59.77; H, 3.39. ESI-MS:  $m/z$  (100%) 302.0429 [M]<sup>+</sup>.

**Synthesis of {Co<sub>2</sub>(cpia)(OH)(bipy)<sub>0.5</sub>}<sub>n</sub> (1).** A mixture containing cpiaH<sub>3</sub> (0.04 g, 0.13 mmol), bipy (0.02 g, 0.13 mmol), Co(OAc)<sub>2</sub>·6H<sub>2</sub>O (0.12 g, 0.5 mmol) and 1 M NaOH (0.15 mL) in 3 mL water, was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Block-shaped pink crystals of **1** were collected in 55% yield. The crystals were washed with water followed by acetone and air-dried. Anal. Calcd. for C<sub>20</sub>H<sub>12</sub>NO<sub>8</sub>Co<sub>2</sub>: C, 46.90; H, 2.36; N, 2.73%. Found: C, 46.75; H, 2.41; N, 2.78%. IR (cm<sup>-1</sup>): 3466(s), 3086(s), 2923(s), 1615(m), 1572(s), 1545(s), 1453(m), 1384(s), 1245(m), 1200(m), 1163(m), 969(m), 854(m), 817(m), 780(m), 728(s), 704(m).

**Synthesis of {[Co<sub>2</sub>(cpia)(OH)(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O]<sub>n</sub> (2).** A mixture of cpiaH<sub>3</sub> (0.04 g, 0.13 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.07 g, 0.26 mmol) in 3 mL of water and 0.5 mL of methanol was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Block-shaped pink crystals of **2** collected in 48% yield, washed with water and acetone. Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>11</sub>Co<sub>2</sub>: C, 36.90; H, 2.89%. Found: C, 36.63; H, 2.81%. IR (cm<sup>-1</sup>): 3562(s), 3423(s), 3097(s), 2924(s), 1616(m), 1561(s), 1422(m), 1351(s), 1244(m), 1216(m), 1167(m), 976(m), 868(m), 857(m), 782(m), 708(s), 697(m).

**Synthesis of {Co<sub>1.5</sub>(cpia)(bipyethane)<sub>n</sub> (3).** A mixture containing cpiaH<sub>3</sub> (0.04 g, 0.13 mmol), bipyethane (0.03 g, 0.13 mmol), Co(OAc)<sub>2</sub>·6H<sub>2</sub>O (0.13 g, 0.5 mmol) and 1(M) NaOH (0.15 mL) in 3 mL water, was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per minute. Block-shaped pink crystals of **3** along with a white solid were collected. The crystals were separated mechanically under microscope, washed

with water followed by acetone. Yield 30%. Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>N<sub>2</sub>O<sub>7</sub>Co<sub>1.5</sub>: C, 56.71; H, 3.34; N, 4.89%. Found: C, 56.56; H, 3.45; N, 4.75%. IR (cm<sup>-1</sup>): 3107(s), 2924(s), 1615(m), 1572(s), 1454(m), 1382(s), 1249(m), 1207(m), 1159(m), 1017(m), 834(m), 773(m), 712(s), 666(m).

**Synthesis of {Co<sub>1.5</sub>(cpia)(pyridine)<sub>2</sub>}<sub>n</sub> (4).** A mixture containing cpiaH<sub>3</sub> (0.04 g, 0.13 mmol), Co(OAc)<sub>2</sub>·6H<sub>2</sub>O (0.13 g, 0.13 mmol) and pyridine (0.15 mL) in 3 mL water, was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 180 °C for three days and then allowed to cool to room temperature at the rate of 1 °C per min. Block-shaped pink crystals of **4** with white solid impurities were collected. The crystals were separated mechanically under microscope, washed with water followed by acetone and finally dried in air. Yield 22%. Anal. Calcd. For C<sub>25</sub>H<sub>17</sub>N<sub>2</sub>O<sub>7</sub>Co<sub>1.5</sub>: C, 55.01; H, 3.13; N, 5.13%. Found: C, 54.73; H, 3.23; N, 5.08%. IR (cm<sup>-1</sup>): 3107(s), 2924(s), 1603(m), 1565(s), 1454(m), 1391(s), 1254(m), 1212(m), 1162(m), 1012(m), 852(m), 778(m), 722(s), 698(m).

**Single-Crystal X-ray Studies.** Single crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Data integration and reduction were processed with SAINT<sup>13</sup> software. An empirical absorption correction was applied to the collected reflections with SADABS<sup>14</sup> using XPRED.<sup>15</sup> The structure was solved by the direct method using SHELXTL<sup>16</sup> and refined on F<sup>2</sup> by full-matrix least-squares technique using the SHELXL-97 program package. Non-hydrogen atoms were refined anisotropically. The H atoms have been refined as follows; the hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The hydrogen atoms of water molecules were located from difference Fourier maps and refined freely keeping the O–H bond distances constrained to ~0.90 Å with the DFIX command. The crystal and refinement data are collected in Table 1 while selective bond distances and angles are given in Table S1 (Supporting Information).

## Results and Discussion

The new tripodal ligand, cpiaH<sub>3</sub> (Scheme 1) has been designed to provide some rotational freedom for the aromatic carboxylates that can facilitate bridging of Co(II) centers. All the coordination polymers, once isolated are stable in air and insoluble in common organic solvents and water. The IR spectra of all the compounds show strong absorption bands between 1422 and 1616 cm<sup>-1</sup> that are diagnostic<sup>17</sup> of coordinated carboxylate groups (Figure S2–S5, Supporting Information). The sharp peak at 3466 cm<sup>-1</sup> in the case of **1** indicates<sup>18</sup> the presence of hydroxyl group. The IR spectrum of **2** gives broad peaks around 3560 and 3420 cm<sup>-1</sup> due to coordinated and noncoordinated water and the hydroxyl group as well. The binding modes of the carboxylates observed in these polymers are shown in Figure 1.

Solid-state UV–vis spectrum of these compounds could be important because of its characteristic distorted coordination geometry (Figure S12, Supporting Information). It is common for a Co(II) ion in octahedral coordination to have different colors and to exhibit weak d–d absorption bands. Compound **1** has an intense violet color and **2–4** show a red to pink color. The absorption spectra of **1–4** show three strong absorption bands in the visible region 400–650 nm. The large splitting bands in the visible region and their enhanced intensities are in accordance with the large distortion from octahedral geometry of the metal center.<sup>10g</sup>

Compound **1** crystallizes in triclinic space group  $P\bar{1}$  with two crystallographically independent cobalt ions, one cpia<sup>3-</sup>, a half bipy, and one oxygen from a  $\mu_3$ -OH group in the

