

Hydrothermal synthesis and characterization of the first oxalate–bta mixed-ligand three-dimensional frameworks: $\{[M_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2\}_n$ ($M = \text{Co}^{\text{II}}, \text{Fe}^{\text{II}}$; bta = benzene-1,2,4,5-tetracarboxylate)

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Two new metal–organic complexes formulated as $\{M_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2\}_n$ (**1**: $M = \text{Co}^{\text{II}}$; **2**: $M = \text{Fe}^{\text{II}}$; bta = benzene-1,2,4,5-tetracarboxylate) have been hydrothermally synthesized at 160 °C for 120 h. Their structures were determined by single-crystal X-ray diffraction analysis and characterized by XPS, IR, ICP, elemental, TG and magnetic analysis. Complexes **1** and **2** are isostructural and represent the first coordination network structure constructed by bridging oxalate and bta mixed ligands. In the crystallographic independent unit each metal ion center is in a distorted octahedral geometry and coordinated by four O atoms from the four COO groups of four bta ligands and by two other O atoms from a bis-chelating oxalate ligand. The interconnected independent units create different types of channels running in different directions. The complexes **1** and **2** contain helical chains composed of left-handed and right-handed helices interlaced in pairs. Uncoordinated water molecules occupy the channels in the two complexes. Both of the complexes have intramolecular antiferromagnetic interactions.

Introduction

Self-assembled extended metal complexes as functional solid materials with specific network topologies are of great interest due to their fascinating molecular structures and potential applications to magnetism,¹ electrical conductivity,² ion exchange,³ separation,⁴ biology,⁵ and catalysis.⁶ Especially, the assembly of organic molecules and metal-ion building blocks can yield a new generation of multi-dimensional networks, which contain channels, or cavities of various sizes and shapes.⁷

The bridging ligand is one of the important factors that greatly influence the structures of coordination polymers. So far, a variety of coordination polymers with different structures and different bridging ligands have been synthesized. In particular, bi- or multi-dentate bridging ligands containing N- or O-donors, for example, 4,4'-bipyridine and $\text{C}_2\text{O}_4^{2-}$, two excellent bridging ligands, are used to bind metal centers, generating a number of one- two- and three-dimensional infinite metal–4,4'-bipy⁸ and metal– C_2O_4 ⁹ frameworks. The coordination chemistry of aromatic polycarboxylate–transition metal complexes has attracted considerable interest in inorganic chemistry and in some applied sciences. So far, supramolecular structures based on multidentate aromatic polycarboxyl bridging ligands such as rigid 1,4-benzenedicarboxylate,¹⁰ rigid benzene-1,3,5-tricarboxylate,¹¹ rigid benzene-1,2,4-tricarboxylate¹² and rigid benzene-1,2,4,5-tetracarboxylate,¹³ have been reported. Among these ligands, benzene-1,2,4,5-tetracarboxylate (bta) has eight oxygen atoms that can possibly induce a variety of coordination modes, and interesting structures with higher dimensions. Scheme 1 illustrates the versatile coordination abilities of the bta ion. However, so far, most of the coordination frameworks are built with only one type of bridging ligand. Although several interesting examples of combining two ligands including EDTA and 4,4'-bipy,¹⁴ pyrazine and 4,4'-bipy,¹⁵ oxalate and pyrazine,¹⁶ oxalate and 4,4'-bipy,¹⁷ pyridine-4-carboxylate and 4,4'-bipy,¹⁸ phthalate and 4,4'-bipy,¹⁹ and terephthalate and 4,4'-bipy,^{10b} have been reported, the design and synthesis of systems containing two or more different bridging ligands are much less well explored. Additionally, it is generally impossible as yet to predict either the composition of the product or its

structure and much more work is required for rational design and synthesis. Our recent efforts in designing new coordination network structures have focused largely on systems containing mixed multifunctional ligands. In this article, we describe the rational design and hydrothermal synthesis of a new type of the first oxalate–bta mixed-ligand 3-D metal coordination frameworks $[M_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2$ ($M = \text{Co}^{\text{II}}, \text{Fe}^{\text{II}}$).

