Synthesis, Crystal Structure, and Fluorescence of a New 3D Nd(III) Coordination Polymer Based on the Pyridine-3,5-Dicarboxylate and In Situ Generated Oxalate Ligand

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A new three-dimensional neodymium(III)-containing coordination polymer, \([\text{Nd}_2(\mu_2-\text{ox})(\mu_4-\text{PDC})_2(H_2O)_4]\cdot 2H_2O (1)\) (H_2PDC \text{ = pyridine-3,5-dicarboxylic acid, H}_2\text{ox \text{ = oxalate acid})}, has been successfully synthesized under hydrothermal conditions via mixed-ligand of pyridine-3,5-dicarboxylate and in situ generated oxalate, and characterized by elemental analysis, IR, and single-crystal X-ray diffraction. The crystal structural analysis reveals that complex 1 displays an unusual three-dimensional framework with a pillared-layer containing a two-dimensional metal-organic layer architecture, and possesses a rare bimodal (4,5)-connected net with (4.6.6.8) topology. Moreover, complex 1 exhibits intense fluorescent emission at room temperature in the solid state.

Keywords: lanthanide coordination polymer, crystal structure, network topology, luminescent property

Introduction

Recently, the rational design and synthesis of lanthanide coordination polymers has attracted considerable attention in various area owing to their versatile coordination fashions, intriguing molecular topologies, and potential application, such as unique optical, magnetic, gas adsorptive, and catalytic applications.\(^{[1-9]}\) Especially, the lanthanide (4f) coordination complexes usually exhibit intense and long-lived emission over narrow wavelength ranges which are potentially applicable as fluorescent probes and electroluminescent devices.\(^{[10-12]}\) Additionally, the lanthanide coordination polymers base on multifunctional ligands containing nitrogen and oxygen donors, such as pyridine-3,5-dicarboxylic acid, pyridine-2,4,6-tricarboxylic acid, pyridine-2,3,5,6-tetracarboxylic acid, and others have become a particularly important subject, some of them showing diverse architecture and interesting properties.\(^{[13-16]}\) Moreover, oxalate is now widely employed in crystal engineering of coordination polymers due to it may serve as “template” for new functional materials.\(^{[17]}\) However, the coordination chemistry of pyridine-3,5-dicarboxylate and oxalate mixed ligands has been much less explored with rare earth ions so far.\(^{[18]}\) We have previously reported the synthesis and crystal structure of series of lanthanide carboxylate polymers,\(^{[19-21]}\) which display strong photoluminescent emission in the solid-state at room temperature. Herein, during our attempt to prepare new lanthanide carboxylate polymers, we selected pyridine-3,5-dicarboxylate and in situ generated oxalate as linkers in this work. As a result, hydrothermal reactions of the above ligands with Nd(III) nitrate resulted in a new 3D lanthanide coordination polymer \([\text{Nd}_2(\mu_2-\text{ox})(\mu_4-\text{PDC})_2(H_2O)_4]\cdot 2H_2O (1)\). Complex 1 has a three-dimensional pillared-layer architecture displaying a rare bimodal (4,5)-connected network with \((4.6.6.8)\) topology. The photoluminescent property associated with its crystal structure has been measured at room temperature.

Experimental

Materials and General Methods

All chemicals were commercially purchased and used without any further purification. Elemental analysis for C, H, and N was performed on a Perkin Elmer 240C elemental analyzer. Fourier transform IR spectrum was carried out on a Nicolet AVATAR-360 FT-IR spectrophotometer with a KBr disk in the range of 400–4000 cm\(^{-1}\). The solid-state emission spectrum was measured on a Hitachi F-4500 fluorescence spectrometer equipped with a xenon lamp at room temperature.

Synthesis of the Complex \([\text{Nd}_2(\mu_2-\text{ox})(\mu_4-\text{PDC})_2(H_2O)_4]\cdot 2H_2O (1)\)

The single crystals of complex 1 were produced by hydrothermal reaction. A mixture containing \(\text{Nd(NO}_3)_2\cdot 6H_2O\)
(37.6 mg, 0.1 mmol), AgNO₃(34.0 mg, 0.2 mmol), and H₂PDC (3.34 g, 0.2 mmol) in H₂O (12 mL) was stirred for 30 min in air, and then sealed in 25 mL Teflon-lined stainless steel container and kept at 170°C for 72 h under autogenous pressure, followed by slow cooling to room temperature. Brown needle-like single crystals of complex 1 were picked out, washed with doubly deionized water several times, and then dried in air. Yield: 57% (based on Nd). Anal. Calcd. (%): C, 23.63; H, 2.26; N, 3.41. IR (KBr/pellet)/cm⁻¹: 3436 (br), 2924(m), 1634(s), 1557(m), 1471(w), 1399(m), 1384(s), 1147(w), 769(w), 719(w), 593(w), 470(w), 427(w).

