Three Dimensional Polymer Bis(nitrilotriacetato)-samarium(III) Hydrate: Hydrothermal Synthesis and Crystal Structure

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Received December 2, 2008

Abstract—Hydrothermal reaction of Sm₂O₃ with nitrilotriacetic acid gives rise to a lanthanide coordination polymer, [Sm(NTA)(H₂O)]ₙ (I). Its solid state structure has been characterized by elemental analysis and IR spectroscopy. X-ray single-crystal diffraction analysis indicates that I is a three-dimensional coordination polymer with eight-coordinated Sm(III) ion.

DOI: 10.1134/S0036023610080139

Lanthanide complexes have received much attention because of their interesting photophysical properties which have potential applications in the luminescence probes for chemical or biological macromolecules and the active center for luminescent materials [1–9]. Nitrilotriacetic acid (H₃NTA) is one of the important derivatives of glycine, and is widely used in biochemistry and medicine. Lanthanide complexes with nitrilotriacetate have been studied for a long time, and the crystal structures of a series of lanthanide complexes have been reported. Some lanthanide complexes have multiple dimensional polymeric structures, such as [Ln(NTA)(H₂O)] (Ln = La, Pr, Nd, Eu) [10], [Pr(NTA)] · 3H₂O [11], [Dy(NTA)] · 4H₂O [12], [Tm(NTA)(H₂O)₂] · 2H₂O [13]; the other typical lanthanide complexes are monomers, which include [Eu(NTA) · 2H₂O] and [Tb(NTA) · 2H₂O] [14], K₃[Nd(NTA) · 2H₂O] · 6H₂O, K₃[Er(NTA)₂(H₂O)] · 5H₂O [15], K₃[Y(NTA)(H₂O)] · 6H₂O [16], K₃[Ho(NTA)₂(H₂O)] · 5H₂O [17], but until now only one samarium(II) complex with NTA ligand was reported by our group [18]. Nonetheless, it is still worth investigating the structural diversity of such lanthanide coordination polymers with NTA. In our previous studies some lanthanide coordination polymers with NTA have been reported [18, 19], in order to continue our work, here we report the hydrothermal synthesis, crystal structure of a novel coordination polymer [Sm(NTA)(H₂O)]ₙ (I).

EXPERIMENTAL

Synthesis of I. An aqueous mixture (15 mL) containing H₂NTA (0.7 mmol, 0.1337 g), Sm₂O₃ (0.25 mmol, 0.0872 g), and KOH (0.5 mmol, 0.0400 g) was placed in a teflon-lined stainless steel vessel (25 mL). Ethanol (5.0 mL) was added to the mixture. The vessel was sealed and heated to 130°C for 3 days. Upon cooling to room temperature, yellow block crystals of I were obtained.


Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. IR data: (KBr pellet, cm⁻¹): 3559 (m), 3552 (s), 2961 (w), 2912 (w), 1647 (s), 1591 (s), 1559 (s), 1471 (m), 1439 (m), 1426 (m), 1404 (m), 1352 (m), 1332 (m), 1300 (m), 1254 (m), 1244 (m), 1116 (m), 1023 (m), 996 (m), 970 (m), 944 (m), 931 (m), 743 (m), 644 (w), 515 (w), 472 (w), 412 (w).

Crystal data for I: C₆H₈NO₇Sm, FW = 356.48, monoclinic, space group P2(1)/c, a = 6.8363(2) Å, b = 6.6686(2) Å, c = 20.8039(7) Å, β = 106.442(2)°, V = 909.64(5) Å³, Z = 4, Dc = 2.603 Mg/m³, T = 296(2) K, R₁ = 0.0197, wR₂ = 0.0501 (final R indices [I > 2σ(I)]). Crystallographic data for title complex I is deposited to the Cambridge crystallographic data center with deposition number CCDC 703316.

The X-ray single crystal data collection for complex I was performed on a Bruker SMART CCD diffractometer equipped with a graphite monochromator MoKα radiation (λ = 0.71073 Å). Multi-scan absorption correction was applied using the SADABS program [20]. The structure was solved by a direct method using the SHELXS-97 program [21]. Refinements on F² were performed using SHELXL-97 [22] by a full-

1 The article is published in the original.
matrix least-square method with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms of the ligands were generated geometrically, while the H atoms of the coordination water molecule were located from difference Fourier synthesis and refined with restraints.

### RESULTS AND DISCUSSION

The yellow block crystals of I were obtained by the reaction of H₃NTA, Sm₂O₃ and KOH at pH 6–7 [20]. The IR spectrum of ν(C–N) of I is at 1116 cm⁻¹, undergoing red-shifts 84 cm⁻¹ compared with that of H₃NTA (1200 cm⁻¹), indicates that the N atom of NTA ligand coordinated to Sm(III) ion. For the COOH group, the vibration peak at 1725 cm⁻¹ of NTA disappeared in the complex I, which indicating that H₃NTA is deprotonated completely. νₐ(COO⁻) at 1620 cm⁻¹ of H₂NTA red-shifts to 1591 cm⁻¹, and νₐ(COO⁻) at 1340 cm⁻¹ of H₂NTA blue-shifts to 1404 cm⁻¹ in complex I, confirming that the O atoms of COO⁻ also coordinate with Sm(III). There is a broad and strong ν(OH) band of H₂O about 3550 cm⁻¹, showing that there are hydrogen bonds between H₂O and NTA ligand in complex I.

The title complex I is different from that of {[Sm(NTA)(H₂O)₂]·H₂O}ₙ [18]. Single crystal X-ray determination reveals that the NTA ligand coordinates to the Sm(III) ion in a tetradeutate mode through three oxygen atoms (O1, O3 and O6) of three different carboxyl groups and a nitrogen atom (N1), forming three five-membered chelating rings: A (C₁/C₂/O₆/N₁/Sm₁), B (N₁/C₃/C₄/O₃/Sm₁) and ring C (N₁/C₅/C₆/O₁/Sm₁). There are three dihedral angles among the three least-square planes A, B and C are 18.6°, 64.2° and 82.9° for A/B, A/C and B/C, respectively. The Sm(III) ion is eight-coordinated, the geometry around each Sm(III) ion can be described as a distorted square antiprism with four sites occupied by one NTA ligand (O1, O3, O6 and N1) (Fig. 1). The remaining four sites occupied by carboxylate groups (O2A, O4B, O5C) from three different NTA ligands, and from one water ligand (O7).

### Table 1. Selected bond distances (Å) and bond angles (°) for compound I

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>d(D–H), Å</th>
<th>d(H···A), Å</th>
<th>d(D···A), Å</th>
<th>&lt;(DHA), deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(7)–H(7A)...O(5)#1</td>
<td>0.850(10)</td>
<td>2.13(2)</td>
<td>2.947(4)</td>
<td>162(6)</td>
</tr>
<tr>
<td>O(7)–H(7B)...O(2)#2</td>
<td>0.852(10)</td>
<td>2.31(5)</td>
<td>2.910(4)</td>
<td>128(6)</td>
</tr>
<tr>
<td>O(7)–H(7B)...O(1)#2</td>
<td>0.852(10)</td>
<td>2.141(16)</td>
<td>2.985(4)</td>
<td>170(7)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 –x, –y + 2, –z + 1; #2 –x + 1, –y + 1, –z + 1.