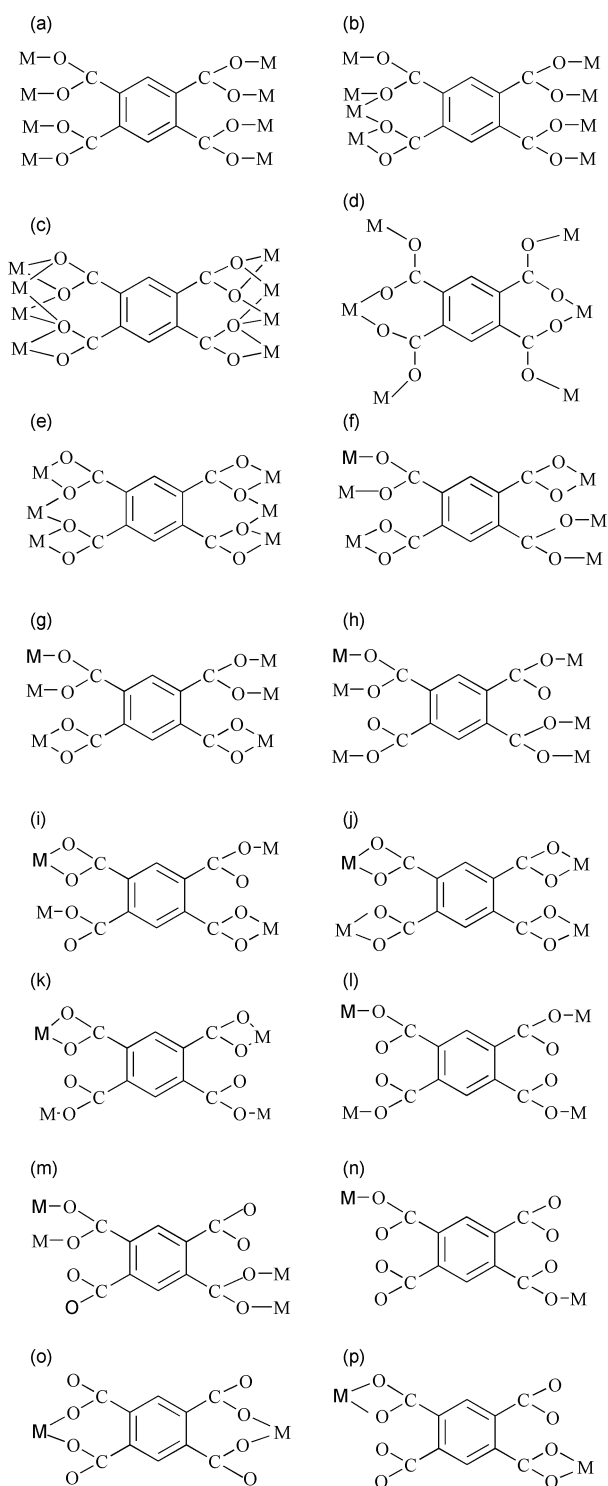
Experimental

Synthesis

All reagents were of analytical grade. The two complexes were hydrothermally prepared in 30 mL Teflon-lined stainless steel vessels filled to ~70% capacity. For complex **1**, a mixture of $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.091 g, 0.5 mmol), $\text{Na}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.085 g, 0.5 mmol), Na_4bta (0.17 g, 0.5 mmol) and H_2O (20 mL) in a mole ratio of 1 : 1 : 1 : 2222 was heated at 160 °C for five days under autogenous pressure. After cooling to room temperature, the mauve columnar product isolated by filtration was purified by repeated cycles of treating the aqueous slurry in an ultrasonic bath. The yield of the crystalline material **1** based on $\text{Co}(\text{II})$ was approximately 72%. Anal. Calc. for $\text{C}_6\text{H}_6\text{CoO}_8$: C, 27.16; H, 2.26; Co, 22.23. Found: C, 27.47; H, 1.99; Co, 22.19%. IR (KBr pellet, cm^{-1}): 3370m, 1683s, 1606vs, 1507m, 1440m, 1398m, 1349m, 1302m, 1147m, 945m, 875s, 821s, 771m, 721m, 680m, 603m, 558m, 491s. Complex **2** (brown columnar) was synthesized using the same molar ratios and the same procedure as for complex **1**, except that $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ was replaced by $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$. The yield of the crystalline material **2** based on $\text{Fe}(\text{II})$ was approximately 56%. Anal. Calc. for $\text{C}_6\text{H}_6\text{FeO}_8$: C, 27.49; H, 2.29; Fe, 21.38. Found: C, 27.71; H, 1.84; Fe, 21.61%. IR (KBr pellet, cm^{-1}): 3366m, 1679s, 1605vs, 1504m, 1442m, 1392m, 1345m, 1304m, 1147m, 946m, 873s, 820s, 773m, 716m, 677m, 600m, 554m, 494s.

Characterization

The elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analyses



Scheme 1 Typical coordination modes for the bta ligand.

were performed on a Perkin-Elmer Optima 3300DV spectrometer. Infrared spectra were measured on KBr disks with a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} region. XPS analysis was performed on an EASY ESCA spectrometer with an Mg-K α achromatic X-ray source. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in air. Magnetic measurements were obtained using an MPMS-XL magnetometer at $H = 5000$ Oe in the temperature range 4–300 K.