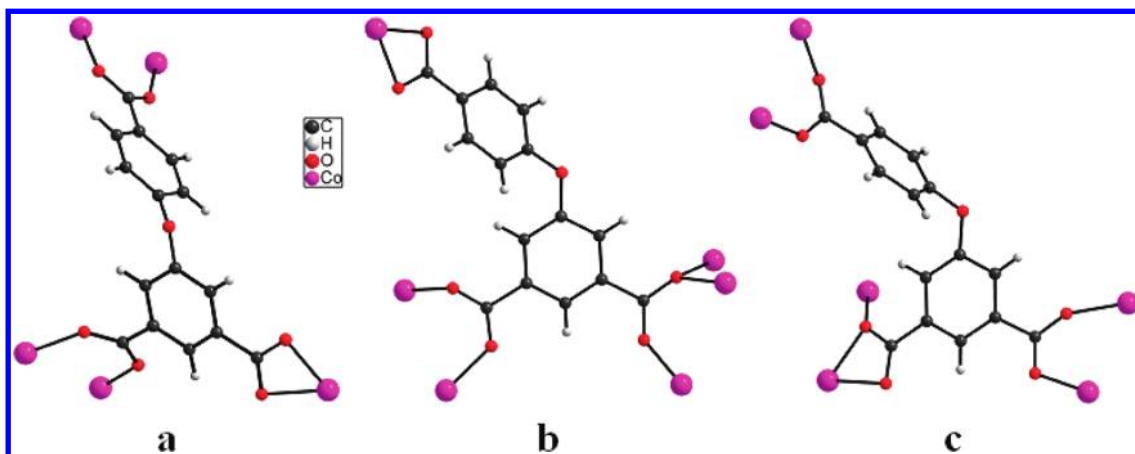


Figure 1. (a–c) Coordination modes of ligand  $\text{cpia}^{3-}$  in 1–4.

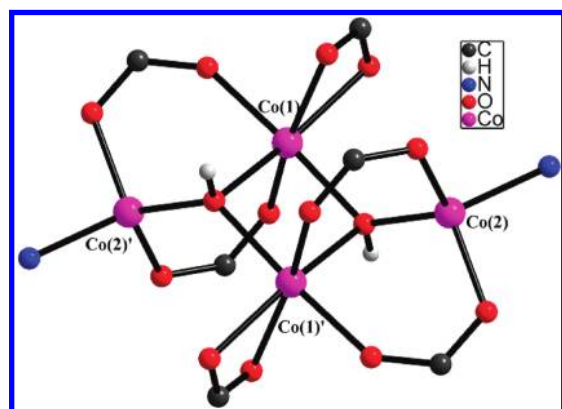


Figure 2. Metal cluster formed by ligand in compound 1.

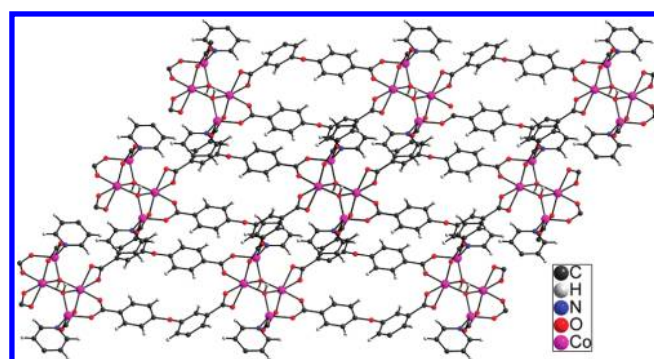


Figure 3. Propagation of the tetranuclear clusters in compound 1 into a 3D structure.

Table 1. Crystal and Structure Refinement Data for 1–4

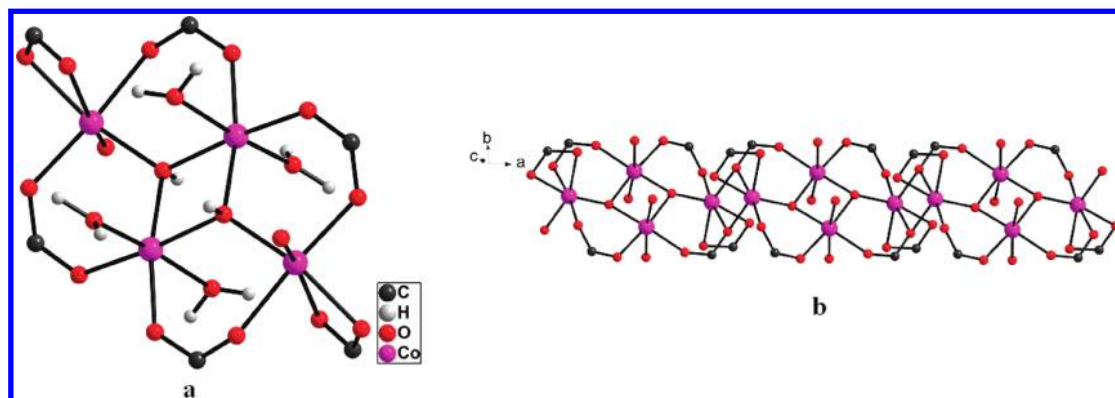
| compound                               | 1  | 2  | 3   | 4   |
|--|--|--|---|---|
| empirical formula                      | $\text{C}_{20}\text{H}_{12}\text{NO}_8\text{Co}_2$ | $\text{C}_{15}\text{H}_{14}\text{O}_{11}\text{Co}_2$ | $\text{C}_{27}\text{H}_{19}\text{N}_2\text{O}_7\text{Co}_{1.5}$ | $\text{C}_{25}\text{H}_{17}\text{N}_2\text{O}_7\text{Co}_{1.5}$ |
| formula wt                             | 512.17   | 488.12   | 571.84  | 545.80  |
| crystal system                         | triclinic  | triclinic  | triclinic   | triclinic   |
| space group                            | $P\bar{1}$   | $P\bar{1}$   | $P\bar{1}$  | $P\bar{1}$  |
| $a$ , Å                                | 9.682(2)   | 7.839(3)   | 9.584(5)  | 9.435(4)  |
| $b$ , Å                                | 10.102(2)  | 10.710(3)  | 10.422(6)   | 10.818(4)   |
| $c$ , Å                                | 11.134(2)  | 10.935(6)  | 12.375(6)   | 12.970(6)   |
| $\alpha$ (°)                           | 67.128(3)  | 100.064(7)   | 100.584(3)  | 66.065(3)   |
| $\beta$ (°)                            | 77.118(3)  | 110.271(6)   | 104.738(8)  | 70.289(5)   |
| $\gamma$ (°)                           | 66.641(3)  | 97.693(7)  | 94.047 (5)  | 87.504(7)   |
| $U$ , Å <sup>3</sup>                   | 918.1(3)   | 828.9(6)   | 1166.6(11)  | 1132.4(8)   |
| $Z$                                    | 2  | 2  | 2   | 2   |
| $\rho_{\text{calc}}$ Mg/m <sup>3</sup> | 1.85   | 1.96   | 1.63  | 1.60  |
| $\mu$ , mm <sup>-1</sup>               | 1.860  | 2.065  | 1.132   | 1.162   |
| $F(000)$                               | 514  | 492  | 583   | 555   |
| refln collected                        | 5939   | 5386   | 7674  | 6777  |
| independent refln                      | 4303   | 3922   | 5513  | 4821  |
| GOOF                                   | 1.192  | 1.123  | 1.129   | 1.139   |
| final $R$ indices [ $I > 2\sigma(I)$ ] | $R1 = 0.0535$ ,<br>$wR2 = 0.1467$                  | $R1 = 0.0602$ ,<br>$wR2 = 0.1356$                    | $R1 = 0.0701$ ,<br>$wR2 = 0.1868$                               | $R1 = 0.0879$ ,<br>$wR2 = 0.2462$                               |
| $R$ indices (all data)                 | $R1 = 0.0786$ ,<br>$wR2 = 0.2240$                  | $R1 = 0.1012$ ,<br>$wR2 = 0.2050$                    | $R1 = 0.1073$ ,<br>$wR2 = 0.2915$                               | $R1 = 0.1125$ ,<br>$wR2 = 0.2982$                               |

