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Metathesis in Single Crystal: Complete and Reversible Exchange of Metal Ions Constituting the Frameworks of Metal−Organic Frameworks

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Metal organic frameworks (MOFs) composed of metal ions or metal clusters as nodes and multitopic organic ligands as linkers have received considerable attention over a decade because of their potential applications such as in gas storage, separation, and catalysis.[1] Although the structure and internal environment of pores can be in principle controlled through judicious selection of nodes and organic linkers, the direct synthesis of such materials with desired functionalities in the pores or channels is often difficult to achieve due to their thermal/chemical sensitivity or high reactivity. While exchange of free guest molecules or counterions from the cavities, or removal of solvent molecules weakly bound to metal centers constituting frameworks has been frequently exercised, the modification or selective replacement of integral parts of the framework remains rare.[2] In particular, the complete metal metathesis from the integral part of the framework without altering the framework or pore structure is hitherto unknown in MOFs, except a few examples of the partial exchange of the framework forming metal ions.[3] Herein, we report for the first time the complete and reversible exchange of metal ions constituting a robust microporous framework while maintaining not only the structural integrity of the framework but also single crystallinity.

Solvothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with a new coplanar C_3-symmetric ligand H_3hett (ethyl substituted truxene tricarboxylic acid, Figure 1b) in DMF produced a new crystalline MOF **1**, $Cd_{1.5}(H_3O)_3[(Cd_4O)_3(hett)_8] \cdot 6H_2O$ (formulated from dried sample), as colorless block-shaped crystals.[4] X-ray diffraction analysis revealed that **1** possesses a cubic network (Figure 1a), similar to that of sodalite.[5] The basic building unit of the structure is an octahedron consisting of six $\{Cd_4O\}^{6+}$ units and eight $hett^{3-}$ ligands at the vertices and faces, respectively. The cubic framework is generated by sharing the vertices of the octahedra. The Cd^{2+} ions of the μ_4-oxo-bridged, square-planar $\{Cd_4O\}^{6+}$ units, which behave as secondary building units (SBUs) (Figure 1c), are connected through the carboxylate groups of eight surrounding $hett^{3-}$ ligands. Each carboxylate group of $hett^{3-}$ is coordinated to two metal ions; while O1 binds to a single metal ion, O2 bridges two metal ions in a μ_2-fashion (Scheme 1). In turn, each triangular $hett^{3-}$ ligand is connected to three $\{Cd_4O\}^{6+}$ vertices to generate a rare 3,8-connected network.[6] Each metal ion is thus coordinated by eight oxygen atoms including one from H_2O. The coordination geometry around the cadmium metal ions in **1** is best described as a distorted square antiprism. The framework is negatively charged (−6 per formula unit), but no countercations were found by X-ray diffraction analysis. The presence of 1.5 Cd^{2+} and three solvated protons ($3H_3O^+$) per formula unit balancing the framework charge was, however, suggested by elemental analysis.

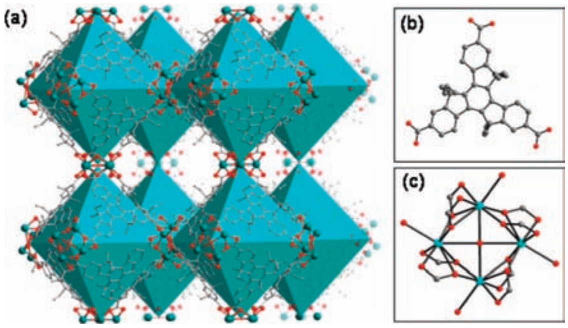
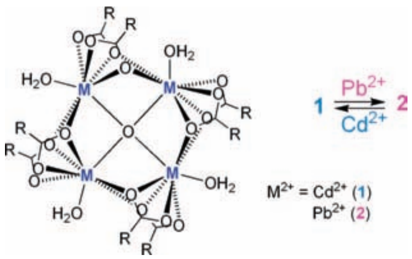


Figure 1. Parts of crystal structure of **1**, (a) a cube of eight octahedral cages sharing $\{Cd_4O\}$ vertices leaving a ∼2 nm void space at the center, (b) molecular structure of ligand H_3hett, and (c) a square-planar Cd_4O cluster behaving as a SBU.

Scheme 1. Reversible Exchange of Central Metal Ions at the SBU



The framework of **1** is stable in air as well as in various solutions. It is also stable up to 350 °C even after removal of guest molecules in the large channels. The exceptional stability and the accessibility of metal ions constituting the framework of **1** from the large channels prompted us to explore the possibility of metal ion exchange from the integral part of the framework. When **1** was immersed in aqueous $Pb(NO_3)_2$ solution for a week, a complete exchange (as analyzed by inductively coupled plasma atomic emission spectroscopy (ICP−AES)) of the framework Cd(II) ions by Pb(II) ions was observed without losing the structural integrity. The powder X-ray diffraction (PXRD) pattern of the Pb(II) exchanged MOF (**2a**) is similar to that of the parent compound **1** (Figure 2a). Furthermore, this ion exchange process occurs without losing single crystallinity, as confirmed by single crystal X-ray diffraction (SXRD) studies. The X-ray structural analysis of the Pb(II)-exchanged crystal (**2a**)[4] clearly indicated that the overall framework structure of **2a** is the same as that of **1**. The only significant difference is that the M−O bond distances in **2a** (Pb−O1 2.489; Pb−O2 2.526; Pb−O2′ 2.833; Pb−O3 3.070 Å) are substantially longer than those in **1** (Cd−O1 2.327; Cd−O2 2.289; Cd−O2′ 2.477; Cd−O3 2.641 Å) reflecting the larger size of Pb^{2+} than Cd^{2+} (ionic radius, 1.43 Å vs 1.24 Å, respectively). We have also confirmed that the crystal structure of **2a** is essentially identical to that of **2** directly synthesized from lead nitrate and H_3hett.[7]