Structural determination

Suitable single crystals with dimensions of 0.112 \times 0.146 \times 0.267 mm for **1** and 0.212 \times 0.120 \times 0.114 mm for **2** were

Table 1 Crystal data and structure refinement for complexes **1** and **2**

	1	2
Empirical formula	$\text{C}_6\text{H}_6\text{CoO}_8$	$\text{C}_6\text{H}_6\text{FeO}_8$
Formula weight	265.04	261.96
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
$a/\text{\AA}$	9.3343(19)	9.3825(19)
$b/\text{\AA}$	13.738(3)	13.791(3)
$c/\text{\AA}$	6.7078(13)	6.7346(13)
$\beta/^\circ$	122.60(3)	122.37(3)
$V/\text{\AA}^3$	724.6(2)	736.0(3)
Z	4	4
μ/mm^{-1}	2.397	2.078
Obs. refl. [$I > 2\sigma(I)$]	782	719
Goodness-of-fit on F^2	1.090	1.066
$R1$ [$I > 2\sigma(I)$]	0.0275	0.0307
$wR2$ (all data)	0.0797	0.0735

selected for single-crystal X-ray diffraction analysis. The data of complex **1** were collected at 293(2) K on a Rigaku R-AXIS RAPID IP diffractometer (graphite monochromated Mo-K α radiation: $\lambda = 0.71073$ \AA); the data of complex **2** were collected at 293(2) K on Bruker SMART-CCD diffractometer (graphite monochromated Mo-K α radiation: $\lambda = 0.71073$ \AA). The two structures were solved by direct methods (SHELXTL Version 5.10)²⁰ and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were easily found from the difference Fourier map. In complex **1**, atom OW1 was disordered over two sites OW1/OW1', with occupancy of 0.35/0.65, respectively. OW1 and OW1' were refined with fixed thermal parameters. In complex **2**, atom OW1 was disordered over two sites OW1/OW1', with occupancy of 0.61/0.39, respectively. OW1 was refined with fixed thermal parameters. The H1 atom attached to the C1 atom was placed geometrically. In both of the structures, Co(or Fe), C4, C1, H1 had the same occupancy of 0.5. All of the non-hydrogen atoms were refined anisotropically. Experimental X-ray data for complexes **1** and **2** are listed in Table 1.

CCDC reference numbers 183360 (**1**) and 183361 (**2**).

