An unusually high thermal stability within a novel lanthanide 1,3,5-cyclohexanetricarboxylate framework: synthesis, structure, and thermal data

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A novel three-dimensional lanthanide–organic framework has been synthesized; this material has an exceptionally high thermal stability (600 °C) and an unusually low coordination number for a lanthanide ion (CN = 6).

The use of multifunctional organic linker molecules to polymerize metal centers into microporous and framework materials has led to the development of a rich field of chemistry.[1–8] These metal–organic framework (MOF) materials hold the potential for very useful applications, ranging anywhere from molecular recognition and separation to gas storage and sensing.[9–17] Their thermal stability, however, is moderate (often in the range of 150–300 °C) and usually related to the decomposition of the organic component(s). Traditional microporous materials (zeolites, AlPOs) or various metal oxides typically dominate these areas in terms of practical functions.[18–24] Just the same, the versatility and topological diversity demonstrated through MOF materials is perhaps the primary reason why these materials have been studied so enthusiastically over the past few years.

The use of structure-directing agents in the syntheses of these materials is of interest to our research efforts.[25,26] We have had much success with the use of 4,4′-dipyridyl in this regard. As such, we attempted to use 4,4′-dipyridyl in the synthesis of a previously reported structure[27] in hopes of inducing a change in topology that would occur upon inclusion of a guest molecule. This structure, $[Er(C_9H_9O_6)(H_2O)_2]\cdot 2.5H_2O$, consists of ErO_9 polyhedra, where seven of the oxygen atoms are from the carboxylate groups of the organic linker and the remaining two oxygen atoms are bound water molecules. Channels along the [001] direction are approximately 4.7 Å in diameter and contain several unbound water molecules. We believed that the 4,4′-dipyridyl would displace the excess water and act to change the overall channel topology as a structure-directing agent. Instead, a novel material ($[Ln(C_9H_9O_6)]$, where Ln = Er^{3+}, Tb^{3+}) was synthesized that did not include the intended guest molecule. This serendipitous discovery has led to a very interesting, highly symmetric lanthanide-containing MOF material. Perhaps the most interesting features of this material are the low coordination of the lanthanide metal center (coordination number = 6) and the high thermal stability of this material (stable to 600 °C), as will be discussed herein.

Initial synthesis of this material was conducted *via* hydrothermal methods. Erbium nitrate hydrate (Strem Chemicals), 1,3,5-cyclohexanetricarboxylic acid (Aldrich Chemical Company), 4,4′-dipyridyl (Aldrich Chemical Company), and distilled water were placed into a Teflon-lined Parr bomb in the relative molar ratios of 1 : 1 : 1 : 830 (pH = 2.6). The reaction vessel was then sealed and placed in a 170 °C oven for 24 hours. Upon cooling to room temperature, a clear bright yellow solution of pH 1.7 was decanted from pink, spherical crystals. The crystals were rinsed with distilled water followed by ethanol and allowed to air dry at room temperature. An analogous reaction was done, replacing the erbium source with terbium nitrate hexahydrate (Strem Chemicals), to yield light yellow, cube-shaped crystals (pH initial = 2.6; pH final = 1.7). Subsequent syntheses without 4,4′-dipyridyl produced the title compound, thus suggesting merely a spectator role for the dipyridyl. Further reactions were done wherein the water ratios were varied (420 and 85). It appears that the amount of water in this reaction has little to no effect on the final product, as all products from these reactions are isomorphous.

A single crystal of each sample was selected and mounted on a glass fiber for single crystal X-ray diffraction.† Since both the spherical crystals obtained from the erbium and the cubic crystals from the terbium were quite large and appeared to be polycrystalline, they were first crushed under a glass slide and a single crystal fragment was selected from the resulting powder. Powder X-ray diffraction data were also collected on all samples with a Scintag XDS 2000 diffractometer (Cu Kα, 3–60°, 0.05° step, 1.0 s $step^{-1}$) and manipulated using the JADE software package.[28] The observed powder patterns were compared to those calculated from single crystal X-ray diffraction and both were in agreement, indicating phase purity. Elemental analyses were also performed and found to be in good agreement: $Er(C_9H_9O_6)$ Found: C, 28.38%; H, 2.38%. Calc.: C, 28.42%; H, 2.38% and $Tb(C_9H_9O_6)$ Found: C, 28.95%; H, 2.46%. Calc.: C, 29.05%; H, 2.44%.

