A Novel Three-Dimensional Metal-Organic Framework Constructed from Two-Dimensional Interpenetrating Layers Based on Trinuclear Cobalt Clusters: $[Co_3(btec)(C_2O_4)(H_2O)_2]_n$

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Keywords: Hydrothermal synthesis / Carboxylate ligands / Cobalt / Coordination polymers / Magnetic properties

A novel coordination polymer $[Co_3(btec)(C_2O_4)(H_2O)_2]_n$ (**1**; btec = 1,2,4,5-benzenetetracarboxylate) has been hydrothermally synthesized and characterized by IR, XPS, XRPD, TG analysis and single-crystal X-ray diffraction. The structural analysis reveals that **1** exhibits a new three-dimensional metal-organic framework constructed from two-dimensional parallel interpenetrating networks based on trinuclear cobalt cluster building blocks. Such interpenetrating composite networks in **1** represent the first example in the {M-btec} (M = transition metal) system. Variable-temperature magnetic susceptibility measurements indicate an antiferromagnetic behavior in **1**.

Introduction

The design and synthesis of infinite high-dimensional (especially two- and three-dimensional) metal-organic frameworks has attracted extensive interest in recent years, not only due to their intriguing structural motifs but also their potential applications in catalysis, molecular adsorption, and optical, electronic and magnetic materials.[1−2] Although it is not yet possible to prepare fully predictable metal-organic frameworks on the basis of rational design, recent exciting developments in coordination and organic chemistry provide great possibilities for the creative synthesis of desired novel frameworks.[3−5]

Among various metal-organic frameworks, the entangled structure, in which two or more infinite networks interpenetrate each other, is an attractive structural feature and has been widely researched.[6] In general there are two important factors for the formation of interpenetrating structures: one is that infinite networks contain large pores or cavities for interpenetration, and the other is that the individual 2-D networks should possess some appropriate elements of corrugation or undulation.[5] The use of long organic bridging ligands is often regarded as an effective strategy for the construction of such compounds.[7] In this aspect, organic aromatic polycarboxylate ligands, such as 1,4-benzenedicarboxylate and 1,3,5-benzenetricarboxylate, have been widely used in the construction of high-dimensional structures with large pores and/or undulated layers;[8] some interpenetrating frameworks have also been successfully prepared.[9] More recently, 1,2,4,5-benzenetetracarboxylate (btec) has proved to be a good candidate for assembling high dimensional metal-organic architectures owing to its two interesting structural features. In the first place, it contains multiple bridging moieties, which leads to a variety of connection modes with transitional metal centers and provides abundant structural motifs. Secondly, it can act both as a hydrogen-bond donor and as a hydrogen-bond acceptor due to the existence of protonated and/or deprotonated carboxyl groups.[10a] To date, a series of 2-D and 3-D metal-organic compounds in the {M-btec} (M = transition metal) system with large pores or undulated networks have been reported,[10] however, no interpenetrating structural feature in this system has hitherto been observed.

During our research on the hydrothermal synthesis of metal-organic frameworks in {M-btec} systems, another kind of organic bis-chelating oxalate ligand ($C_2O_4^{2-}$) has been introduced and a new coordination polymer, $[Co_3(btec)(C_2O_4)(H_2O)_2]_n$ (**1**), has been synthesized. Compound **1** exhibits a 3-D metal-organic framework consisting of 2-D interpenetrating networks on the basis of trinuclear cobalt cluster building blocks. To the best of our knowledge, compound **1** represents the first example in the {M-btec} system that possesses the interpenetrating structural feature. Furthermore, the btec ligand shows an unusual coordination mode linked with ten metal centers.

Results and Discussion

The hydrothermal reaction of an alkaline aqueous solution of $Co(C_2O_4)\cdot 2H_2O$, H_4btec and NaOH gives rise to

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DOI: 10.1002/ejic.200300221

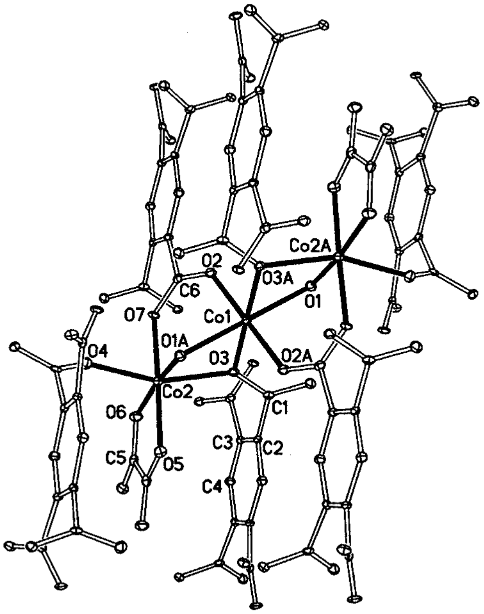
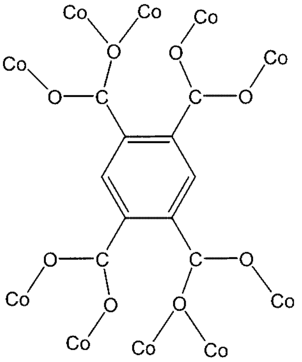


