828 *Inorg. Chem.* **2001,** *40,* 828−830

Synthesis, Characterization and Structural Transformation of A Condensed Rare Earth Metal Coordination Polymer

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Received June 29, 2000

There has been tremendous interest in the synthesis and crystal structure of open-framework materials due to their potential applications in catalysis, separations, and ion exchange processes.[1] A variety of organic molecules, including bi-, tri-, and tetradentate (diamondoid) ligands,[2] have been used in the construction of many fascinating structures. 1,4-Benzenedicarboxylic acid (H_2bdc), a rodlike bifunctional ligand, has afforded a number of extended structures by virtue of an exodentate coordination mode.[3] An interesting lanthanide−bdc system has been reported recently that consists of a microporous structure generated upon removal of water from a condensed phase. This system is potentially important as a fluorescent probe.[4]

Our previous studies on dicarboxylic acids have shown that they are highly reactive toward metals under hydrothermal conditions.[5] In this work, 1,4-benzenedicarboxylic acid has been selected as a ligand and a water/ethanol solution as a solvent. Hydrated $Er(NO_3)_3$ (0.075 g), H_2bdc (0.036 g), H_2O (10 mL), and EtOH (1 mL) in the mole ratio of 1:1:2645:83 were placed in a 23 mL acid digestion bomb and heated at 160 °C for 3 days. The pH of the final solution was 4.5. The pink crystals of $Er_4(bdc)_6\cdot 6H_2O$ (**1**) (0.074 g, 74.2%) were collected after washing by water (3 × 10 mL) and by acetone (3 × 10 mL), respectively.[6a] A microcrystalline sample of $Er_4(bdc)_6$ (**2**) resulted after **1** (23 mg) was heated to 300 °C under nitrogen gas.[6b] A thermogravimetric (TG) curve indicated clearly the weight loss of six water molecules. $Er_2(bdc)_3\cdot 4H_2O$ (**3**) was obtained by allowing **2** to be exposed to saturated water vapor for 2 h.[6c] This structural transformation was confirmed by PXRD, IR, and elemental microanalysis. **3** is isostructural to $Tb_2(bdc)_3\cdot 4H_2O$[4] and can also be prepared using the same method described in ref 4.[6d]

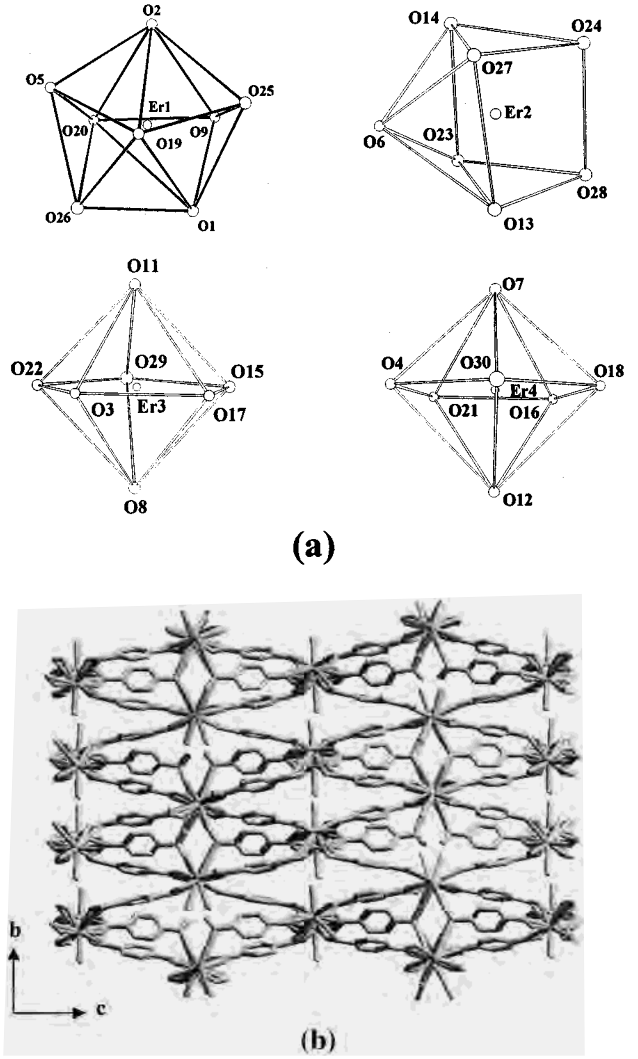

Figure 1. (a) Coordination polyhedra for the four crystallographically independent Er ions in **1**. (b) A perspective view of the crystal structure of **1** along the *a*-axis. Er1′, Er2′, Er3′, and Er4′ are crystallographically equivalent to Er1, Er2, Er3, and Er4, respectively.

