

## Reversible Repositioning of Zinc Atoms within Single Crystals of a Zinc Polycarboxylate with an Open-Framework Structure

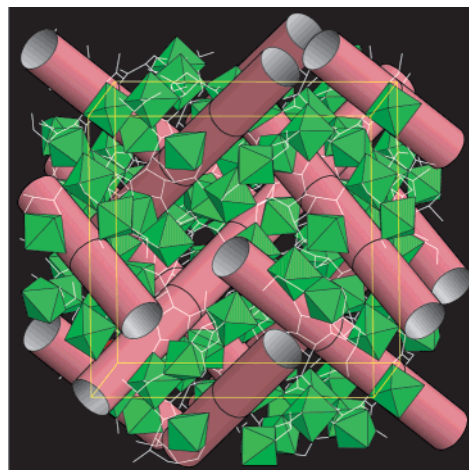
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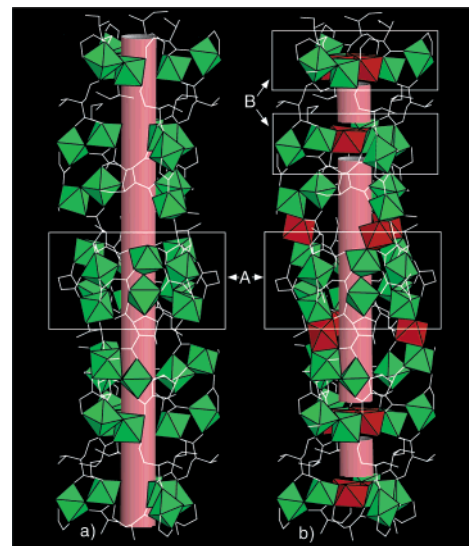
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Synthesis of compounds with open-framework structures built of metal centers interconnected by organic linkers has become one of the most popular areas of research in synthetic materials chemistry. The reasons for this include: (a) the huge variety of readily available organic groups that can serve as linkers, (b) the large number of transition- and main-group metals that can play the role of metal centers, (c) the easy synthetic approach, usually heating a mixture of metal salts and organic compounds in an appropriate solvent, and (d) the almost unprecedented structural diversity and many novel phenomena exhibited by such compounds. Some groups, among which those of Clearfield, Férey, Rao, Yaghi, and Zaworotko, have made extensive progress in this area, and some of them have even made successful attempts in predicting the structures.<sup>1</sup> The diversity of the linkers, however, is so vast that structure prediction works only for specific classes of linkers. Luckily, there is a vast territory populated with unpredictable compounds. Thus, complex linkers with large numbers of potential coordinating sites fall in the latter category. Here we present the results of using tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA, also referred to as  $H_4L$ )  $C_4H_4O(COOH)_4$  with nine coordinating oxygen atoms to link Co and Zn in extended open-framework structures. While studying the resulting new compounds, we observed an unprecedented phenomenon. Upon heating under vacuum, the zinc compound not only loses water, but some of the zinc atoms move to different positions in the structure while preserving the crystallinity of the single crystals. Even more astonishing was the observation that upon exposure to air at room temperature, the dehydrated zinc compound reabsorbs all of the water, and the zinc atoms move back to their original positions, again without any deterioration of the crystals.

The two new compounds with general formulas  $[Co_2L(H_2O)_2] \cdot 2.33H_2O$  (**1**) and  $[Zn_3L(OH)_2(H_2O)_{1.33}] \cdot 3H_2O$  (**2**) were synthesized hydrothermally from mixtures of THFTCA and  $CoCl_2$  or  $ZnCl_2$ , respectively.<sup>2</sup> Despite their different formulas, the two compounds crystallize in the same cubic space group  $Pa\bar{3}$  with similar lattice parameters,  $a = 20.5213(3)$  and  $20.7929(3)$  Å for **1** and **2**, respectively, and similar but quite complex structures.<sup>3</sup> The major difference is that in addition to the two different metal positions in **1**, compound **2** has an additional third zinc position. The structures are built of  $MO_6$  octahedra interconnected by the 9-dentate tetracarboxylate linkers (Figure 1). Large nonintersecting channels along the cubic body diagonals are found in **1** (Figures 1 and 2a). These channels are filled with noncoordinated water while their walls are made of coordinated water and carboxylic oxygen atoms. The building motif of **1** has a ring of six pairs of corner-sharing octahedra (fragment **A** in Figures 2a and 3). The same rings and similar channels are found in **2** (Figure 2b), but additional  $ZnO_6$  octahedra (red in Figure 2b) block the channels. The latter octahedra are made of four  $H_2O/OH$  molecules and two carboxylic oxygens. Three such octahedra form a triangle by sharing edges with each