asymmetric unit. The four cobalt ions Co1, Co2, Co1', and Co2' form a tetranuclear unit through bondings from two bridging  $\mu_3$ -OH and carboxylate groups of  $\text{cpia}^{3-}$  ligands (Figure 2).

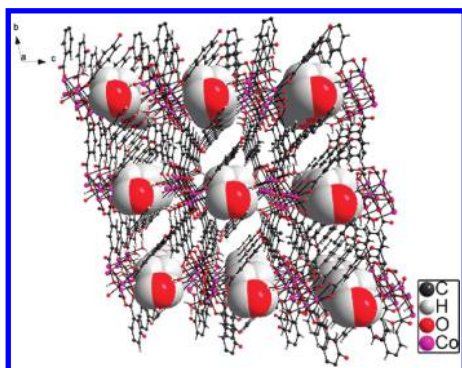
In this centrosymmetric tetramer, Co1 shows distorted octahedral  $\text{CoO}_6$  coordination from one chelating and two bridging carboxylates of  $\text{cpia}^{3-}$  ligands ( $\text{Co}-\text{O} = 2.064$ – $2.077$  Å) besides two  $\mu_3$ -OH groups ( $\text{Co}-\text{O} = 2.092$ – $2.115$  Å).

The Co2 center, on the other hand, adopts a distorted tetrahedral  $\text{CoNO}_3$  coordination provided by two O atoms from two bridging carboxylates ( $\text{Co}-\text{O} = 1.961$ – $1.963$  Å), one nitrogen atom from a bipy ligand ( $\text{Co}-\text{N} = 2.031$  Å) and one  $\mu_3$ -OH group ( $\text{Co}-\text{O} = 1.942$  Å). These tetrameric units propagate into a 3D network via bridging carboxylates of  $\text{cpia}^{3-}$  and N atom of the bipy ligands (Figure 3). Thus, the structure of 1 can be described as a 3D framework, consisting





**Figure 4.** (a) Tetranuclear cluster formed in compound **2**. (b) An array of puckered chains of Co(II) ions along the *a* direction of a unit cell.



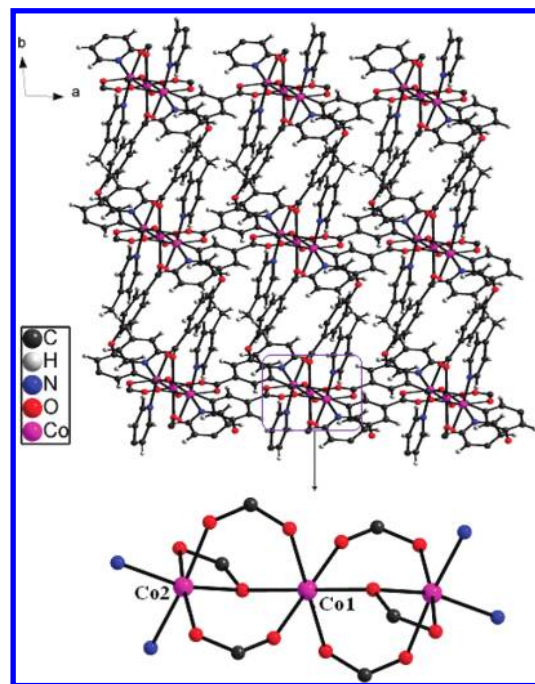
**Figure 5.** Perspective 3D view of compound **2** viewed along the *a* axis with embedded water molecules.

of  $[\text{Co}_4(\mu_3\text{-OH})_2]^{6+}$  subunits connected through  $\text{cpia}^{3-}$  and bipy ligands.

Compound **2** also crystallizes in the triclinic space group  $P\bar{1}$  with two Co(II), one  $\text{cpia}^{3-}$ , two coordinated and one lattice water molecules and one  $\mu_3\text{-OH}$  group in the asymmetric unit. It contains the tetranuclear core  $[\text{Co}_4(\mu_3\text{-OH})_2]^{6+}$  similar to the one present in **1**. Instead of a discrete tetranuclear core unit in **1**, it extends along the crystallographic *a* axis via bridging carboxylates and sharing Co(II) ions to form an infinite chain (Figure 4). These chains are further connected through available carboxylate groups to generate a neutral 3D coordination polymer with voids occupied by water molecules (Figure 5) and also exhibit  $\pi\cdots\pi$  interactions between arene cores of two independent  $\text{cpia}^{3-}$  (3.227 Å). Here, the three carboxylate groups of the  $\text{cpia}^{3-}$  ligand bind in three different modes: chelating, syn-syn, and syn-syn-anti bridging (Figure 1b). The Co1 atom is coordinated by two OH groups (Co–O = 2.074–2.090 Å), two O atoms in a bridging fashion from two different  $\text{cpia}^{3-}$  ligands (Co–O = 2.029–2.046 Å), and two water molecules (Co–O = 2.145–2.205 Å), in a distorted octahedral fashion.

The Co2 atom also has a distorted octahedral geometry and is ligated by one OH group (Co–O = 2.009 Å) and five oxygen atoms from one chelating and three bridging  $\text{cpia}^{3-}$  ligands (Co–O = 2.045–2.211 Å).

In contrast to the previous two structures, **3** has an acyclic trimeric Co(II) subunit constructed from bridging carboxylates (Figure 6). It also crystallizes in the triclinic space group  $P\bar{1}$  where the asymmetric unit consists of two crystallographically independent Co(II) ions, one  $\text{cpia}^{3-}$  and one bipyethane. Here, the three carboxylate groups of the  $\text{cpia}^{3-}$  ligand bind the metal ions in different ways viz., syn-syn, chelating, and bridging (Figure 1c).