X-Ray Crystallography

A brown needle-like crystal with dimensions of 0.20 mm × 0.14 mm × 0.13 mm was selected for measurement. Diffraction data of complex 1 were collected at 293(2) K on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated MoKα radiation (λ = 0.71073 Å). A total of 8410 reflections were collected in the range of 2.47 ≤ θ ≤ 25.05° by using a φ-ω scan mode, of which 2,005 were unique and 1,800 were observed with I > 2σ(I) and 172 variable parameters. The structure of complex 1 was solved by direct methods using the SHELXS-97 program[22] and refined on F² by full-matrix least-squares method with the SHELXL-97 program.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and re

Table 1. Crystallographic data and structure refinement summary for complex 1

| Parameter | Value |
|-----------|-------|
| Formula   | C₅H₁₂N₀₆Nd |
| Formula weight | 407.40 |
| T (K)     | 293(2) K |
| Crystal system | Monoclinic |
| Space group | P2₁/c |
| a (Å)     | 7.702 2(5) |
| b (Å)     | 9.915 2(7) |
| c (Å)     | 15.820 2(9) |
| β (°)     | 110.305(3) |
| V (Å³)    | 1133.09(13) |
| Z         | 4 |
| Dcalc. (g·cm⁻³) | 2.388 |
| F(000)    | 784 |
| θ range (°) | 2.47–25.05 |
| Refns. collected | 8410 |
| Data/restraints/parameters | 2005/0/172 |
| Goodness-of-fit on F² | 1.001 |
| R indices [I > 2σ(I)] | R1 = 0.0193, wR2 = 0.0430 |
| R indices (All data) | R1 = 0.0230, wR2 = 0.0441 |
| Largest diff. peak and hole (e Å⁻³) | 0.734 and –0.513 |

Results and Discussion

In the FT-IR spectrum of complex 1, the broad band centered at 3436 cm⁻¹ shows the O–H band stretching vibration of the water molecules. Moreover, the infrared spectrum further confirms that the absence of the characteristic absorption band of carboxyl group about 1700 cm⁻¹ indicates their complete deprotonation. The strong significant shift absorption peak of carboxylate groups at 1634, 1557, 1399, and 1384 cm⁻¹ should be attributed to metal coordination of the

| Bond Lengths (Å) | Value |
|------------------|-------|
| Nd(1)–O(1)       | 2.495(3) |
| Nd(1)–O(2)       | 2.524(3) |
| Nd(1)–O(3)       | 2.424(3) |
| Nd(1)–O(4)#3     | 2.393(3) |
| O(5)#1–Nd(1)–O(6)#2 | 101.21(10) |
| O(5)#1–Nd(1)–O(4)#3 | 89.51(9) |
| O(6)#2–Nd(1)–O(4)#3 | 150.34(10) |
| O(5)#1–Nd(1)–O(3) | 148.83(9) |
| O(6)#2–Nd(1)–O(3) | 83.88(9) |
| O(4)#3–Nd(1)–O(3) | 101.16(9) |
| O(5)#1–Nd(1)–O(1) | 80.55(10) |
| O(6)#2–Nd(1)–O(1) | 137.26(9) |
| O(4)#3–Nd(1)–O(1) | 71.48(9) |
| O(3)–Nd(1)–O(1)  | 75.41(9) |
| O(5)#1–Nd(1)–O(1W) | 68.28(10) |
| O(6)#2–Nd(1)–O(1W) | 75.70(9) |
| O(4)#3–Nd(1)–O(1W) | 82.98(9) |
| O(3)–Nd(1)–O(1W)  | 141.61(9) |
| Nd(1)–O(5)#1     | 2.364(3) |
| Nd(1)–O(6)#2     | 2.365(3) |
| Nd(1)–O(1W)      | 2.519(3) |
| Nd(1)–O(2W)      | 2.522(3) |
| O(1)–Nd(1)–O(1W) | 139.68(9) |
| O(5)#1–Nd(1)–O(2W) | 138.32(10) |
| O(6)#2–Nd(1)–O(2W) | 78.57(9) |
| O(4)#3–Nd(1)–O(2W) | 75.20(9) |
| O(3)–Nd(1)–O(2W) | 72.83(9) |
| O(1W)–Nd(1)–O(2W) | 127.65(9) |
| O(5)#1–Nd(1)–O(2) | 71.46(9) |
| O(6)#2–Nd(1)–O(2) | 74.67(9) |
| O(4)#3–Nd(1)–O(2) | 135.34(9) |
| O(3)–Nd(1)–O(2)  | 77.29(9) |
| O(1)–Nd(1)–O(2)  | 64.92(8) |
| O(1W)–Nd(1)–O(2) | 125.80(9) |
| O(2W)–Nd(1)–O(2) | 141.34(9) |