Figure 1. ORTEP drawing of **1** showing the local coordination environment of Co^{II} (thermal ellipsoids at 50% probability)



Scheme 1. The coordination mode of the btec ligand in compound **1**

1 as purple block crystals. Single-crystal X-ray diffraction analysis revealed that **1** exhibits a novel 3-D metal-organic framework based on trinuclear cobalt cluster building blocks. The fundamental unit is shown in Figure 1. There are two crystallographically unique Co centers in the asymmetric unit, both displaying a distorted octahedral coordination geometry. The Co(1) center coordinates to four oxygen atoms of four different carboxylate groups, with Co(1)−O$_{(carboxyl)}$ distances in the range 1.9966(18)−2.0639(19) Å, and to two oxygen atoms of water molecules, with Co(1)−O$_{(water)}$ distances of 2.1991(19) Å. The O−Co(1)−O bond angles vary from 78.43(7)° to 180.00(14)°. The Co(2) center coordinates to three oxygen atoms of three different carboxylate groups [Co(2)−O$_{(carboxyl)}$ 2.0765(18)−2.1607(19) Å], two oxygen atoms of the oxalate ligand [Co(2)−O$_{(oxalate)}$ 2.0638(19)−2.131(2) Å] and one oxygen atom of a water molecule [Co(2)−O$_{(water)}$ 2.234(2) Å]. The O−Co(2)−O bond angles range from 75.71(7)° to 174.70(8)°. The three {CoO_6} octahedra are connected together to form a linear trinuclear Co cluster in an edge-sharing mode. In addition, four carboxylate groups of the btec ligand exhibit two kinds of coordination modes with Co centers, as shown in Scheme 1. Two carboxylate groups act as a bidentate ligand, bridging two Co centers, while the other two exhibit an unusual bidentate bridging mode, linking three Co centers. Thus, one btec ligand is connected to ten Co centers, which has rarely been observed in previous reports.[10h] Furthermore, the oxalate groups ($C_2O_4^{2-}$) act as a bidentate bridging ligand to link trinuclear Co clusters into an interesting 1-D undulated chain. All these undulated chains are further connected by the btec ligands to form a 2-D grid-like network with large pores, as shown in Figure 2. The pore size is ca. 9.16 × 10.03 Å. The most important structural feature of **1** is that two such individual 2-D grid-like networks are self-entangled to form an interesting 2-D parallel interpenetrating layer (see Scheme 2 and Figure S1). To the best of our knowledge, no interpenetrating composite

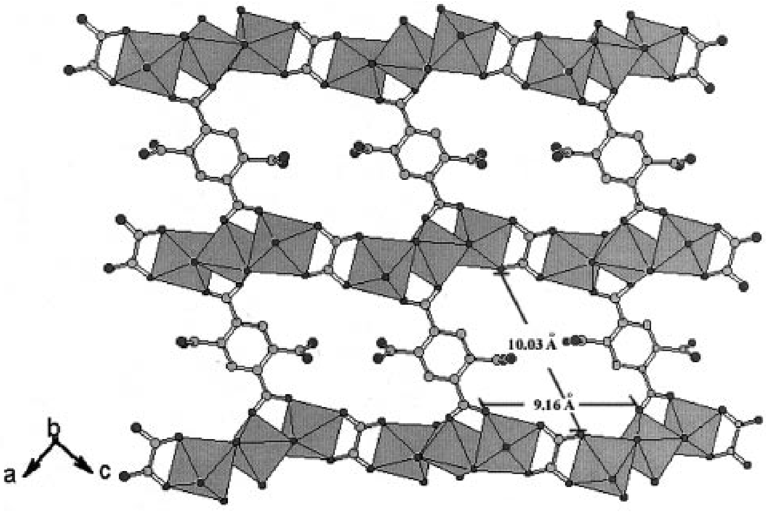
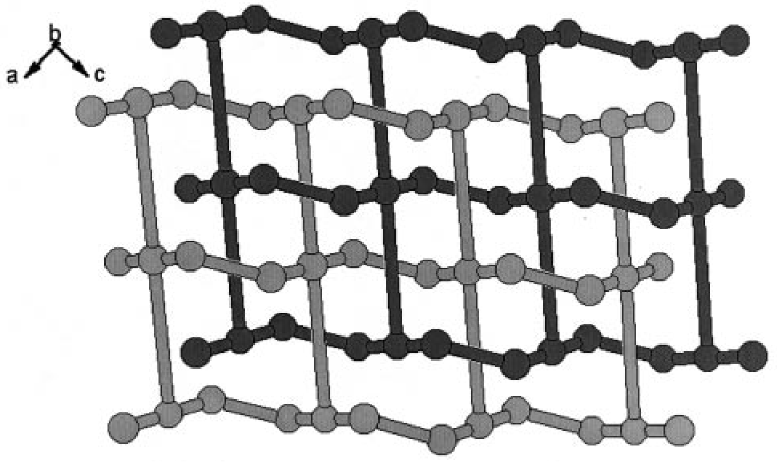