See <http://www.rsc.org/suppdata/dt/b2/b209491f/> for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

The complexes **1** and **2** are constructed *via* a self-assembly process under mid-temperature hydrothermal conditions. The application of the hydrothermal technique to synthetic crystal growth has been established for some time.²¹ The generation of supramolecular frameworks is influenced by factors such as the solvent system, templates, counter-ions, ligand geometry, temperature, reaction time, pH level and the ratio between metal salts and ligands, *etc.*^{22–27} When different cobalt(II) and iron(II) sources (halide or acetate) are introduced in the reaction system the same products are obtained, which means that $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is the source of $\text{C}_2\text{O}_4^{2-}$ ligand. In an attempt to prepare polymers with different structures, the reactions of $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (or MCl_2), $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and Na_4bta in different molar ratios were conducted. These reactions, however, led to the same products in spite of their different yields. This fact indicates that the complexes isolated in this reaction system are the most stable under hydrothermal conditions. The XPS spectra for complex **1** shows a peak at 781.6 eV attributed to Co^{2+} and the XPS spectra for complex **2** shows a peak at 709.4 eV ascribed to Fe^{2+} . ICP analysis shows that there is no sodium in either of the complexes. The results of ICP analysis and elemental analysis, as shown in the Experimental section, are in good agreement with the formula $\{[\text{M}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)] \cdot (\text{H}_3\text{O})_2(\text{H}_2\text{O})_2\}_n$ ($\text{M} = \text{Co}^{\text{II}}, \text{Fe}^{\text{II}}$). For entropic reasons, the synthesis at a higher temperature can promote the formation of

polymer frameworks of higher dimensionality through the loss of terminal ancillary ligands.^{11a,13e} Thus, for example, Wood and co-workers synthesized a 3-D open-framework complex $[\text{Co}_5(\text{OH})_2(\text{bta})_2(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ at 190 °C,^{13c} while Rochon and Massarweh synthesized discrete molecular complexes $[\text{Co}(\text{H}_2\text{O})_5]_2(\text{bta}) \cdot 6\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_5]_2(\text{bta}) \cdot \text{H}_2\text{O}$ at room temperature.^{13f}

Crystal structures

Single-crystal X-ray diffraction analysis revealed that complexes **1** and **2** are isostructural having a novel three-dimensional (3-D) structure with different types of channels running in different directions. Viewed down the *b* axis, the structure consists of layers from double helical chains, which extend parallel to the *ab* plane of the crystal and are bridged by bta ligands along the *c* direction (Fig. 1(c)). The double helical chains are composed of left-handed and right-handed helices interlaced in pairs (Fig. 1(a)). The central axis of each helical chain is a twofold screw axis. The double helical chains linked by bridging oxalate ligands form a layer motif parallel to the *ab* plane (Fig. 1(b)). As is evident in Fig. 1(b), adjacent metal ions are linked by distinct ligands COO and C₂O₄ in two essentially orthogonal directions and in the ratio of 4 : 1. The M centers are coordinated by COO ligands along the *a* axis to form eight-membered M₂(COO)₂ narrow elliptical rings with dimensions of 4.823(1) × 3.720(4) Å and 4.836(1) × 3.773(4) Å for complexes **1** and **2**, respectively. In each of the elliptical rings, the major axis is the distance between two metal centers, and the minor axis is the distance between two atomic centers of carboxylate carbons. The repeated rings are fused to form a 1-D double helix array. On the double helical chain, each of two adjacent M ions is linked with the bridging C₂O₄ ligand alternately in opposite directions parallel to the *b* axis to form a 24-membered macrometallacyclic ring. Adjacent rings are fused to give a unique 2-D network (Fig. 1(b)) with the smaller rings disposed along the *a* axis. Sharing their bta bridges, the adjacent [M(C₂O₄)(COO)₄]_∞ layers are linked together to form a 3-D structure (Fig. 1(c)) with 14-membered (M–O–C–C=C–O)₂ “rhombic” channels. Using the four C atoms from the four carboxylate groups as the points of a “rhomb”, the lengths of its diagonals were measured as 9.654(5) and 7.926(1) Å for complex **1**, and 9.686(6) and 7.949(1) Å for complex **2**.