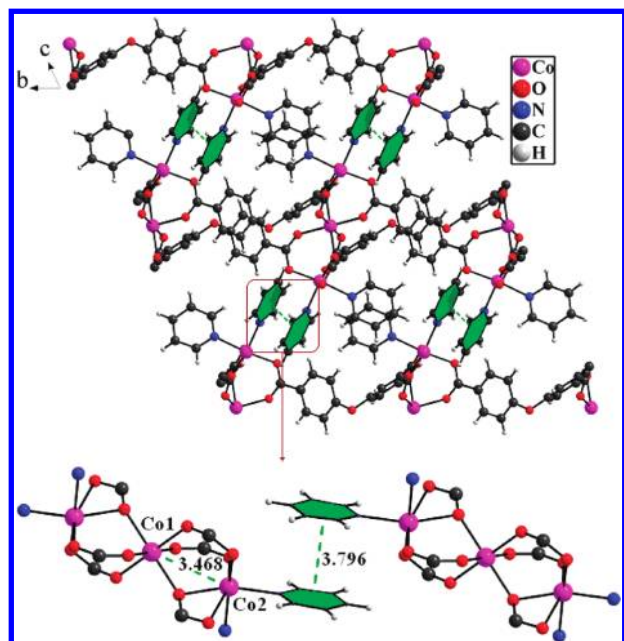


**Figure 6.** 3D view of compound **3** showing a section of trimeric cobalt subunit.

The central Co1 atom is located at the crystallographic inversion center. It is coordinated to six O atoms from the six bridging carboxylate groups of the  $\text{cpia}^{3-}$  ligands forming a distorted octahedral geometry (Co–O = 2.004–2.161 Å). Each of the two terminal Co(II) ions also has an octahedral coordination environment provided by four O atoms from two bridging and one chelating carboxylates (Co–O = 2.025–2.353 Å) and two N atoms from two bipyridylethane ligands (Co–N = 2.101–2.152 Å). The linear trinuclear Co(II) clusters are further connected via the  $\text{cpia}^{3-}$  ligand to generate the 3D network (Figure 6) and also show  $\pi\cdots\pi$  interactions between arene cores of two independent  $\text{cpia}^{3-}$  (3.294 Å).

Compound **4** also forms a trinuclear cluster with a bonding mode similar to **3**. Both the Co–O and Co–N bond distances are also similar. The 2D framework constructed by trimeric Co(II) subunits exhibits strong  $\pi\cdots\pi$  interactions between pyridine molecules to generate an overall 3D framework (Figure 7).

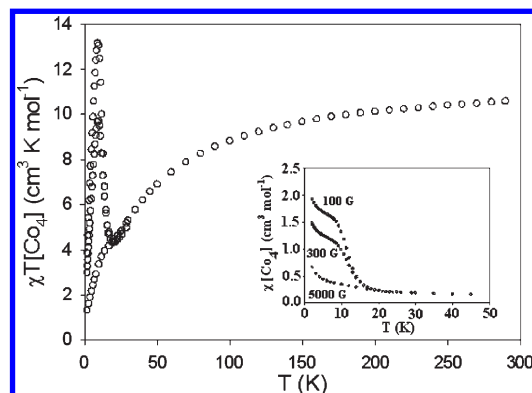
Thermal stability of the compounds were examined (Figure S1, Supporting Information). Compound **1** is thermally stable up



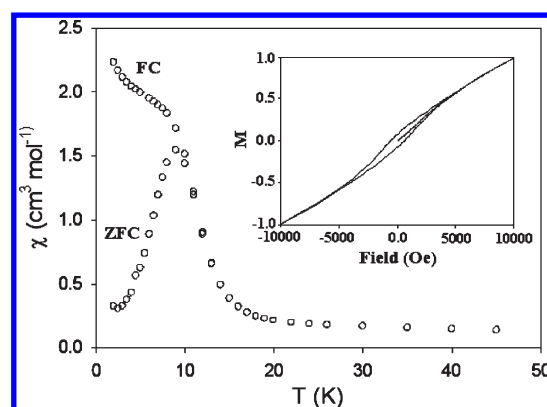
**Figure 7.** 3D packing diagram of compound **4** showing a  $\pi \cdots \pi$  interaction between the pyridine molecules.

to 450 °C. Compound **2** shows a weight loss of 11.2% (expected = 11.1%) in the temperature range of 80–120 °C that corresponds to the loss of two coordinated and one lattice water molecules. Decomposition of this compound is accomplished only above 460 °C. Compound **3** is found to be stable up to 350 °C. Compound **4** shows a weight loss of 29.1% (expected = 29.0%) in the temperature range of 80–200 °C, corresponding to the loss of two coordinated pyridine molecules. Complete decomposition is observed beyond 340 °C. In order to check whether the framework is intact after heating or not, we have collected powder X-ray diffraction patterns (PXRD) of samples **1** and **3** at different temperatures (Figures S13 and S14, Supporting Information). The peak positions and intensities are very similar to each other, showing the frameworks are stable and intact at the mentioned temperatures in TGA.

**Magnetic Studies.**  $\{\text{Co}_2(\text{cpia})(\text{OH})(\text{bipy})_{0.5}\}_n$  (**1**). From the magnetic point of view, **1** will be treated as  $\{\text{Co}_4(\text{cpia})_2(\text{OH})_2(\text{bipy})\}_n$ , since the magnetic behavior will be better understood taking into account the repeating tetranuclear Co(II) unit. As previously discussed, two Co(II) ions (Co1 and Co1') are distorted octahedral, while the other two Co(II) ions (Co2 and Co2') are distorted tetrahedral. This results in the two metal centers Co1 and Co1' displaying strong spin–orbit coupling while Co2 and Co2' do not. The four metal centers are bridged by two triply bridging hydroxides forming a core similar to the known “butterfly” core. Although this is a common structural motif for the trivalent 3d metals such as Mn,<sup>19</sup> Fe,<sup>20</sup> V,<sup>21</sup> and Cr,<sup>22</sup> it is not often found for divalent metals.<sup>23</sup> In the common butterfly complexes, the triply bridging ligand is an oxide, while in **1** it is a hydroxide. Magnetically, this arrangement results in intermediate spin-states for the tetranuclear complexes, due to competing antiferromagnetic interactions, since the M–O–M angles around the triply bridging oxide are about 120°. In **1**, the Co–O(H)–Co angles range between 128.57° and 96.93°, resulting in competing antiferromagnetic and ferromagnetic interactions. Magnetic susceptibility data were collected with the crushed crystals of **1** at variable

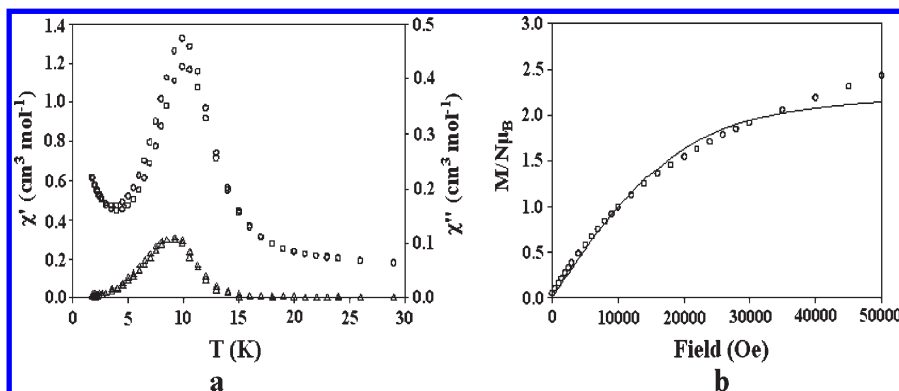


**Figure 8.**  $\chi T$  vs  $T$  plot for compound **1**. The inset shows the susceptibility at three different applied fields in the 2 to 50 K region.

