Rare Earth Ion Center in Distorted Square Anti-Prism Coordination Environment: A Novel Three-Dimensional Coordination Polymer with Channels

Xu Haitao, Zheng Nengwu,* Jin Xianglin,† Yang Ruyi, and Li Zhengquan
Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China
†Department of Chemistry, Beijing University, BeiJing 100871 P. R. China

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The hydrothermal synthesis and the structure of the coordination polymer $[La_2(ATPT)_3{\cdot}(H_2O)_5]\ (H_2O)_2$ (ATPT = 2-aminoterephthalic acid) were reported. The Rare-earth ion center was in the distorted square anti-prism coordination environment. These carboxyl groups linking La^{3+} ion centers engendered one-dimension channels with pending groups. Guest water molecules in these channels joined these pending groups via hydrogen bond.

Because of its potential applications,[1] 3-D coordination polymer with pores or channels has attracted considerable interest in materials. Many reports focused on coordination polymers containing transition metals.[2] Coordination polymer with rare-earth (RE) ion has rarely been studied. However, RE ions, as nodes of high-dimension coordination polymers, would be up to much for diverse coordination-mode and variable coordination numbers.[3] It prefers to O atoms. Some successful examples were reported.[4]

As building block to furnish coordination polymer, ATPT is considered as follows: a) it could furnish various coordination-mode due to multifunctional groups. b) Being one type of rigid ligand, ATPT would allow multi-dimension framework. c) As modifying groups, amino groups would be designed in channels or pores to connect small molecule via hydrogen bond. In this paper, the synthesis and the structure of $[La_2(C_8H_5NO_4)_3(H_2O)_5]{\cdot}2H_2O$ (**1**), being the first open framework furnished by ATPT, is reported.

The title compound was obtained by hydrothermal synthesis. A mixture of ATPT (0.0551 g), NaOH (0.0120 g) and distilled water (20 ml) was heated till boiling. When cooled, the solution was put into a 40-ml Teflon-lined stainless autoclave which was added $La(NO_3)_3$ (0.0979 g). The Teflon-lined stainless autoclave was sealed and heated at 154 °C for 72 h, then cooled to 122 °C for 1.5 h, and then kept this temperature for 2 h before finally declined to room temperature. Light-brown lamellar crystals of **1** suitable for X-ray diffraction analysis[5] were collected after washing by H_2O.

Compound **1** was stable in air and insoluble in water and common organic solvent. Infrared spectra exhibited broad absorption peaks at 3480, 3428, 3369 cm^{-1} due to N-H, O-H stretching modes. Two medium-intensity bands at 1621 and 1495 cm^{-1} could be ascribed to carboxyl groups' (CO_2^-) stretching mode. Intense features at 1534, 1424 cm^{-1} were assigned to the δ (N-H) and δ (O-H) modes.

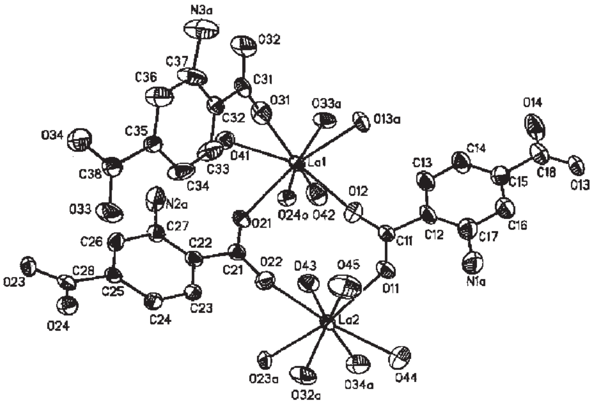

Figure 1. ORTEP plot of coordination structure of **1**.

As shown in Figure 1, there was two crystallographically independent La(III) ions. Each La^{3+} ion coordinated with eight oxygen atoms and was in the distorted square anti-prism center. For $La1^{3+}$ ion, O_{13a}, O_{33a}, O_{31}, and O_{41} form the top plane of the distorted square anti-prism and the bottom plane was completed by O_{12}, O_{42}, O_{24a}, and O_{21}. Six oxygen atoms were from carboxylate anions and the La1-O distances were in the range of 2.422(4)–2.592(3). The other two, the bond lengths 2.608(4) and 2.616 (4) respectively, were provided by two coordinated water molecules. These were comparable with those reported for $[La(Hpdc)_3(H_2O)_4]{\cdot}2H_2O$.[4] The bond angles around $La1^{3+}$ center were in the range from 69.37° (13) to 81.69° (13). Like $La1^{3+}$ ion, O_{45}, O_{11}, O_{43}, and O_{22} was in the top plane of the distorted square anti-prism and the bottom plane was occupied by O_{12}, O_{42}, O_{24a}, and O_{21} for $La2^{3+}$. Five were from carboxyl groups and the La2-O bond length was in the range of 2.397(4)–2.546(3), the rest were from three water molecules and their La2-O bond length was in the range of 2.582(4)–2.662 (5). The bond angles around $La2^{3+}$ ion center were from 70.17°(16) to 78.14°(13). As illustrated above, RE-O bond distances with O atoms from coordinated water was longer than those with O atoms from carboxyl groups. To the best of our knowledge, the chelated-bond distance should be longest, the mono-dentate-bond distance was middle and the bridged-bond distance was shortest for the RE-O bond. If the chelated-bond would come into being, its distance must be beyond La_2-O_{45} bond distance (2.662(5)). In fact, the chelated-bond couldn't form in the compound **1**.