Each metal ion center is in a distorted octahedral geometry and coordinated by four O atoms from the COO groups of four different bta ligands and by two other O atoms from a bis-chelating oxalate ligand. Atoms O(3), O(3A), O(1) and O(1A) occupy the equatorial positions with an average bond length of 2.1156(2) Å for Co–O and 2.1408(2) Å for Fe–O, while atoms O(2) and O2(A) occupy the axial positions with an average bond length of 2.1618(2) Å for Co–O and 2.1906(1) Å for Fe–O. The framework is electrically neutral and the eight oxygen atoms from the four deprotonated carboxylate groups of each bta unit are all used as coordinating atoms, and bind to eight metal ions. When bta functions as a bridging ligand it usually has many coordination modes, in the case reported here it acts as a μ₈-bridging organic ligand; to our knowledge, this coordination mode has not been observed in other compounds.

Viewed down the *c* axis, the honeycomb network has prominent channels parallel to the *c* axis (Fig. 2(c)). Viewing the *ab* plane, the layer has two different types of cavities (A and B), as shown in Fig. 2(a). Cavity B is constructed with a 16-membered ring while cavity A, larger than the former, is surrounded by a 22-membered ring. The 2-D honeycomb layers stack along the *c* axis in the sequence *ABAB* where layers *B* are displaced by 8 Å along the *b* axis. Identical repeated units each consisting of a cavity A and a cavity B are aligned vertically to form 1-D channels along the *c* axis. The mean interlayer separations are about 4.67 Å for complex **1** and about 4.69 Å for complex **2**.

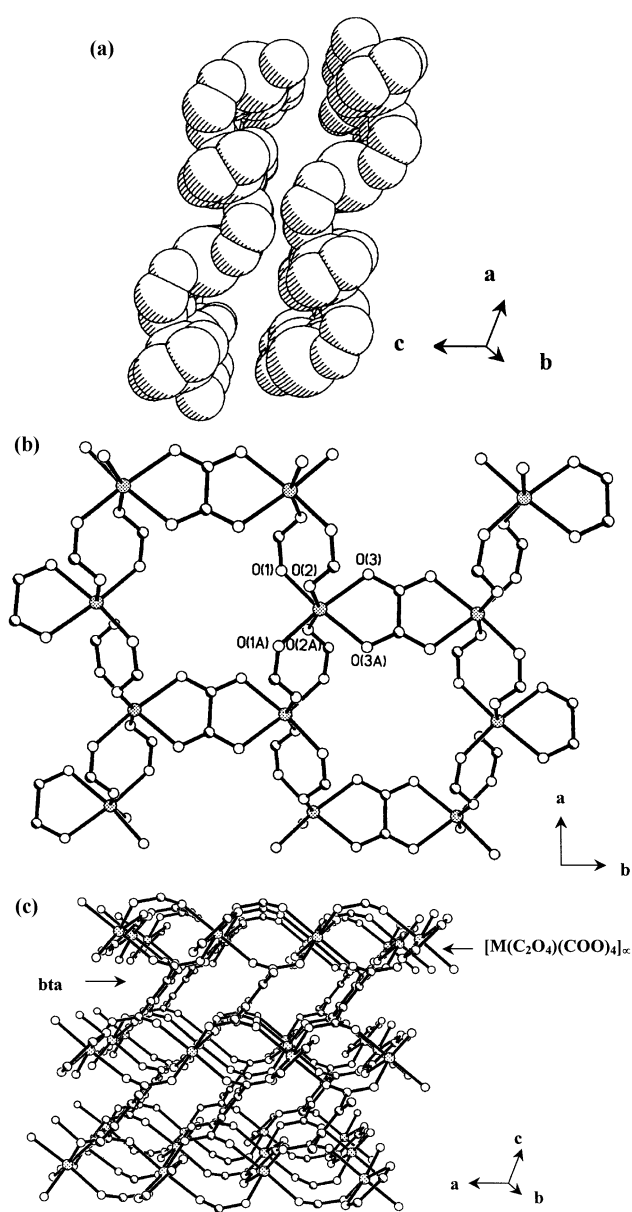


Fig. 1 (a) A view of the space-filling diagram of the left-helical and right-helical M/COO chains. (b) A view of the structure of the [M(C₂O₄)(COO)₄]_∞ layer. (c) A view of the structure of complexes **1** and **2** along the (101) plane, showing the channels.