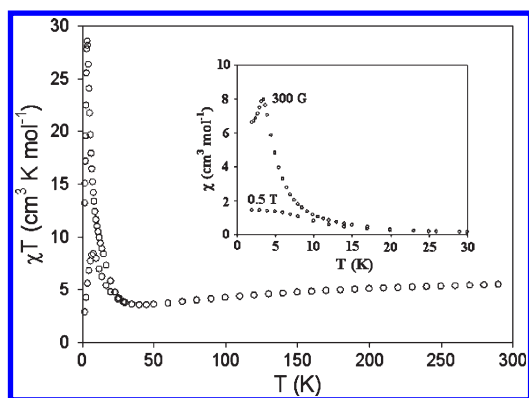


**Figure 9.** Zero-field cool (ZFC) and field-cool (FC) plot for compound **1** at 50 G applied field. The inset shows a hysteresis plot at 2 K.

temperatures and variable fields. A  $\chi T$  vs  $T$  plot is shown in Figure 8. The  $\chi T$  product at 300 K affords a value of 10.55  $\text{cm}^3 \text{K mol}^{-1}$  per tetranuclear Co(II) unit, above the expected value for four Co(II) with  $S = 3/2$  and  $g = 2.0$  ( $7.50 \text{ cm}^3 \text{K mol}^{-1}$ ). With lowering of the temperature, the  $\chi T$  product decreases partly due to depopulation of the  $J = 5/2$  state and the preferential population of  $J = 1/2$  of the Co1 and Co1' ions. At a field of 5 kG, a plateau is reached around 20 K, and below this temperature the  $\chi T$  product further decreases and is strongly field-dependent, as shown in the inset of Figure 8. At lower than 5 kG, a sharp peak in the  $\chi T$  product is observed at 9 K, the maximum  $\chi T$  value of which is also field dependent. The sudden rise of the susceptibility below 13 K is also accompanied by a strong divergence of the zero field-cool/field cool measurements, shown in Figure 9, indicating the onset of a ferromagnetic state. This is confirmed by the appearance of the out-of-phase signal in the AC magnetic susceptibility at 9 K, shown in Figure 10a, which does not depend on the frequency. The weak ferromagnetic nature of **1** is further confirmed by the small hysteresis loops (inset of Figure 9) observed at 2 K, with  $H_c = 400 \text{ G}$ . The magnetization vs field data for **1** shown in Figure 10b suggest a nonzero spin ground-state for the  $[\text{Co}_4]$  units with low lying excited states, and the data can be modeled with the Brillouin function of  $S = 1$  and  $g = 2.0$ ; the agreement is not excellent due to the presence of two hexacoordinated Co(II) ions per tetranuclear unit with strong spin–orbit coupling. Each  $[\text{Co}_4]$  unit can have a ground state between  $S = 0$  and  $S = 4$  (the hexacoordinated Co(II) ions possess an effective



**Figure 10.** (a) AC magnetic susceptibility plot for compound **1** (triangles: out-of-phase susceptibility, right axis, circles: in-phase susceptibility, left axis). (b) Magnetization vs field plot for compound **1** at 2 K. The solid line is the Brillouin function for an  $S = 1$  with  $g = 2.0$ .

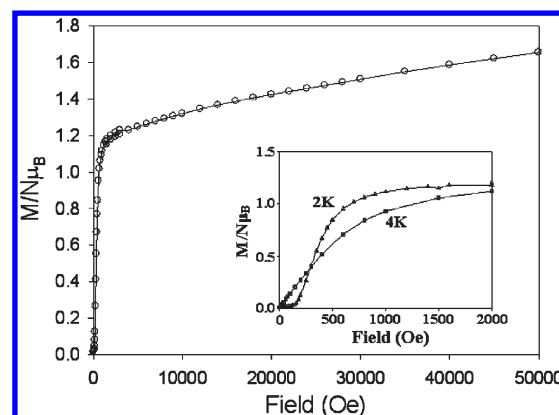


**Figure 11.**  $\chi T$  vs  $T$  plot for compound **2** at two applied fields. The inset shows the susceptibility plot in the 2–30 K temperature range.

$S = 1/2$  at low temperature), but the observed  $S = 1$  is an intermediate spin-state resulting from the competing interactions within each  $[\text{Co}_4]$  unit. In the crystal, the  $[\text{Co}_4]$  units that form **1** are linked by bipy and the tricarboxylate ligands into an ordered 3D network. The shortest distance between  $[\text{Co}_4]$  units is 5.511 Å, enabling dipolar interactions that give rise to the weak ferromagnetic state observed.

$[\{\text{Co}_2(\text{cpia})(\text{OH})(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O}]_n$  (**2**). Magnetic susceptibility data were collected for a sample of crushed crystals of **2** at variable temperatures and variable fields. A  $\chi T$  vs  $T$  plot is shown in Figure 11. The  $\chi T$  product at 300 K shows a value of  $5.49 \text{ cm}^3 \text{ K mol}^{-1}$  per dinuclear  $\text{Co}(\text{II})$  unit, above the expected value for two  $\text{Co}(\text{II})$  ions with  $S = 3/2$  and  $g = 2.0$  ( $3.75 \text{ cm}^3 \text{ K mol}^{-1}$ ). With lowering of temperature, the  $\chi T$  product decreases to the value of  $3.01 \text{ cm}^3 \text{ K mol}^{-1}$  at 38 K. In part, this is due to depopulation of the  $J = 5/2$  state and the preferential population of the  $J = 1/2$  state of the Co1 and Co2 ions. Below 38 K, the  $\chi T$  product rises again and becomes strongly field-dependent. This indicates onset of a weak ferromagnetic state induced by the external magnetic field. The field dependence of the magnetization is shown in Figure 12.