The ion exchange process monitored by ICP−AES confirmed the rapid and facile exchange of Cd(II) by Pb(II). Almost 98% of Cd(II) from the framework was replaced by Pb(II) within 2 h and

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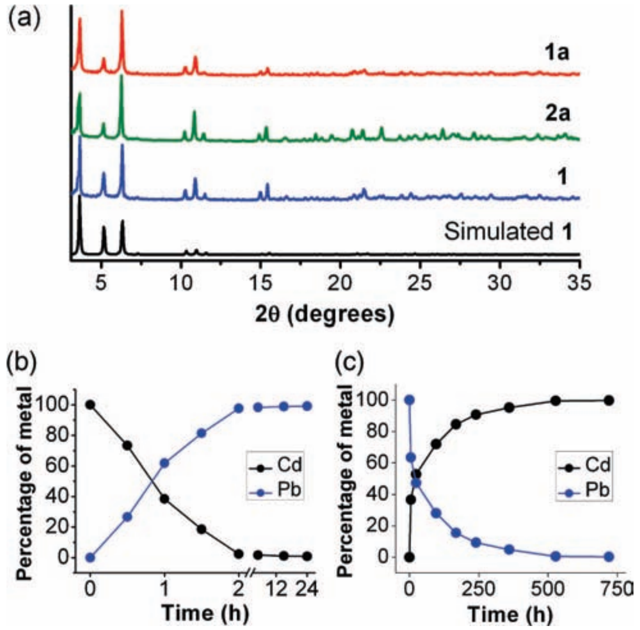

Figure 2. (a) Powder X-ray diffraction profiles for the parent and ion exchanged materials demonstrating the maintenance of the framework integrity. Kinetic profiles of the framework metal ion exchange of (b) Cd(II) with Pb(II) from **1** and (c) Pb(II) with Cd(II) from **2a**.

a complete exchange was observed within 2 d (Figure 2b). To make sure that this is a single-crystal to single-crystal transformation, we followed the metal ion exchange process of **1** by optical microscopy, in situ PXRD and SXRD. A series of optical microscope images of crystals of **1** (Supporting Information, Figures S1 and S2) showed little change in their size, shape, and appearance (except some coloring) during the exchange process. The in situ SXRD study of **1** revealed essentially the same framework structure with a gradual decrease of the Cd occupancy (and concomitant increase of the Pb occupancy) with increasing soaking time (Figure S6). Finally, the in situ PXRD patterns of **1** confirmed the preservation of bulk crystallinity during the process (Figure S11).

The ion exchange process is reversible, but the reverse process takes a longer time. The ICP−AES analysis showed ∼50% exchange of Pb(II) of **2a** by Cd(II) in 1 d, and the complete exchange took almost 3 weeks (Figure 2c). Single crystal X-ray analysis showed that the complete exchange of Pb(II) by Cd(II) to convert **2a** to **1a** occurred with retention of the framework. The TGA and PXRD profiles of **1a** are similar to those of **1**, which also support the regeneration of the parent framework.[7] Optical microscopy (Figures S3 and S4) and in situ PXRD studies (Figure S12) also confirmed the maintenance of single crystallinity and bulk crystallinity, respectively, during the ion exchange process.

We then decided to extend this work to exchange the framework Cd(II) ions of **1** with the lanthanide ions, as all our efforts to prepare open frameworks from lanthanides and H_3hett by direct synthesis were unsuccessful. Preliminary results indicated that the framework Cd(II) ions of **1** were successfully exchanged with lanthanide ions (Dy(III) (**3**) or Nd(III) (**4**)) without losing crystallinity, as proved by ICP−AES and PXRD analysis (Figures S16 and S17).[4] The ICP−AES data showed a complete ion exchange within 12 d. Single crystal X-ray diffraction studies of the frameworks of **3** revealed the retention of the original framework topology except hydroxy-bridged square planar $\{Dy_4(\mu_2\text{-}OH)\}^{11+}$ units at the vertices of the octahedron instead of $\{Cd_4(\mu_4\text{-}O)\}^{6+}$ units in the parent compound **1**. In addition, because of the trivalent lanthanide ions, the frameworks of **3** and **4** are positively charged, which is balanced by NO_3^- ions as suggested by elemental analysis. We are currently studying the extent, rate, and reversibility of the exchange of the framework Cd(II) ions with these and other lanthanide ions in details.

In conclusion, we have successfully demonstrated, for the first time, a single-crystal to single-crystal transformation involving the complete and reversible exchange of the metal ions constituting the framework of a robust MOF under mild conditions. This work may be extended to other MOFs having accessible framework metal ions. As the process involves the replacement of metal ions from their coordination sites, the size and preferred coordination number and geometry of the leaving and incoming metal ions seem to play an important role for the facile exchange of metal ions from the framework. Further studies are required to elucidate the factors governing the framework metal exchanges in MOFs. Nevertheless, the facile and complete exchange of framework metal ions without losing single crystallinity as illustrated here suggests an easy route to MOFs of different metal ions with the same framework structure/topology.

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Supporting Information Available: Experimental details for synthesis of **1** and **2**, process of ion exchange, optical microscope images, IR, PXRD, SXRD, TGA, and N_2 adsorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The TGA profiles and BET surface areas of MOFs produced by ion exchange (**1a** and **2a**) are almost the same as those of MOFs directly synthesized from the metal ions and ligand (**1** and **2**); see Supporting Information.

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