The crystal structure of **1** is a condensed three-dimensional network.[7] There are four crystallographically independent erbium ions in this structure. The local coordination geometry around

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(6) (a) Found (calcd) for $Er_4O_{30}C_{48}H_{36}$ (**1**): C, 32.59 (32.72); H, 1.95 (2.06). The purity of the bulk sample was confirmed by comparison of the observed and calculated PXRD patterns. FT-IR (KBr): $\nu_{as}(COO^-)$ = 1554.6 cm^{-1}, $\nu_s(COO^-)$ = 1418.6 cm^{-1}. It does not dissolve in common organic solvents such as benzene, diethyl ether, acetonitrile, *N,N′*-dimethylformamide, and dimethyl sulfoxide. (b) Found (calcd) for $Er_4O_{24}C_{48}H_{24}$ (**2**): C, 34.71 (34.86); H, 1.43 (1.47). (c) Found (calcd) for $Er_2O_{16}C_{24}H_{20}$ (**3**): C, 32.11 (32.06); H, 2.43 (2.25). (d) Found (calcd) for $Er_2O_{16}C_{24}H_{20}$ (**3**) following the preparation procedure described in ref 4: C, 32.09 (32.06); H: 2.30 (2.25).

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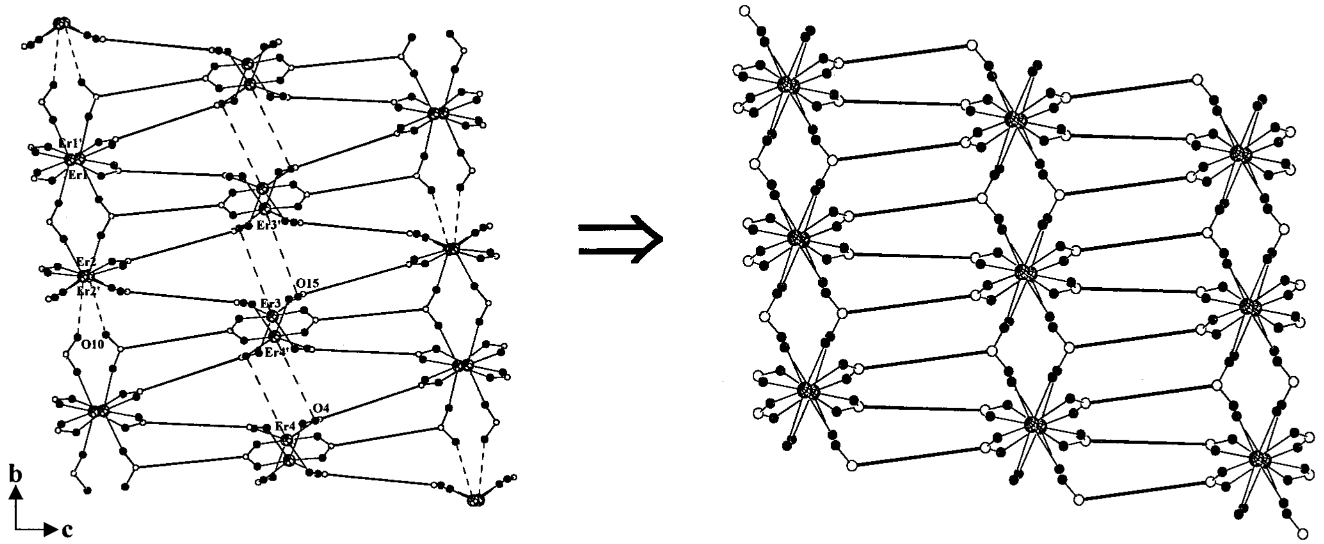

Figure 2. Structural transformation from $Er_4(bdc)_6{\cdot}6H_2O$ (**1**, left) to $Er_2(bdc)_3{\cdot}4H_2O$ (**3**, right). Water molecules are omitted in both structures for clarity.