Figure 2. Polyhedral representation of the individual 2-D gridlike network of **1** viewed along the *b* axis; the polyhedra represent {CoO_6} octahedra



Scheme 2. Simplified schematic representation of the 2-D parallel interpenetrating network of **1** along the *b* axis

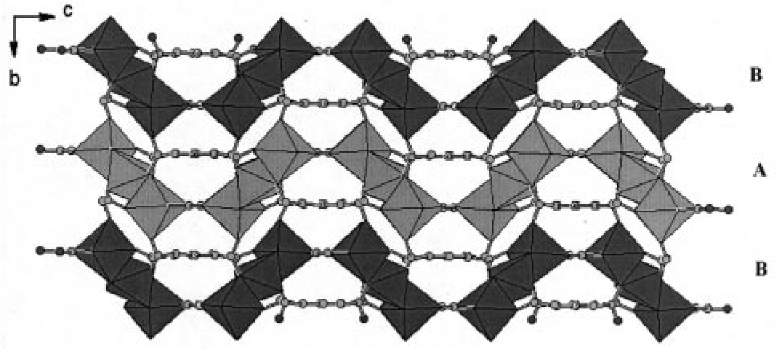


Figure 3. Polyhedral representation of the 3-D metal-organic framework of compound **1** viewed along the *a* axis; the light and dark colors represent two 2-D interpenetrating layers with different extending directions, respectively

network has hitherto been observed in the {M-btec} system. It is noteworthy that the presence of both large pores and an undulated element in the individual 2-D grid-like network provides the possibility of assembling interpenetrating architectures.

It is also interesting that these 2-D interpenetrating networks exhibit a wavelike layered structure along the *a* axis with each arched unit supported by the btec bridging ligand (see Figure 3). The adjacent 2-D interpenetrating layers extend perpendicular to each other in the *ac* plane and are alternately arranged in an ABAB mode along the *b* axis as shown in Figure 3. Thus, a 3-D metal-organic framework is formed by the connection of btec ligands (see Figure 3 and Figure S2).

The valence sum calculations of Co and O atoms are listed in Table S1. The bond-valence calculations (Co, 2.00) suggest all Co atoms are in the +2 oxidation state.[11] This result is also supported by an XPS measurement of the compound in the energy region of $Co2p^{1/2}$ and $Co2p^{3/2}$. The XPS spectrum (shown in Figure S3) gives one peak at 780.8 eV, attributable to Co^{2+}.[12] The O(1) atom has a bond-valence sum of 0.48, suggesting that it belongs to a coordinated water molecule. The O(2)−O(7) atoms have bond-valence sums of 1.90, 1.80, 1.92, 1.86, 1.85 and 1.81, respectively. These results indicate that all the oxygen atoms of the btec ligand and oxalate groups are deprotonated.[13] These results are consistent with the charge-balance considerations and alkaline synthetic conditions of compound **1**.

The variable-temperature magnetic susceptibility was measured from 2 K to 300 K at 5000 Oe for **1**. The magnetic data of **1** are displayed in Figure 4, plotted as the thermal variation of $\chi_m T$ and $1/\chi_m$. The $\chi_m T$ vs. T plot has a value of 9.32 emu·K·mol^{-1} at 300 K, and decreases continuously on cooling to a value of 0.54 emu·K·mol^{-1} at 2 K. The inverse susceptibility ($1/\chi_m$) plot as a function of temperature (T) is linear, closely following the Curie−Weiss law with C = 10.17 emu·K·mol^{-1}, corresponding to about one $S = 3/2$ spin per formula unit with $g = 2.31$ for Co^{II} centers. The effective magnetic moment per metal atom at 300 K, 4.47 μ_B, is in the range of experimentally observed values for high spin Co^{II} ions. The Weiss temperature, $\theta = -25.59$ K, indicates that predominantly antiferromagnetic interactions exist between metallic Co^{II} centers. According to the structure of compound **1**, it could be presumed that the main magnetic interactions between the metal centers might happen in 1-D $\{Co_3(H_2O)_2(C_2O_4)\}$ chains, while the superexchange interactions between Co ions through the btec bridge can be ignored owing to the length of the btec ligands.[14]