The structures (Fig. 1) of both materials are identical, thus only the Er^{3+} structure will be described. This material consists of a single 6-coordinate Er^{3+} metal center in octahedral geometry with six oxygen atoms (O1 and symmetry equivalents). Each oxygen atom is from a carboxylate group from six different ligands, thus each ligand is coordinated to six symmetry equivalent lanthanide centers (Fig. 2). It is interesting to note that each carboxylate group exhibits only a bridging bidentate connectivity (Fig. 3), with a complete lack of more complex connectivities that are readily seen within lanthanide-containing solid-state extended structures.[29] It is also quite remarkable that the lanthanide ions are in such low coordination, even without excess water molecules to fulfill the

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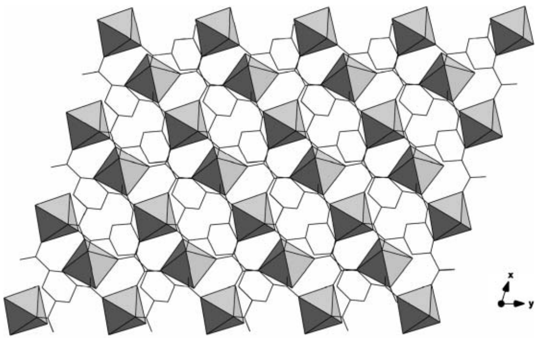

Fig. 1 View of the title compound down the [001] direction. Polyhedra represent the LnO_6 building unit and black lines represent the organic linker, 1,3,5-cyclohexanetricarboxylate.

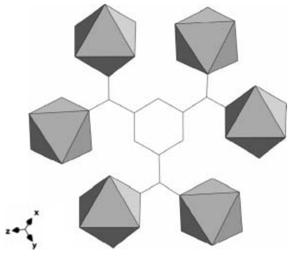

Fig. 2 View of the coordination of the organic linker to six unique LnO_6 polyhedra.

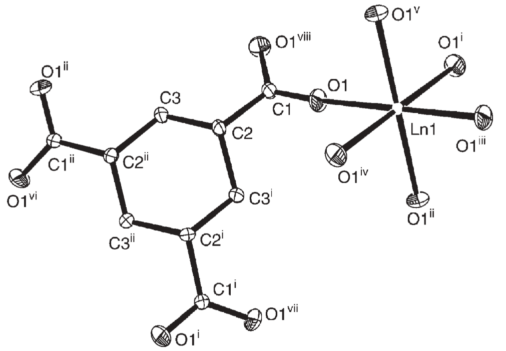

Fig. 3 ORTEP drawing of the title compound. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity, as is the disordered component of C2. Superscript indicates symmetry transformation: i = $-y, x - y, z$; ii = $-x + y, -x, z$; iii = $-x, -y, -z$; iv = $y, -x + y, -z$; v = $x - y, x, -z$; vi = $y + 1/3, x + 2/3, -z + 1/6$; vii = $x - y + 1/3, -y + 2/3, -z + 1/6$; viii = $-x + 1/3, -x + y + 2/3, -z + 1/6$.

usually high coordination numbers inherent to the lanthanide ions. In a search of the Cambridge Structural Database (using ConQuest Version 1.8, updated January 2006),[30] approximately 100 structures were found where the lanthanide center has a coordination number of 6. Most of these structures, however, are molecular species or complexes, often made in non-aqueous solutions and in many instances have sterically bulky ligands. The reason for this unique coordination is unclear, yet may be related to sterics resulting from the dense nature of the framework. The cyclohexane ring of the ligand shows static disorder on the C2 site, indicating that the ligand crystallizes in both the chair and boat conformations. Using SQUEEZE within PLATON,[31] no accessible void space was found in this structure.

Thermogravimetric analysis was performed on both the Er and Tb analogues using a Perkin-Elmer Pyris1 over a temperature range of 30–1000 °C (10 °C min^{-1}) with flowing $N_2(g)$. Initial weight loss begins at 600 °C and continues in one step to 1000 °C. The total weight loss over this range is 45%, which corresponds to loss of most of the organic component. Based on powder X-ray diffraction data (PXRD), the final product is isostructural with lanthanum nitride (PDF #15-0892), indicating that upon loss of the organic at such extreme temperatures, the lanthanide is reacting with the N_2 gas flow. Complete loss of the organic component would require a 55% weight loss, thus the 10% discrepancy between the calculated and observed weight losses can be attributed in part to the formation of the lanthanide nitride. Additionally, the final PXRD spectrum shows some very minor peaks, but attempts to identify these were not successful. Likewise, a powder pattern collected from the sample after heating to 600 °C shows no change from that prior to thermal treatment, further demonstrating the high thermal stability of this material (Fig. 4).