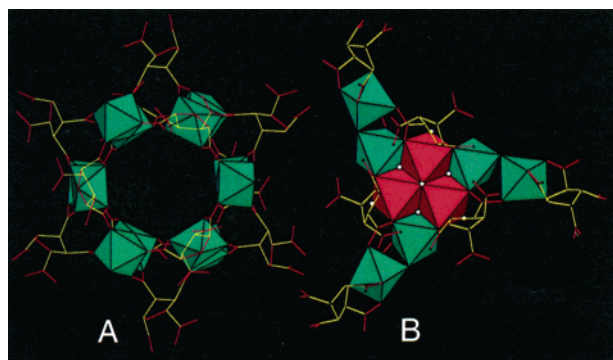
**Figure 1.** Polyhedral view of the structure of **1** (cell outlined) built of  $MO_6$  octahedra and tetracarboxylic linkers. Channels filled with noncoordinated water, shown as tubes, run along the body diagonals.



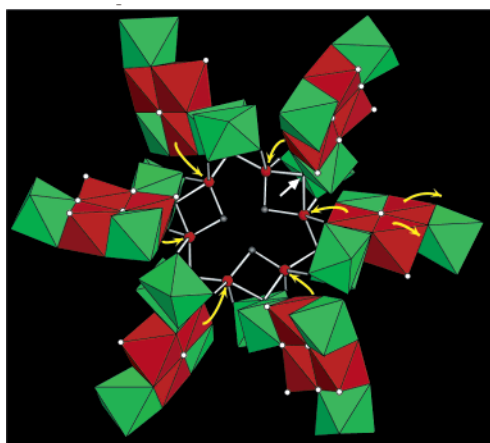
**Figure 2.** Closer view of the channels in **1** (a) and the same but blocked channels in **2** (b). Fragments **A** and **B** (see also Figure 3) are the building blocks in **1** and **2**, respectively. The additional zinc octahedra in **2** that block the channels are shown in red.

other. This core shares edges with three pairs of corner-sharing octahedra and forms fragment **B** (Figures 2b and 3) that builds structure **2**.

Single crystals of the two compounds can be dehydrated by heating under vacuum, and the crystals remain single up to 210 °C for **1** and 230 °C for **2**. The structures of such crystals were determined in sealed glass capillaries. It was found that above 170 °C compound **1** loses all noncoordinated and single-bonded water



**Figure 3.** Closer view of fragments **A** and **B** in **1** and **2**, respectively (see also Figure 2). **A** is a ring of six pairs of corner-sharing octahedra, while **B** has the same pairs of corner-sharing octahedra as in **A** but they are fused further with a triangle of additional edge-sharing octahedra (red). The zinc atoms in the latter are coordinated by four  $\text{H}_2\text{O}/\text{OH}$  groups (white circles) and only two carboxylic oxygen atoms.



**Figure 4.** Upon heating under vacuum, the zinc atoms forming the core (red) of fragments **B** (shown as six incomplete fragments) move to positions inside the ring of fragment **A** (yellow arrows). Additional water molecules (gray) are shared between pairs of neighboring new positions. Some  $\text{H}_2\text{O}/\text{OH}$  ligands are completely deprotonated to four-bonded oxygen atoms (white arrow).

to become blue-purple  $\text{Co}_2\text{L}(\text{H}_2\text{O})$ .<sup>4</sup> Furthermore, upon exposure to air for a few days, the crystals reabsorb the lost water to the original formula  $\text{Co}_2\text{L}(\text{H}_2\text{O})_2 \cdot 2.33(\text{H}_2\text{O})$  and color.<sup>4</sup> Such reversible single crystal to single crystal transformations are relatively rare and somewhat unexpected.<sup>1,5</sup>