(Fig. 2(b)). The channels are filled with guest water molecules, there being four water molecules per unit cell.

Characterization

The infrared spectra of complexes **1** and **2** are similar. Their IR spectra exhibit three characteristic bands of the bridging oxalate group (*i.e.* a strong band near 1660 cm⁻¹, a doublet in the 1350–1310 cm⁻¹ range and a band near 820 cm⁻¹) assignable to ν_{as}(CO), ν_s(CO) and δ(OCO), respectively. Furthermore, they exhibit the absorption bands of the asymmetric (ν_{as}(CO₂)) and symmetric (ν_s(CO₂)) vibration of bta appearing between 1600 and 1440 cm⁻¹. The Δν(ν_{as}(CO₂) – ν_s(CO₂)) values of 166 cm⁻¹ in complex **1** and of 163 cm⁻¹ in complex **2**, respectively, suggest bidentate bridge coordination modes of each carboxylate group of bta.²⁸ This is also in agreement with the crystal structure. An additional broad strong band near 3370 cm⁻¹ is assigned to the O–H stretching vibration of H₂O.

Thermogravimetric analysis for the two complexes was determined as shown in Fig. 3. There were three weight losses in complex **1**. The first weight loss of 3.54% in the range from 70 to 95 °C corresponds to loss of one of the four guest water