The thermal stability of this material is quite remarkable. Degradation of the organic components of MOFs typically begins at moderate temperatures (200–350 °C),[32–37] resulting in decomposition of the synthesized material. In rare instances, a metal–organic framework material may be stable above 350 °C and up to around 520 °C,[38–40] but reasons for this are largely unspecified. In many of these materials, residual solvent remains in the framework either coordinated directly to the metal center (*e.g.*, aquo ligands) or uncoordinated in the framework channels. Considering the volatility of these solvent molecules, it is quite common to observe their release from the framework at low temperatures (<200 °C). This release can easily result in a perturbation of the structure and weakening of metal–linker bonds, which may help facilitate decomposition. Lack of such solvent molecules in the structure presented herein may be one factor that contributes to its robustness. An additional factor to consider is the flexibility of the organic linker itself. In more rigid systems (*e.g.*, aromatics), it is perhaps more difficult to accommodate distortions in the structure caused by heating. It is therefore conceivable that the metal–linker bonds will break in order to accommodate any changes, whereas a less rigid linker adds a degree of flexibility that allows for any small

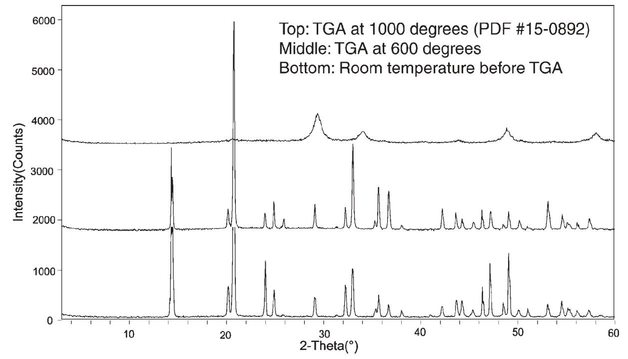

Fig. 4 Powder X-ray diffraction spectra of the title compound. The bottom spectrum was taken at room temperature with no thermal treatment and the middle spectrum is after heating to 600 °C. The top spectrum shows the title compound after heating to 1000 °C.

perturbations in the structure. Both of these factors may play a key role in the high thermal stability of this material.

In conclusion, a new lanthanide-containing metal–organic framework material with exceptional thermal stability has been synthesized. It has been shown that this material contains a coordination number of six, which is rather rare for the large lanthanide ions.

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Notes and references

† Crystallographic data: the data were collected at room temperature using a Bruker SMART diffractometer with an APEX II CCD detector[41] using both phi and omega scans. The structures of both materials solved readily in both the $R3c$ and $R\bar{3}c$ space groups with direct methods and refined using SHELXL-97.[42] During refinement in the acentric space group, PLATON indicated missed symmetry and suggested the $R\bar{3}c$ space group. When both materials were refined in $R\bar{3}c$, however, disorder appeared on the C2 position, creating two symmetry equivalent C2 positions about 1 Å from each other, indicating static disorder. Samples were tested for second harmonic generation, yielding negative responses, indicating that an acentric space group was not likely. Taking these factors into consideration, final refinement was done in the centric space group $R\bar{3}c$ using the WINGX software suite.[43] $\mathrm{Er(C_9H_9O_6)}$: $M = 380.42$, hexagonal, $a = b = 8.820(3)$, $c = 20.727(13)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1396.4(11)$ Å^3, $T = 295(2)$ K, $Z = 6$, $\mu = 9.025$ mm^{-1}, $R_{\mathrm{int}} = 0.0618$, $R_2 = 0.0176$, w$R_2 = 0.0414$ ($I > 2\sigma(I)$); $\mathrm{Tb(C_9H_9O_6)}$: $M = 372.08$, hexagonal, $a = b = 8.9133(12)$, $c = 20.654(6)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1421.1(5)$ Å^3, $T = 295(2)$ K, $Z = 6$, $\mu = 7.475$ mm^{-1}, $R_{\mathrm{int}} = 0.0605$, $R_2 = 0.0184$, w$R_2 = 0.0412$ ($I > 2\sigma(I)$). The heavy metal atom positions were located immediately upon solution and the remaining atoms (except hydrogen atoms) were located in Fourier-difference maps. Hydrogen atom positions on C3 were located in Fourier-difference maps yet constrained to idealized distances. Hydrogen atoms on C2 were neither located nor calculated due to disorder on this site. CCDC 614837 and 614838. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610012k

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