Carboxylate anions bridged metal ions to furnish an eight-membered $La_2(CO_2^-)_2$ macro-cycle (La1-C_{11}-La2-C_{21}-La1). Compared with the corresponding M•••M distances reported in literature,[6] the shorter La•••La distance (*ca* 5.0) may be attributed to the additional consolidation from bridging-bond. These carboxylate anions (O_{11}-C_{11}-O_{12} and O_{21}-C_{21}-O_{22}) with a dihedral angle of 15.68° lean to different metal ion. Judging from coordination environment, the steric hindrance around La1 was stronger than that around La2. It would lead to various effect of steric hindrance for benzene ring linking different carboxyl group. So the carboxylate plane deflecting its benzene ring presented different dihedral angles. The carboxylate (O_{11}-C_{11}-O_{12}) plane formed dihedral angles (α_1) of 14.18° to its benzene ring. This result was also comparable well with those found in Co(pdc)·$2H_2O$[7] (13.37°). The other carboxylate (O_{21}-C_{21}-O_{22}) plane leaving its benzene ring had dihedral angles (α_2) of 9.69°. Because of the bridged-bond carboxyl groups leaning to different ion centers, the Benzene ring containing carboxyl group (O_{11}-C_{11}-O_{12}) was subjected to steric hindrance stronger than that containing carboxyl group (O_{21}-C_{21}-O_{22}), and the dihedral angle α_1 was larger than the dihedral angles α_2.

CO_2^- anions linking metal ions to form sandwich in *ab* plane (not shown) employed two modes: the bidentate *anti-anti* mode to bind metal layer or bridge adjacent layer and the mono-dentate bond mode to link adjacent-layer. These uncoordinated oxygen atoms would play an important role for hydrogen bonds with guest water molecules between sandwiches.

These ligands linking La^{3+} ion centers engendered one-dimension channels along *a*-axis (Figure 2), which was about 9×6 Å^2 in cross-section. It was interesting to observe coordinated water and amino groups pending in channels. Guest water molecules in these channels join pending groups via hydrogen bonds. So these channels were deemed hydrophilic channels. The highly disordered solvent molecules would trap in the channels. The most intriguing feature of the channel-structure was hydrophilic properties, which would provide new possibilities for shape and nature selective as molecular sieves. Further studies by other methods are required to characterize them in progress.

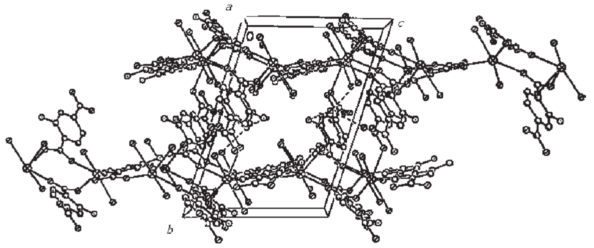

Figure 2. Perspective view of **1** along the X-axis.

The organic ligand symmetry was crucial for open framework. Because of the π-π conjugation, carboxyl groups and benzene would lean to co-plane. Anions bonded metal ions to form quadrangle down Z- and Y-axis and resulted in one-dimension channels along X-axis in compound **1**. For 4-sulfobenzoic acid in compounds Eu_2(1, 4-BDS)$(4SB)_2$·$3H_2O$[8] and Gd_2(1, 4-BDS)$(4SB)_2$·$3H_2O$[8], sulfonic group presented tri-pyramid so as to get twisty building block. This building block furnished not channels but 3-D pillared networks. Another example described in the crystal $Na_2Co(bpdc)_2H_2O$[9], CO_2^- groups attached the adjacent metal layer to give rise to a pillared 3D framework due to anions cross-linked metal ions in $(bpdc)_2^{2-}$ ligand.

Our current works have focused on the synthesis of channel-structure with pending groups and a few achieved.

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5 Crystal data for $[La_2(C_8H_5NO_4)_3(H_2O)_5]\cdot 2H_2O$: $C_{24}H_{29}La_2N_3O_{19}$, $M = 941.32$, triclinic, space group P-1, $a = 10.452(2)$, $b = 15.248(3)$, $c = 10.221(2)$ Å. $\alpha = 101.431(5)$, $\beta = 101.226(6)$, $\gamma = 105.766(5)$°. Z = 2, V = 1482.3(5) Å^3, $D_C = 2.109\ \mathrm{g\,cm^{-3}}$, Crystal size $0.45 \times 0.40 \times 0.10\ \mathrm{mm^3}$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, T = 293(2) K, Absorption coefficient is $2.938\ \mathrm{mm^{-1}}$, $2.55° < 2\theta < 27.48°$, $R_1[I > 2\sigma(I)] = 0.0367$, wR2 (all data) = 0.1030, GOF = 1.085. Deposited in CCDC 166193.

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