A Novel Three-dimensional Structure Based on Both μ_8-Bridging Benzene-1,2,4,5-tetracarboxylate and μ_2-Bridging Oxalate

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This novel crystal structure of the coordination polymers $\{[M(\mu_8\text{-bta})_{1/2}(\mu_2\text{-}C_2O_4)_{1/2}]\cdot(H_2O)_4\}_n$ (**1**: M=Co^{III}; **2**: M=Fe^{III}; bta = benzene-1,2,4,5-tetracarboxylate) is based on both bta and oxalate as bridging ligands and contains helical chains composed of left-handed and right-handed helices interlaced in pairs.

The assembly of organic molecules and metal-ion building blocks can yield a new generation of multi-dimensional networks that contain channels or cavities of various sizes and shapes.[1] The bridging ligand is one of the important factors that greatly influence the structures of coordination polymers.[2] Organic polycarboxyl is one of excellent bridging ligands that constitute coordination polymers. So far supramolecular structures based on one of the multidentate polycarboxyl bridging ligands such as the rigid 1,4-benzenedicarboxylate,[3] rigid benzene-1,3,5-tricarboxylate,[4] oxalate[5] and rigid benzene-1,2,4,5-tetracarboxylate,[6] have been reported more and more often. The coordination polymers **1** and **2** are based on both of bta and oxalate as bridging ligands and possess attractive novel structural features. Here we report the syntheses[7] and X-ray crystal structure analyses[8] of the coordination polymers **1** and **2**, which have not only an infinite helical chain, but also both left-handed and right-handed helical chains in one compound.

Single-crystal X-ray diffraction analysis revealed that compounds **1** and **2** as analogues have a novel three-dimensional structure. Viewed down the *b* axis, the structure consists of layers from helical chains, which extend parallel to the *ab* plane of the crystal and are bridged by bta ligands along the *c* direction (Figure 1). The helical chains are composed of left-handed and right-handed helices interlaced in pairs (Figure 2). The central axis of each helical chain is a twofold screw axis. And these helical chains linked by bridging oxalate ligands form a layer motif in the *ab* plane (Figure 3). Shown as in Figure 3, that the adjacent metal ions are linked by distinct ligands COO and C_2O_4 in two essentially orthogonal directions and in the ratio of 4 : 1. The COO ligand coordinates to M centers along *a* axis to form 8-membered $M_2(COO)_2$ narrow elliptical rings with dimensions of 4.8 × 3.8 Å and the repeating units are fused to form 1D helix array. The adjacent M ions on the helical chain link with, alternately in opposite direction, the bridging C_2O_4 ligands parallel to *b* axis to form a 24-membered macrometallacyclic ring. The adjacent rings are fused to a unique 2D network with the smaller rings disposed along the *a* axis. The adjacent $[M(C_2O_4)(COO)_4]_\propto$ layers are linked together, sharing their bta bridges, to form a 3D structure (Figure 1) with "rhombic" channels. Using the atomic centers of carboxylate carbons as the points of a "rhombic", we measured the edges of the "rhombic" as 4.4 Å or 7.1 Å across its diagonal.

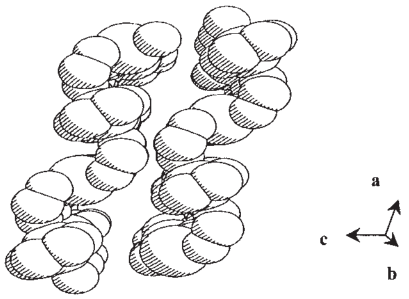

Figure 2. A view of the space-filling plot of the left-helical and right-helical M/COO chains.

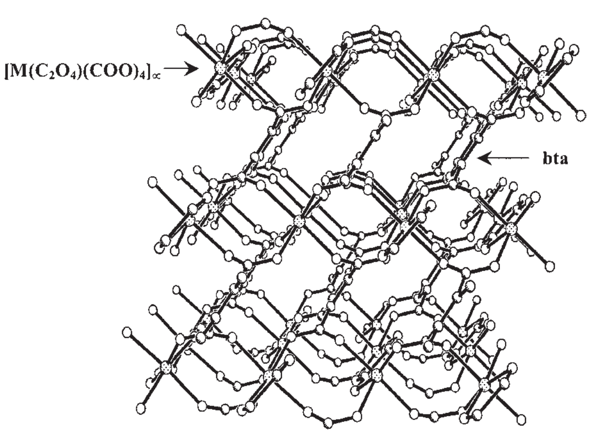

Figure 1. A view of the structure of compound **1** and compound **2** along the (101) plane, showing the channels.