Er1 is a dodecahedron which consists of six oxygen atoms from six bdc and two from water molecules. The coordination polyhedron around Er2 is a capped trigonal prism which contains five carboxylate oxygen and two water oxygen atoms. The coordination environments of Er3 and Er4 are both pentagonal bipyramidal. The pentagonal planes are composed of four carboxylate oxygen atoms and a water oxygen atom, and the two apical sites are taken by another two carboxylate oxygen atoms (Figure 1a). A perspective view of the structure along the *a*-axis is illustrated in Figure 1b. All Er1 and Er2 are located in one plane whereas all Er3 and Er4 are located in the other plane (Figure 2, left side). The separation between the adjacent planes is 9.5 Å. The neighboring Er1 and Er1′ (or Er2 and Er2′) atoms are approximately parallel to the *c*-axis and they are connected by two carboxylic groups from the two bridging bdc ligands,[8] whereas Er1 and Er2 are approximately parallel to the *b*-axis and are connected by one carboxylic group through a bridging bdc. There are no direct connections between the Er3 and Er3′ (or Er4 and Er4′) atoms. The neighboring Er3 and Er4 atoms are connected by three carboxylic groups of three different bridging bdc ligands. There are two μ_4 and one μ_3 coordination modes for bdc. Each of the two μ_4-bdc bridges to four erbium ions through its four carboxylate oxygen atoms,[9] and the μ_3-bdc bonds only to three metals using three of its carboxylate oxygen atoms. A comparison of this structure with that of $Tb_2(bdc)_3{\cdot}4H_2O$ reveals the differences in the two: While metal ions form a single type of dodecahedron in $Tb_2(bdc)_3{\cdot}4H_2O$, there are three different coordination polyhedra for Er in **1**. Similarly, the bdc utilizes two bonding modes in the former structure while it utilizes three in the latter. Following the same procedure described in ref 4, we successfully isolated $Er_2(bdc)_3{\cdot}4H_2O$ (**3**) by replacing Tb (or Eu) salt with erbium nitrate, which is isostructural to $Tb_2(bdc)_3{\cdot}4H_2O$. The formation of **3** was confirmed by PXRD. Attempts to synthesize **1** under hydrothermal conditions in water failed. This suggests that the existence of ethanol was crucial for the formation of **1**. The strong adsorption peaks at $\nu_{as}(COO^-) = 1554.6$ cm^{-1} and $\nu_s(COO^-) = 1418.6$ cm^{-1} in the IR spectrum of **1** showed that carboxylate groups of bdc coordinate to erbium ions in a bridging fashion.[9] This is in agreement with the result of the X-ray structure analysis. **1** is more condensed than $Tb_2(bdc)_3{\cdot}4H_2O$. The unoccupied volume was calculated to be 20.41% for **1**, based on the unit cell volume, and 21.17% for $Tb_2(bdc)_3{\cdot}4H_2O$.

Thermogravimetric analysis (TGA) study revealed that **1** underwent a two-step decomposition process, with its first weight loss occurring at 90−133 °C. The weight lost corresponded to six water molecules per formula unit (found 6.3%, calcd 6.1%). Increasing temperature led to the decomposition of the compound at 510 °C. The final pyrolysis was completed at 800 °C, giving a pink powder of Er_2O_3. Having a flat plateau from 133 to 510 °C (a span of nearly 400 °C), **1** represents one of the most stable coordination polymers encountered so far.[10] Reabsorption of water was probed after **1** lost six water molecules. The IR spectrum of **2**, the sample after the total removal of water at 300 °C, reveals that the broad peak around 3500−3450 cm^{-1} originally assigned to water molecules in **1** disappeared, and the strong peaks $\nu_{as}(COO^-)$ at 1539.2 cm^{-1} and $\nu_s(COO^-)$ at 1426.4 cm^{-1} confirmed the shift of Er−O (metal−carboxylate oxygen) stretches. A comparison on the PXRD patterns of **1** (Figure 3a) and **2** (Figure 3b) also shows significant shifting, broadening, and possibly splitting of some diffraction lines. To our surprise, the PXRD pattern (Figure 3c) of the sample after exposure of **2** to saturated water vapor for 2 h gave an almost perfect match to that of **3** prepared following the procedures described in ref 4 (Figure 3d). The IR spectra of these two samples were almost identical.