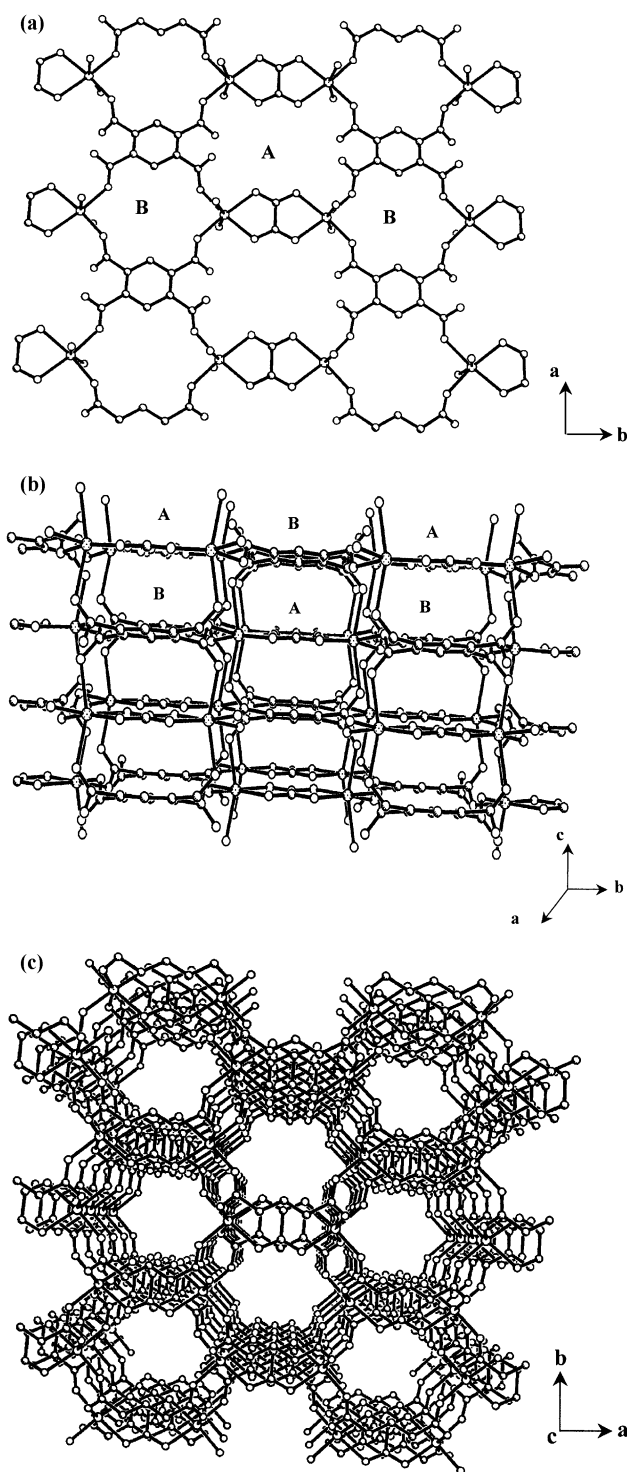


Fig. 2 (a) A view of the *ab* plane of complexes **1** and **2** where two different types of cavities A and B exist in the 2D network. (b) Representation of how the cavities A and B are aligned to form 1D channels along the *c* axis. (c) Projection of complexes **1** and **2** along the *c* axis, showing the stacked layers of the molecular honeycomb.

molecules $(\text{H}_2\text{O}/[\text{Co}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2)$, calc.: 3.40%); the second weight loss of 10.49% in the range from 130 to 175 °C corresponds to that of the other three guest water molecules $(3\text{H}_2\text{O}/[\text{Co}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2)$, calc.: 10.19%); the remaining weight (85.97%) corresponds to the framework $[\text{Co}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]$ (calc.: 86.41%), which does not lose weight until further heating to 380 °C. The final weight loss in the range from 380 to 490 °C was caused by the release of bta and oxalate ligands. The decomposition process was completed at 490 °C giving black cobalt oxides (Co_3O_4) as the final decomposition products, which constituted 30.38% of the ini-

tial weight (calc.: 30.27%). There were two weight losses in complex **2**. The first weight loss of 14.04% in the range from 70 to 170 °C corresponds to that of the four guest water molecules $(4\text{H}_2\text{O}/[\text{Fe}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]\cdot(\text{H}_3\text{O})_2(\text{H}_2\text{O})_2)$, calc.: 13.74%); the remaining weight (85.96%) belongs to the framework $[\text{Fe}_2(\mu_8\text{-bta})(\mu_2\text{-C}_2\text{O}_4)]$ (calc.: 86.26%), which does not lose weight until further heating to 380 °C. The final weight loss in the range from 380 to 470 °C was caused by the release of bta and oxalate ligands. The decomposition process was completed at 470 °C giving black iron oxide (Fe_2O_3) as the final decomposition product, which constituted 30.62% of the initial weight (calc.: 30.54%).

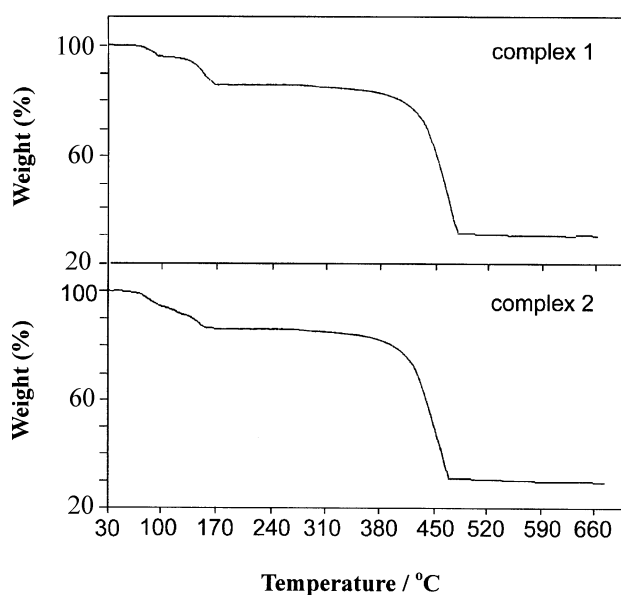


Fig. 3 TG curves for complexes **1** and **2**.