At 2 K, magnetization rises suddenly to a value of  $1.1 \mu_B$  at an applied DC field of 160 G, indicating onset of the weak ferromagnetic state. Saturation is never reached and the maximum magnetization value reached at 5 T is  $1.6 \mu_B$ . The absence of 3D order is further confirmed by the lack of an out-of-phase peak in the  $ac$  magnetic susceptibility, as well as lack of magnetization hysteresis. The crystal structure of **2** consists of 3D array of puckered chains of  $\text{Co}(\text{II})$  ions



**Figure 12.** Magnetization vs field Plot at 2 K for compound **2**. The inset shows the low field region measured at 2 K and 4 K.

along the crystallographic  $a$  axis that are bridged by the triply bridging OH and bridging oxygen donors from the carboxylate. The chains are linked by the carboxylates with inter-chain Co–Co distances of 7.5 Å. Thus, magnetically **2** can be considered as weakly interacting infinite 1D chains. There are two crystallographically distinct  $\text{Co}(\text{II})$  ions, Co1 and Co2. The Co1–OH–Co2 angles are  $119.93^\circ$ , with additional syn,syn-carboxylato bridges to afford antiferromagnetic superexchange pathways between these ions. The Co1–O–Co1' and Co2–O–Co2' are  $98.75^\circ$  and  $99.19^\circ$ , respectively, giving rise to weak magnetic interaction between the metal pairs that could be weakly ferromagnetic.<sup>24</sup> No reliable magneto-structural correlation for  $\text{Co}(\text{II})$ -O complexes is available due to the complication of the large spin–orbit coupling of the hexacoordinated  $\text{Co}(\text{II})$ . However, as reported<sup>24a</sup> by Murrie and co-workers, a Co–O–Co angle of  $96$ – $99^\circ$  leads to weak ferromagnetic coupling. Also, no possible exchange pathways between the Co1–Co1' and Co2–Co2' pairs exist. Thus, the magnetic structures of the metamagnetic **2** can be described as ferromagnetically coupled  $[\text{Co}_2]$  units that form a zigzag chain linked by the triply bridging OH ligands. The coupling between  $[\text{Co}_2]$  units along the chain is antiferromagnetic.

## Conclusion

In summary, we have synthesized four different 3D coordination polymers with  $\text{Co}(\text{II})$  ions under solvothermal conditions using a new tripodal carboxylate ligand. Magnetic studies reveal that compound **1** is a weak ferromagnet,



whereas compound **2** displays a metamagnetic state. Such types of ferromagnetically coupled coordination polymers are under investigation with this and other flexible carboxylate ligands in our laboratory.

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**Supporting Information Available:** Crystallographic data for **1–4** in CIF format, table for selected bonds and distances for **1–4**, IR, TGA analysis, ESI-MS, and NMR. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