In structure **1**, the distances between Er2 and O10 are 4.838−4.854 Å. Upon heating and removal of water from the compound, the structure (**2**) will contract as indicated by the COO$^-$ vibration shift in IR. Simultaneously, the uncoordinated O10 atoms will be highly subject to bonding to the adjacent, unsaturated Er2, resulting in a similar coordination geometry for both Er1 and Er2 as in $Tb_2(bdc)_3{\cdot}4H_2O$. On the other hand, the holes in **2** between Er3 and Er4 will collapse due to the unstable pentagonal coordination of Er3 and Er4 after removal of the two coordinated

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(7) Pink needle crystals of $Er_4(bdc)_6{\cdot}6H_2O$ were analyzed at 298 K: orthorhombic, space group *Pbca*, $a = 9.661(2)$ Å, $b = 26.224(3)$ Å, $c = 37.863(3)$ Å, $V = 9593(3)$ Å^3, $Z = 8$, $D_c = 2.440$ g/cm^3, and μ(Mo Kα) = 71.25 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters for data collection were measured by least-squares analysis of the setting angles of 25 well-centered reflections with 14.57° ≤ θ ≤ 18.66°. A total of 10379 reflections were measured, of which 6288 were observed with $I \geq 3.0\sigma(I)$ and these were used in structure solution and refinement; $R = 0.045$, $R_w = 0.058$, GOF = 1.38. The structure was solved and refined using the TEXSAN package.

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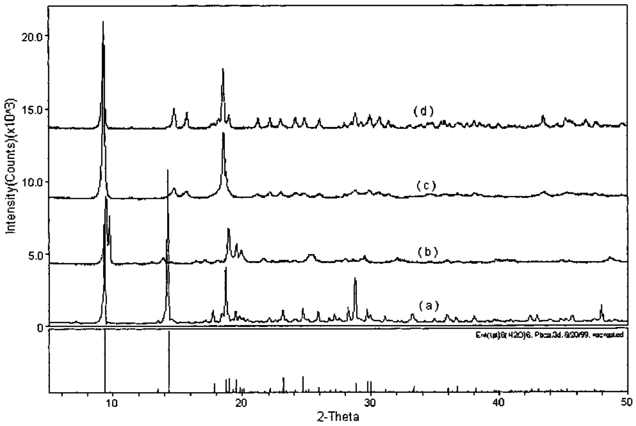

Figure 3. (a) Observed PXRD pattern for crystalline solid $Er_4(bdc)_6\cdot 6H_2O$ (**1**). (b) Observed PXRD pattern of $Er_4(bdc)_6$ (**2**) after removal of six waters in **1**. (c) Observed PXRD pattern of the rehydrated sample after powders of **2** were placed in saturated water for 2 h. (d) PXRD pattern of $Er_2(bdc)_3\cdot 4H_2O$ (**3**) synthesized following the procedure described in ref 4. Bottom: calculated PXRD pattern for **1** from single-crystal data.

water molecules. A reasonable assumption is that such an instability may force the structure to reorganize by breaking the Er3−O15 and Er4−O4 bonds and forming new bonds between Er3′−O15 and Er4′−O4, resulting in a $Tb_2(bdc)_3\cdot 4H_2O$ type structure (Figure 2, right). Structure rearrangement of this type has been observed only in a few coordination polymers.[11] A reversible process to reproduce **2** from **3** was not successful.

In conclusion, we have synthesized a unique three-dimensional condensed rare-earth metal coordination polymer via hydro(solvo)thermal reactions in water/ethanol. This structure not only exhibits high thermal stability but also can be transformed to a different structure by desorption and reabsorption of water. This unique property may contribute to the current investigations in the field of molecular sorbents, phase separation, and adsorption/desorption processes.

Acknowledgment. We are grateful to the National Nature Science Foundation of China (Grant No. 59872039) and the Anhui Provincial Foundation of Natural Science Research. J.L. would like to acknowledge the partial support from the National Science Foundation.

Supporting Information Available: Crystallographic data for $Er_4(bdc)_6\cdot 6H_2O$: An X-ray crystallographic file (CIF). IR data of **1**, **2**, and **3** and related PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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