The big surprise, however, came from similar experiments with compound **2**. When heated above 170 °C under vacuum, the compound not only loses water, but also the zinc atoms forming the core of motif **B** abandon their positions and move to a different place in the structure, inside the ring of motif **A** (Figure 4).<sup>6</sup> Apparently, the four original  $\text{H}_2\text{O}/\text{OH}$  ligands of the octahedral coordination of these atoms are removed during dehydration, and the atoms end up with very low coordination, as low as two-coordinate. This forces them to “sample” the surrounding area for better coordination sites, perhaps traveling as  $\text{Zn}(\text{OH})_x(\text{H}_2\text{O})_y$  complexes, and the new position, ca. 3 Å away, is found. This position provides two carboxylic and two  $\text{H}_2\text{O}/\text{OH}$  oxygens as ligands. The latter are shared corners of  $\text{ZnO}_6$  octahedra in the as-prepared compound, but become completely deprotonated to a four-bonded oxygen atom (inside a  $\text{Zn}$ -tetrahedron) after dehydration. Each repositioned zinc atom achieves trigonal bipyramidal coordination

by sharing an additional water molecule with another such atom (Figure 4), and the formula becomes  $[\text{Zn}_3\text{L}(\text{O})(\text{H}_2\text{O})_{0.5}]$ .

Even more amazing was the behavior of the dehydrated compound **2** when exposed to air. At room temperature for 2 days, its single crystals not only reabsorb most of the lost water, but most of the disordered zinc atoms (68%) move back to their original positions.<sup>6</sup> Presumably, after a sufficiently long period of time (at room temperature), the compound will return to its original structure.

Perhaps the closest analogue to the observed zinc hopping is the single crystal to single crystal conversion observed in some alkali metal/bismuth/selenium compounds where, upon oxidative removal of cations, whole layers of Bi/Se become closer to each other and form bonds between themselves.<sup>7</sup> Currently, we are carrying out rigorous investigations of the ability of both dehydrated compounds to reabsorb molecules other than water. Furthermore, some of the Zn and Co in the dehydrated compounds are square-pyramidal and present open and accessible coordination sites for further reactivity studies. It is difficult to assess the practical significance of the observed zinc hopping in compound **2** at this time. However, the uniqueness of the phenomenon is unquestionable.

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**Supporting Information Available:** X-ray crystallographic file in CIF format for all structures (as prepared, dehydrated, and hydrated). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (2) Mixtures of THFTCA,  $\text{MCl}_2$ , and  $\text{H}_2\text{O}$  in molar ratios 1:6:1120 for **1** and 1:9:1490 for **2**, both modified with NaOH to pH of 5.5, were loaded in Teflon-lined autoclaves (23-mL capacity) and were heated for 3 days at 140 and 95 °C, for **1** and **2**, respectively. Both compounds form beautiful cuboctahedral crystals, purple for **1** and colorless for **2**. Elemental analysis for **2** (Galbraith, meas./calc. %): Zn, 36.36/35.93; C, 16.41/16.26; H, 2.702/2.4; Na, <0.1/0.0.
- (3) The structures of **1** and **2** were determined from single-crystal X-ray diffraction data of **1** and **2** collected on a Bruker APEX diffractometer with a CCD area detector and  $\text{K}\alpha$  radiation.  $\text{R1/wR2} = 3.5/10.6$  and  $3.0/9.7\%$  ( $I \geq 2\sigma_I$ ) for **1** and **2**, respectively.
- (4) Determined from data collected on an Enraf-Nonius CAD4 diffractometer with  $\text{K}\alpha$  radiation, were the structures of compound **1** that was: (a) heated at 170 °C under vacuum ( $a = 20.329(1)$  Å,  $\text{R1/wR2} = 6.95/14.32\%$ ), (b) treated as (a) and then exposed to air for 2 days ( $a = 20.448(1)$  Å,  $\text{R1/wR2} = 5.41/13.02\%$ ), (c) heated at 200 °C under vacuum ( $a = 20.273(1)$  Å,  $\text{R1/wR2} = 8.21/18.52\%$ ), and (d) treated as (c) and then exposed to air for 2 days ( $a = 20.495(1)$  Å,  $\text{R1/wR2} = 5.31/13.62\%$ ).
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- (6) Determined from data collected on Enraf-Nonius CAD4 with  $\text{K}\alpha$  radiation, were the structures of compound **2** that was: (a) heated at 170 °C under vacuum ( $a = 20.482(1)$  Å,  $\text{R1/wR2} = 7.37/15.79\%$ , new position occupancy of 75%), (b) heated at 220 °C under vacuum ( $a = 20.483(1)$  Å,  $\text{R1/wR2} = 7.66/16.62\%$ , new position occupancy of 100%), and (c) treated as (b) and then exposed to air for 2 days ( $a = 20.713(1)$  Å,  $\text{R1/wR2} = 5.97/13.53\%$ , new position occupancy of 32%). Small and incomplete data set was collected for a dehydrated crystal that was then kept in water for 2 days. The refinement showed only 11% occupancy of the new position.
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