## References

- (1) (a) Perry, J. J., IV; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (b) Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keefe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257. (c) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (d) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (e) Uemura, T.; Yanai, N.; Kitagawa, S. *Chem. Soc. Rev.* **2009**, *38*, 1228. (f) Das, M. C.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2009**, *131*, 10942. (g) Chen, B.; Wang, L.; Xiao, Y.; Fronczek, F. R.; Xue, M.; Cui, Y.; Qian, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 500. (h) Rajput, L.; Biradha, K. *Cryst. Growth Des.* **2009**, *9*, 40. (i) Hong, M. *Cryst. Growth Des.* **2007**, *7*, 10. (j) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 2293. (k) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2948. (l) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (m) Janiak, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1431.
- (2) (a) Li, J. R.; Yu, Q.; Sañudo, E. C.; Tao, Y.; Song, W.-C.; Bu, X.-H. *Chem. Mater.* **2008**, *20*, 1218. (b) Numata, Y.; Inoue, K.; Baranov, N.; Kurmoo, M.; Kikuchi, K. *J. Am. Chem. Soc.* **2007**, *129*, 9902. (c) Gu, Z.-G.; Zhou, X.-H.; Jin, Y.-B.; Xiong, R.-G.; Zuo, J.-L.; You, X.-Z. *Inorg. Chem.* **2007**, *46*, 5462. (d) Kaneko, W.; Ohba, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 13706. (e) Liu, T.; Zhang, Y.; Wang, Z.; Gao, S. *Inorg. Chem.* **2006**, *45*, 2782. (f) Öhrström, L.; Larsson, K. *Molecule-Based Materials: The Structural Network Approach*; Elsevier: Amsterdam, 2005. (g) Mialane, P.; Dolbecq, A.; Rivière, E.; Marrot, J.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 2274. (h) Coronado, E.; Palacio, F.; Veciana, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 2570. (i) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.
- (3) (a) Cheon, Y. E.; Suh, M. P. *Chem. Commun.* **2009**, 2296. (b) Chen, P.-K.; Batten, S. R.; Qi, Y.; Zheng, J.-M. *Cryst. Growth Des.* **2009**, *9*, 2756. (c) Ma, L.-F.; Wang, Y.-Y.; Wang, L.-Y.; Lu, D.-H.; Batten, S. R.; Wang, J.-G. *Cryst. Growth Des.* **2009**, *9*, 2036. (d) He, J.; Zhang, J.-X.; Tsang, C.-K.; Xu, Z.; Yin, Y.-G.; Li, D.; Ng, S.-W. *Inorg. Chem.* **2008**, *47*, 7948. (e) Cheng, J.-W.; Zheng, S.-T.; Liu, W.; Yang, G.-Y. *CrystEngComm* **2008**, *10*, 1047. (f) Tasiopoulos, A. J.; Milligan, P. L., Jr.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *Inorg. Chem.* **2007**, *46*, 9678. (g) Lisnard, L.; Mialane, P.; Dolbecq, A.; Marrot, J.; Clemente-Juan, J. M.; Coronado, E.; Keita, B.; de Oliveira, P.; Nadjio, L.; Secheresse, F. *Chem.—Eur. J.* **2007**, *13*, 3525. (h) Li, Y.-G.; Hao, N.; Wang, E.-B.; Lu, Y.; Hu, C.-W.; Xu, L. *Eur. J. Inorg. Chem.* **2003**, 2567.
- (4) (a) Wang, X.-T.; Wang, X.-H.; Wang, Z.-M.; Gao, S. *Inorg. Chem.* **2009**, *48*, 1301. (b) Huang, Y.-G.; Wang, X.-T.; Jiang, F.-L.; Gao, S.; Wu, M.-Y.; Gao, Q.; Wei, W.; Hong, M.-C. *Chem.—Eur. J.* **2008**, *14*, 10340. (c) Hu, B.-W.; Zhao, J.-P.; Sanudo, E. C.; Liu, F.-C.; Zeng, Y.-F.; Bu, X.-H. *Dalton Trans.* **2008**, 5556. (d) Biswas, C.; Mukherjee, P.; Drew, M. G. B.; Gomez-Garcia, C. J.; Clemente-Juan, J. M.; Ghosh, A. *Inorg. Chem.* **2007**, *46*, 10771. (e) Kurmoo, M.; Kumagai, H.; Akita-Tanaka, M.; Inoue, K.; Takagi, S. *Inorg. Chem.* **2006**, *45*, 1627. (f) Dietzel, P. D. C.; Morita, Y.; Blom, R.; Fjellvaag, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6354. (g) Bu, X.-H.; Liu, H.; Du, M.; Zhang, L.; Guo, Y.-M.; Shionoya, M.; Ribas, J. *Inorg. Chem.* **2002**, *41*, 1855. (h) Gerrard, L. A.; Wood, P. T. *Chem. Commun.* **2000**, 2107. (i) Lawandy, M. A.; Huang, X.; Wang, R.-J.; Li, J.; Lu, J. Y.; Yuen, T.; Lin, C. L. *Inorg. Chem.* **1999**, *38*, 5410.
- (5) (a) Mahata, P.; Sen, D.; Natarajan, S. *Chem. Commun.* **2008**, 1278. (b) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Murcia-Martinez, A. *Chem.—Eur. J.* **2006**, *12*, 3484. (c) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (d) Huang, Z.-L.; Drillon, M.; Masciocchi, N.; Sirono, A.; Zhao, J.-T.; Rabu, P.; Panissod, P. *Chem. Mater.* **2000**, *12*, 2805. (e) Kurmoo, M. *J. Mater. Chem.* **1999**, *9*, 2595.
- (6) (a) Aijaz, A.; Sañudo, E. C.; Bharadwaj, P. K. *Inorg. Chem. Acta* **2009**, *362*, 4246. (b) Yoon, J. H.; Ryu, D. W.; Kim, H. C.; Yoon, S. W.; Suh, B. J.; Hong, C. S. *Chem.—Eur. J.* **2009**, *15*, 3661. (c) Arora, H.; Lloret, F.; Mukherjee, R. *Inorg. Chem.* **2009**, *48*, 1158. (d) Lu, Y.-B.; Wang, M.-S.; Zhou, W.-W.; Xu, G.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem.* **2008**, *47*, 8935. (e) Zheng, Y.-Z.; Xue, W.; Tong, M.-L.; Chen, X.-M.; Grandjean, F.; Long, G. J. *Inorg. Chem.* **2008**, *47*, 4077. (f) Jia, H.-P.; Li, W.; Ju, Z.-F.; Zhang, J. *Chem. Commun.* **2008**, 371. (g) Chen, P.-K.; Che, Y.-X.; Zheng, J.-M.; Batten, S. R. *Chem. Mater.* **2007**, *19*, 2162. (h) Cheng, X.-N.; Zhang, W.-X.; Chen, X.-M. *J. A. Chem. Soc.* **2007**, *129*, 15738. (i) Barrios, L. A.; Ribas, J.; Aromi, G.; Ribas-Arino, J.; Gamez, P.; Roubeau, O.; Teat, S. J. *Inorg. Chem.* **2007**, *46*, 7154. (j) Li, J.-R.; Yu, Q.; Sañudo, E. C.; Tao, Y.; Bu, X.-H. *Chem. Commun.* **2007**, 2602. (k) Li, J.-R.; Yu, Q.; Tao, Y.; Bu, X.-H.; Ribas, J.; Batten, S. R. *Chem. Commun.* **2007**, 2290. (l) Zeng, M.-H.; Zhang, W.-X.; Sun, X.-Z.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3079. (m) Xiang, S.; Wu, X.; Zhang, J.; Fu, R.; Hu, S.; Zhang, X. *J. A. Chem. Soc.* **2005**, *127*, 16352. (n) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.
- (7) (a) Chen, Z.-L.; Jiang, C.-F.; Yan, W.-H.; Liang, F.-P.; Batten, S. R. *Inorg. Chem.* **2009**, *48*, 4674. (b) Choi, S. W.; Kwak, H. Y.; Yoon, J. H.; Kim, H. C.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2008**, *47*, 10214. (c) Zhang, X.-M.; Hao, Z.-M.; Zhang, W.-X.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3456. (d) Das, A.; Rosair, G. M.; El Fallah, M. S.; Ribas, J.; Mitra, S. *Inorg. Chem.* **2006**, *45*, 3301. (e) Zhang, Y.-Z.; Gao, S.; Sun, H.-L.; Su, G.; Wang, Z.-M.; Zhang, S.-W. *Chem. Commun.* **2004**, 1906. (f) Wang, R.; Gao, E.; Hong, M.; Gao, S.; Luo, J.; Lin, Z.; Han, L.; Cao, R. *Inorg. Chem.* **2003**, *42*, 5486.
- (8) (a) Zheng, Y.-Z.; Xue, W.; Zhang, W.-X.; Tong, M.-L.; Chen, X.-M.; Grandjean, F.; Long, G. J.; Ng, S.-W.; Panissod, P.; Drillon, M. *Inorg. Chem.* **2009**, *48*, 2028. (b) Zhang, D.; Wang, H.; Chen, Y.; Ni, Z.-H.; Tian, L.; Jiang, J. *Inorg. Chem.* **2009**, *48*, 5488. (c) Liu, C.-M.; Zhang, D.-Q.; Zhu, D.-B. *Inorg. Chem.* **2009**, *48*, 4980. (d) Tandon, S. S.; Bunge, S. D.; Motry, D.; Costa, J. S.; Aromi, G.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **2009**, *48*, 4873. (e) Miyasaka, H.; Julve, M.; Yamashita, M.; Clerac, R. *Inorg. Chem.* **2009**, *48*, 3420. (f) Bonnet, M.-L.; Aronica, C.; Chastanet, G.; Pilet, G.; Luneau, D.; Mathoniere, C.; Clerac, R.; Robert, V. *Inorg. Chem.* **2008**, *47*, 1127. (g) Coronado, E.; Galan-Mascaros, J. R.; Marti-Gastaldo, Carlos. *J. A. Chem. Soc.* **2008**, *130*, 14987. (h) Bernot, K.; Luzon, J.; Sessoli, R.; Vindigni, A.; Thion, J.; Richeter, S.; Leclercq, D.; Lariouva, J.; van der Lee, A. J. *J. A. Chem. Soc.* **2008**, *130*, 1619. (i) Yoo, H. S.; Kim, J. I.; Yang, N.; Koh, E. K.; Park, J.-G.; Hong, C. S. *Inorg. Chem.* **2007**, *46*, 9054. (j) Xu, H.-B.; Wang, B.-W.; Pan, F.; Wang, Z.-M.; Gao, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 7388. (k) Brockman, J. T.; Stamatatos, T. C.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2007**, *46*, 9160. (l) Bernot, K.; Bogani, L.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. A. Chem. Soc.* **2006**, *128*, 7947. (m) Toma, L. M.; Lescouezec, R.; Pasan, J.; Ruiz-Perez, C.; Vaissermann, J.; Cano, J.; Carrasco, R.; Wernsdorfer, W.; Lloret, F.; Julve, M. *J. A. Chem. Soc.* **2006**, *128*, 4842. (n) Miyasaka, H.; Nezu, T.; Sugimoto, K.; Sugiyama, K.-I.; Yamashita, M.; Clerac, R. *Chem.—Eur. J.* **2005**, *11*, 1592. (o) Pardo, E.; Ruiz-Garcia, R.; Lloret, F.; Faus, J.; Julve, M.; Journaux, Y.; Delgado, F.; Ruiz-Perez, C. *Adv. Mater.* **2004**, *16*, 1597.
- (9) (a) Ma, Y.; Zhang, J.-Y.; Cheng, A.-L.; Sun, Q.; Gao, E.-Q.; Liu, C.-M. *Inorg. Chem.* **2009**, *48*, 6142. (b) Boonmak, J.; Youngme, S.; Chaichit, N.; van Albada, G. A.; Reedijk, J. *Cryst. Growth Des.* **2009**, *9*, 3318. (c) Masciocchi, N.; Galli, S.; Tagliabue, G.; Sironi, A.; Castillo, O.; Luque, A.; Beobide, G.; Wang, W.; Romero, M. A.; Barea, E.; Navarro, J. A. R. *Inorg. Chem.* **2009**, *48*, 3087. (d) Gomez-Coca, S.; Ruiz, E.; Kortus, J. *Chem. Commun.* **2009**, 4363. (e) Compain, J.-D.; Mialane, P.; Dolbecq, A.; Mbomekalle, I. M.; Marrot, J.; Secheresse, F.; Riviere, E.; Rogez, G.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 3077. (f) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Southon, P. D.; Cashion, J. D.; Letard, J.-F.; Moubarki, B.; Murray, K. S.; Kepert, C. J. *J. A. Chem. Soc.* **2008**, *130*, 2869. (g) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 9590. (h) Mereacre, V.; Ako, A. M.; Clerac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2008**, *14*, 3577. (i) He, Z.; Wang, Z.-M.; Gao, S.; Yan, C.-H. *Inorg. Chem.* **2006**, *45*, 6694. (j) Konar, S.; Mukherjee, P. S.; Drew, M. G. B.; Ribas, J.; Chaudhuri, N. R. *Inorg. Chem.* **2003**, *42*, 2545. (k) Tsai, H.-L.; Chen, D.-M.; Yang, C.-L.; Jwo, T.-Y.; Wur, C.-S.; Lee, G.-H.; Wang, Y. *Inorg. Chem. Commun.* **2001**, 511.