Symmetry codes: #1 x, y–1, z; #2 –x + 1, –y + 1, –z + 1; #3 –x + 2, y–1/2, –z + 3/2.
carboxyl group. All the previous IR spectra attributions of complex 1 are consistent with the result of X-ray single-crystal analysis.

The results of crystallographic analysis showed that complex 1 crystallizes in monoclinic system with space group $P2_1/c$, and features a new three-dimensional pillared-layer architecture. The fundamental unit consists of one unique Nd(III) centre, one PDC anion, two coordination water molecules, one free water molecule and half a oxalate anion located on a crystallographic inversion centre, as illustrated in Figure 1. The Nd(III) centre is eight coordinated with four oxygen atoms from four different PDC anions, two oxygen atoms from one oxalate anion and two oxygen atoms from two different coordination water molecules. The Nd-O bond distances range from 2.364(4)–2.524(3) Å, which are similar to those observed in the reported Nd(III) polymers, and O–Nd–O bond angles are range of 68.28(10)–150.34(10)°. Therefore, the Nd(III) centre displays an O₈ distorted dodecahedral geometry. The PDC ligand in complex 1 has a 4-connected geometry to connect four Nd(III) ions (Figure 2). Each carboxyl group behaves as a bidentate to bind two Nd(III) ions, but one carboxyl group bridges two Nd(III) ions in syn-syn fashion with the Nd...Nd distance being 5.1121(4) Å and another bridges two Nd(III) ions in syn-anti fashion with the Nd...Nd distance being 6.2990(4) Å. As shown in Figure 3, Each Nd(III) centre is linked by four equivalent PDC anions to generate an infinite two-dimensional Shubnikov tetragonal grid layer parallel to the (-1 0 2) plane based on the four-connected Nd(III) center and 4-connected PDC anion. Moreover, very intriguingly, the two-dimensional Shubnikov tetragonal grid layers are further connected by oxalate anion, acting as a bidentate chelating-bridging ligand (Figure 2), to generate a three-dimensional pillared-layer framework featuring a three-dimensional inorganic-organic alternate architecture. Additionally, the versatile hydrogen bonding (Table S1) and π...π stacking interaction (Table S2) in complex 1 stabilize the whole crystal structure. From the
topological perspective view, each neodymium atom can be considered as a five-connected node, each PDC anion may be considered as four-connected node and each oxalate anion can be considered as a linker. According to the simplification principle, the whole framework can be topologically represented as a binodal (4,5)-connected network with the short vertex symbol (44.62)(44.64.82) indicating a typical xww topology (Figure 4).

Due to the excellent luminescent properties of lanthanide coordination compounds, the luminescent property of complex 1 was explored in the solid state at room temperature. As shown in Figure 5, complex 1 exhibits two intense emission peaks in visible region at the excitation of 265 nm. Obviously, the two peaks at 470 and 550 nm are attributed to the characteristic emission peaks of Nd(III) ions in the visible region. According to the literature and our experimental verification, the emission bands at 550 nm and 470 nm can be assigned to the transition of Nd(III) ions from $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$, and $^4I_{9/2} \rightarrow ^2P_{1/2}$, respectively.

**Conclusion**

In summary, we have successfully synthesized and structurally characterized a new Nd(III) coordination polymer containing both pyridine-3,5-dicarboxylate and in situ generated oxalate ligand. It represents an unusual 3D structural example of pillared-layer coordination architecture by spontaneous assembly of mixed-carboxylic ligands. Moreover, the complex 1 shows intense solid-state luminescence emission in the visible region at room temperature. The further investigations upon such a successful example are still in progress.

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**Supplementary Material**

Supplemental data for this article can be accessed at the publisher’s website. CCDC 857791 contains the supplementary crystallographic data for complex 1. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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