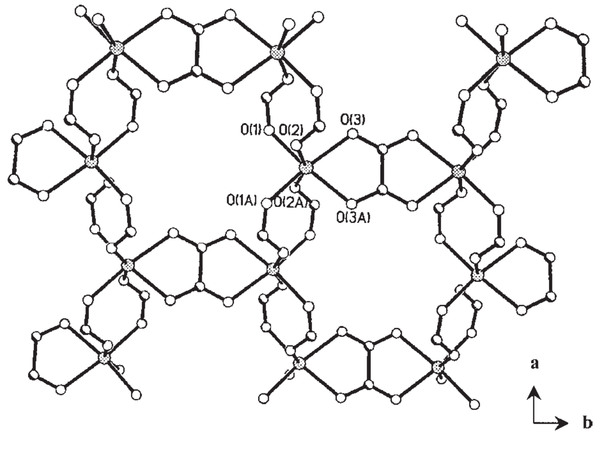

Figure 3. A view of the structure of the $[M(C_2O_4)(COO)_4]_\propto$ layer.

Each metal ion center is six-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. Here the metal ion completes its pseudooctahedral coordination sphere in which the atoms O(3) O(3A) O(1) O(1A) occupy the equatorial positions. The eight oxygen atoms from four deprotonated carboxyl groups of each bta unit, all used as coordinating ones, 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 μ_8-bridging organic ligand, to our knowledge, this coordination mode has not been observed in other compounds.

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7 Compound **1** was prepared by mixing CoC_2O_4(146.9 mg, 1.0 mmol) and Na_4bta (342 mg, 1.0 mmol) in an aqueous solution (20 mL), being stirred in the basic mixture for 6 h. The resulting solution was heated at 160 °C for 120 h under autogenous pressure. After cooling to room temperature, the mauve columnar crystals of **1** (192 mg, 64% yield) were obtained and washed with distilled water and ethanol, and dried in air. Anal. Calcd for $C_3H_{4.5}Co_{0.5}O_5$: C, 24.00; H, 3.00; Co, 19.67. Found: C, 23.87; H, 3.19; Co, 19.59. Compound **2** (145 mg, 49% yield) was synthesized through the same procedure as compound **1**, but CoC_2O_4 was replaced by FeC_2O_4. Anal. Calcd for $C_3H_{4.5}Fe_{0.5}O_5$: C, 24.24; H, 3.03; Fe, 18.85. Found: C, 24.01; H, 3.24; Fe, 18.81. The infrared spectra of compounds **1** and **2** are similar. **1**: IR (KBr) ν/cm^{-1}: 3366(m), 1605(vs), 1504(m), 1442(m), 1392(m), 1345(m), 1304(m), 1147(m), 946(m), 873(s), 820(s), 773(m), 716(m), 677(m), 600(m), 554(m), 494(s). The thermal decomposition of compound **1** and compound **2** takes place by three separate steps in the range of 30–700 °C. The first step is at 120–210 °C corresponding to the loss of crystal water molecules. The second and third steps (270–380 °C) are contributed to the loss of organic acids and the collapse of the framework.

8 Crystal structure analysis: The data of compound **1** were collected at 293(2) K on a Rigaku R-AXIS RAPID IP diffractometer (graphite-monochromated Mo Kα radiation: $\lambda = 0.71073$ Å); the data of compound **2** were collected at 293(2) K on a Bruker SMART-CCD diffractometer (graphite-monochromated Mo Kα radiation: $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXTL Version 5.10) and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Crystal data: Compound **1**: for $C_3H_{4.5}O_5Co_{0.5}$, $M_r = 150.03$, monoclinic, $C2/m$, $a = 9.3343(19)$ Å, $b = 13.738(3)$ Å, $c = 6.7078(13)$ Å, $\beta = 122.60(3)°$, $Z = 4$, $V = 724.6(2)$ Å^3, $D_{calcd} = 1.375$ g cm^{-3}, μ(Mo Kα) = 1.217 mm^{-1}, $F(000) = 304$, GoF = 1.086. A total of 828 reflections were collected and 828 are unique ($R_{int} = 0.0148$). The final $R1$ and $wR2$ are 0.0315 and 0.0839, respectively, for 82 parameters and 782 reflections ($I > 2\sigma(I)$). Compound **2**: $C_3H_{4.5}O_5Fe_{0.5}$, $M_r = 148.49$, monoclinic, $C2/m$, $a = 9.3825(19)$ Å, $b = 13.791(3)$ Å, $c = 6.7346(13)$ Å, $\beta = 122.37(3)°$, $Z = 4$, $V = 736.0(3)$ Å^3, $D_{calcd} = 1.340$ g cm^{-3}, μ(Mo Kα) = 1.057 mm^{-1}, $F(000) = 302$, GoF = 1.050. A total of 2101 reflections were collected and 808 are unique ($R_{int} = 0.0385$). The final $R1$ and $wR2$ are 0.0372 and 0.0900, respectively, for 82 parameters and 766 reflections ($I > 2\sigma(I)$).