The simulated and experimental XRPD patterns of compound **1** are shown in Figure S4. Their peak positions are

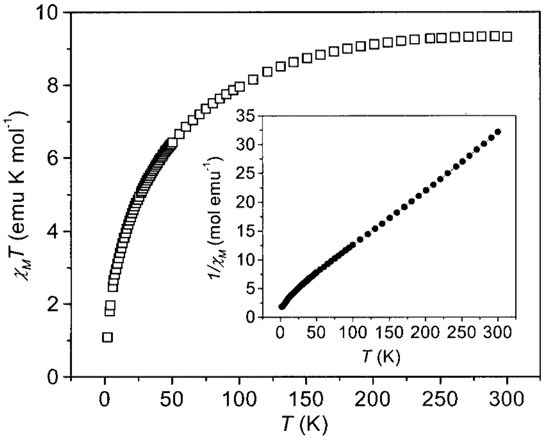


Figure 4. Thermal variation of $\chi_m T$ and $1/\chi_m$ for compound **1**

in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples. In the TG curve of compound **1** (see Figure S5), there is only one weight loss of 58.6% in the temperature range 200−450 °C, corresponding to the successive release of coordinated water, oxalate and btec ligands. Elemental analysis found that the brown residue might be CoO. The whole weight loss (58.6%) is in good agreement with the calculated value (59.2%).

Conclusion

In this work, a novel 3-D metal-organic framework $[Co_3(btec)(C_2O_4)(H_2O)_2]_n$ with 2-D parallel interpenetrating networks has been reported. Compound **1** is the first example in the {M-btec} system that possesses this interpenetrating structural feature. Both the large porous network and the undulated structural features are realized in the individual 2-D network (Figure 2) of **1** by the self-assembly of btec, $C_2O_4^{2-}$ and the linear trinuclear Co cluster building blocks, which provide great feasibility for the construction of interpenetrating network. The successful preparation of **1** indicates that metal-organic frameworks might be designed and synthesized according to specific structural features and inherent stereochemical and interactive information stored in the metal ions and organic ligands.[10a]

Experimental Section

Synthesis of 1: Compound **1** was synthesized from the reaction of $Co(C_2O_4)\cdot 2H_2O$ (0.091 g, 0.5 mmol), H_4btec (0.13 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and H_2O (8 mL, 444 mmol) in an 18 mL Teflon-lined autoclave under autogenous pressure at 160 °C for two days, followed by slow cooling (10 °C/h) to room temperature. The pH value of the reaction solution was ca. 8 and the final pH value was ca. 8.5. The product was washed with distilled water and air-dried at 50 °C. The product was of high quality in the form of purple block crystals (Yield: 0.079 g, 86% based on Co). $C_{12}H_6Co_3O_{14}$ (551.0): calcd. C 26.2, H 1.1, Co 32.1; found C 26.9, H 0.9, Co 31.9. Selected FT-IR data (KBr pellet): $\tilde{\nu}$ = 1638(s) cm^{-1}, 1589(s), 1509 (s), 1457(s), 1396(s), 1352(w), 1309(s), 1209(w), 1155(w), 1105(m), 915(s), 887(s), 836(s), 827(w), 808(w), 794(s), 763(w), 736(w), 698(w), 684(w), 635(w), 587(s), 535(s), 485 (s), 460 (w).

X-ray Crystallography: A purple crystal of **1** with dimensions of 0.578 ×0.378 × 0.258 mm^3 was glued onto a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-K_α monochromated radiation (λ = 0.71073 Å) at 93 K in the range of $2.12 < \theta < 27.12°$. An empirical absorption correction was applied.[15] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXL-97 software package.[16] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on C atoms were located from difference electron-density maps. Crystal data: $C_{12}H_6Co_3O_{14}$, M_r = 550.96, orthorhombic, *Pbcn*, a = 7.0821(14), b = 12.557(3), c = 15.997(3) Å, $\alpha = \beta = \gamma = 90°$, U = 1422.6(5) Å^3, Z = 4, D_c = 2.572 gcm^{-3}, μ = 3.550 mm^{-1}, $F(000)$ = 1084, $R1$ = 0.0263, $wR2$ = 0.0831 and S = 1.065 for 1625 reflections with $I > 2\sigma(I)$ and 133 parameters ($R1$ = 0.0309, $wR2$ = 0.0845 for all 2988 data). CCDC-205531 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (20171010).

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Received April 17, 2003