- (10) (a) Luo, F.; Che, Y.-X.; Zheng, J.-M. *Cryst. Growth Des.* **2009**, *9*, 1066. (b) Jia, Q.-X.; Wang, Y.-Q.; Yue, Q.; Wang, Q.-L.; Gao, E.-Q. *Chem. Commun.* **2008**, 4894. (c) Pan, Z.; Song, Y.; Jiao, Y.; Fang, Z.; Li, Y.; Zheng, H. *Inorg. Chem.* **2008**, *47*, 5162. (d) Gavrilenko, K. S.; Cadot, O.; Bernot, K.; Rosa, P.; Sessoli, R.; Golhen, S.; Pavlishchuk, V. V.; Ouahab, L. *Chem.—Eur. J.* **2008**, *14*, 2034. (e) Rodriguez-Dieguez, A.; Cano, J.; Kivekaes, R.; Debdoubi, A.; Colacio, E. *Inorg. Chem.* **2007**, *46*, 2503. (f) Sanselme, M.; Greneche, J. M.; Riou-Cavellec, M.; Ferey, G. *Chem. Commun.* **2002**, 2172. (g) Kumagai, H.; Kepert, C. J.; Kurmoo, M. *Inorg. Chem.* **2002**, *41*, 3410.
- (11) (a) Chen, Q.; Zhou, Y.-L.; Zeng, M.-H. *J. Mol. Struct.* **2009**, 932, 55. (b) Calvo, R.; Rapp, R. E.; Chagas, E.; Sartoris, R. P.; Baggio, R.; Garland, M. T.; Perec, M. *Inorg. Chem.* **2008**, *47*, 10389. (c) Maspoch, D.; Vidal-Gancedo, J.; Ruiz-Molina, D.; Rovira, C.; Veciana, J. *J. Phys. Chem. Solids* **2004**, *65*, 819. (d) Maspoch, D.; Ruiz-Molina, D.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190.
- (12) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3477.
- (13) *SAINT+*, 6.02ed.; Bruker AXS: Madison, WI, 1999.
- (14) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Germany, **1997**.
- (15) *XPRED*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.
- (16) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
- (17) (a) Lisnard, L.; Mialane, P.; Dolbecq, A.; Marrot, J.; Clemente-Juan, J. M.; Coronado, E.; Keita, B.; de Oliveira, P.; Nadjio, L.; Secheresse, F. *Chem.—Eur. J.* **2007**, *13*, 3525. (b) Li, X.-J.; Wang, X.-Y.; Gao, S.; Cao, R. *Inorg. Chem.* **2006**, *45*, 1508.
- (18) (a) Luo, J.; Zhao, Y.; Xu, H.; Kinnibrugh, T. L.; Yang, D.; Timofeeva, T. V.; Daemen, L. L.; Zhang, J.; Bao, W.; Thompson, J. D.; Currier, R. P. *Inorg. Chem.* **2007**, *46*, 9021. (b) Jia, H.-P.; Li, W.; Ju, Z.-F.; Zhang, J. *Inorg. Chem. Commun.* **2007**, 265.
- (19) Wang, S.; Wemple, M. S.; Yoo, J.; Folting, K.; Huffman, J. C.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2000**, *39*, 1501.
- (20) Boudalis, A. K.; Laloti, N.; Spyroulias, G. A.; Raptopoulou, C. P.; Tezris, A.; Bousseksou, A.; Tangoulis, V.; Tuchagues, J.-P.; Perlepes, S. P. *Inorg. Chem.* **2002**, *41*, 6474 and references therein.
- (21) Castro, S. L.; Sun, Z.; Grant, C. M.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 2365.
- (22) Bino, A.; Chayat, R.; Pedersen, E.; Schneidert, A. *Inorg. Chem.* **1991**, *30*, 856–858.
- (23) (a) King, P.; Clerac, R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Dalton Trans.* **2004**, 2670. (b) Luo, J.; Zhao, Y.; Xu, H.; Kinnibrugh, T. L.; Yang, D.; Timofeeva, T. V.; Daemen, L. L.; Zhang, J.; Bao, W.; Thompson, J. D.; Currier, R. P. *Inorg. Chem.* **2007**, *46*, 9021. (c) Jia, H.-P.; Li, W.; Ju, Z.-F.; Zhang, J. *Inorg. Chem. Commun.* **2007**, 265.
- (24) (a) Galloway, K. W.; Whyte, A. M.; Wernsdorfer, W.; Sanchez-Benitez, J.; Kamenev, K. V.; Parkin, A.; Peacock, R. D.; Murrie, M. *Inorg. Chem.* **2008**, *47*, 7438. (b) Isele, K.; Gigon, F.; Williams, A. F.; Bernardinelli, G.; Franz, P.; Decurtins, S. *Dalton Trans.* **2007**, 332.