The magnetic susceptibilities χ_M of the two complexes were measured in the temperature range 4–300 K at 5000 Oe. Fig. 4 and 5, for complexes **1** and **2**, respectively, show plots of χ_M and μ_{eff} vs. *T*. As illustrated in Fig. 4, the effective magnetic moments of complex **1** at 300 K is $3.93 \mu_B$, slightly higher than the spin-only value ($3.87 \mu_B$) of an octahedral cobalt(II) ion ($S = 3/2$, $g = 2.0$). As illustrated in Fig. 5, the effective magnetic moments for complex **2** at 300 K is $4.20 \mu_B$, lower than the spin-only value ($4.90 \mu_B$) of an octahedral iron(II) ion ($S = 2$, $g = 2.0$). When the temperature was lowered, the effective magnetic moment in both of the complexes decreased gradually, which indicates the occurrence of antiferromagnetic interaction between the metal ions. Figs. 4 and 5 reveal antiferromagnetic behavior with the same maximum in the two susceptibility curves at 18 K for both of the complexes **1** and **2**. The molar susceptibilities χ_M of complexes **1** and **2** in the temperature range 100–300 K fit to the Curie–Weiss law. The calculated values of C_m were 0.2177 and $2.169 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for complexes **1** and **2**, respectively, while the corresponding Weiss temperatures θ were -12.56 and -6.77 K.

Conclusions

Two new three-dimensional complexes containing mixed oxalate–bta ligands have been designed and synthesized *via* a hydrothermal route. Both complexes consist of helical chains that form layers through bridging oxalate ligands. Adjacent layers are linked together, sharing their bta bridges, to form a 3-D structure with “rhombic” channels. Many fascinating structures will be assembled by both of the remarkably versatile bta and $\text{C}_2\text{O}_4^{2-}$ ligands. The complexes could be of great interest in terms of the characteristics of helical inorganic–organic compounds as well as their rational synthesis. The magnetic

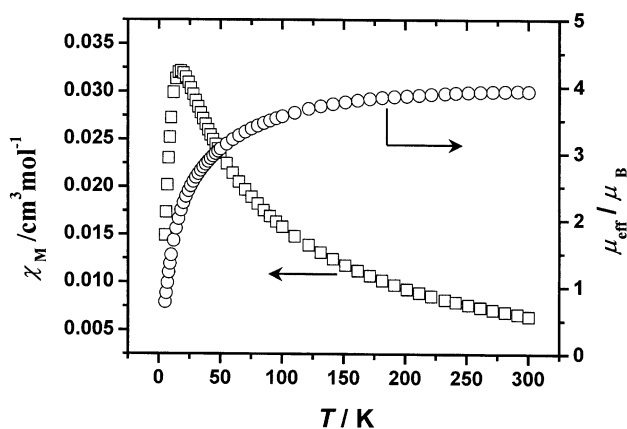


Fig. 4 Experimental χ_M vs. T and μ_{eff} vs. T curves for complex 1.

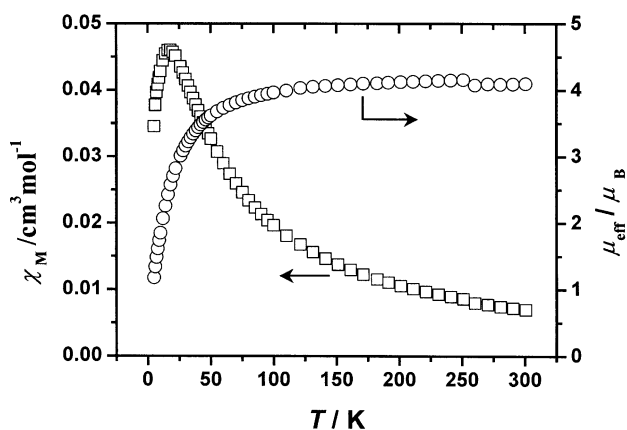


Fig. 5 Experimental χ_M vs. T and μ_{eff} vs. T curves for complex 2.

property studies suggest that metal–metal exchange interactions in the two complexes are antiferromagnetic.

Acknowledgements

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