Hydrothermal Synthesis of Highly Robust 2-D Layered Coordination Polymer of La

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The crystal structure of the coordination polymer: $[La(C_8H_5NO_4)_{1.5}H_2O]_n$ is reported, and some properties are characterized. It is interesting to observe 2-D layer-structures parallel to *ac* plane. The TAG reveals it's thermal high stability and the EPR spectra show that there is no odd spin electron.

The construction of infinite solid-state arrays by employing the coordinate covalent bond and the principle of self-assembly has resulted in numerous metal-ligand networks with fascinating structural topologies. For example, there are chain,[1,2] ladder,[3–5] grid,[6] brick wall,[7] honeycomb,[8] diamond,[9] and channel.[10] And their applications in material science including in the separation, the absorption and catalysis have attracted much attention. As reported in literatures, most organic-building blocks are ligands with N atom[11–13] and the nodes are usually transition metal ions. In this study, we employed the ligand with carboxyl groups and Rare-earth ion to assemble a new coordination polymer. 5-Aminoisophthalic acid has a C_{2v} symmetry and possesses two carboxyl-groups furnishing various coordination modes. Moreover, amino groups, as modifying groups, would be very important for formation of hydrogen bond. In our pursuit of high-dimensional open-framework, we chose 5-aminoisophthalic acid as an organic-building block to obtain an unexpected coordination polymer: $[La(C_8H_5NO_4)_{1.5}\cdot H_2O]_n$[14] by hydrothermal synthesis.

The compound **1** was prepared under the hydrothermal condition: A mixture of 5-aminoisophthalic acid (0.0550 g), NaOH (0.0118 g) and distillated water (20 ml) was heated till boiling. When cooling, the solution was put into a 40-ml Teflon-lined stainless autoclave to which was added $La(NO_3)_3$ (0.0980 g). The Teflon-lined stainless autoclave was sealed and heated at 154 °C for 52 h, then cooling to room temperature. The light-brown lamellar crystals of **1** suitable for X-ray diffraction analysis were collected after washing by H_2O, which was stable in air and insoluble in water and common organic solvent.

Infrared spectra showed broad absorption peaks at 3455, 3417, and 3360 cm^{-1} owing to O-H and N-H stretching modes. Two medium-intensity bands at 1620 and 1556 cm^{-1} could be ascribed to carboxylate anions (CO_2^-) stretching modes. There was no absorption peak of any protonated ligand (1730–1680 cm^{-1}), which confirms complete deprotonation of 5-aminoisophthalic acids by sodium hydroxide. Intense features at 1530, 1471 cm^{-1} are assigned to δ (N-H) and δ (O-H) modes.

As shown in Figure 1, there is only one crystallographically distinct lanthanide atom that is in nine-membered coordination environment–eight oxygen atoms from six 5-aminoisophthalic acid ligands and another one from water-molecule. Carboxylate anions of two ligands chelate the metal La^{3+} ion to get two four-membered rings and the chelating angles are 49.95(6)° (O_{4c}–La(1)–O_{3c}) and 48.05(6)° (O_{6a}–La(1)–O_5) respectively. The rest carboxylate anions bridge the metal La^{3+} ions using u_2 or u_3 modes. The chelated carboxylate anion' plane is tilted with respect to its benzene ring with dihedral angle of 1.46 °, and the bridged carboxyl group' plane deflecting its benzene ring presented dihedral angles of 17.09 °. These La-O bond-distances were ranged in 2.4136–2.826 Å and the average La-O length was 2.5826 Å.

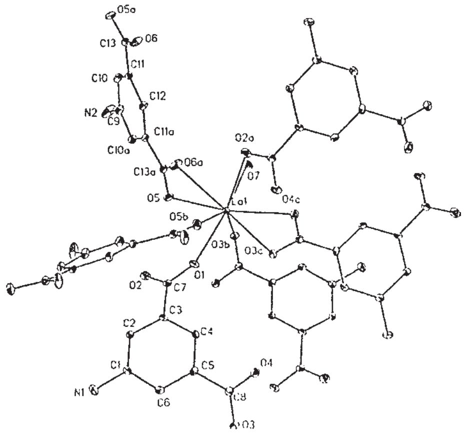

Figure 1. ORTEP plot of coordination structure of **1**. Selected bond lengths (Å) and angles (°): La(1)–O(1) 2.4136(18), La(1)–O(5)#1 2.4674(19), La(1)–O(7) 2.501(2), La(1)–O(6)#2 2.509(2), La(1)–O(4)#3 2.545(2), La(1)–O(2)#1 2.6122(19) La(1)–O(3)#4 2.665(2) La(1)–O(3)#3 2.704(2) La(1)–O(5) 2.826(2). O(1)–La(1)–O(5)#1 75.59(7), O(5)#1–La(1)–O(5) 104.49(7), O(5)–La(1)–O(6)#2 48.05(6), O(2)#1–La(1)–O(6)#2 68.13(7), O(2)#1–La(1)–O(4)#3 76.89(7), O(4)#3–La(1)–O(3)#3 49.95(6), O(3)#4–La(1)–O(3)#3 99.23(6), O(3)#3–La(1)–O(1) 81.79(6), O(7)–La(1)–O(2)#1 71.63(7).

The organic building block of 5-aminoisophthalic acids has a C_{2v} symmetry, but two-carboxyl groups employ in u_2 ($\eta^1\eta^1$) and u_3 ($\eta^2\eta^1$) fashion to link metal La^{3+} ions respectively. Each ligand bonds four metal ions (La^{3+}). One carboxyl group of a unit ligand combines two metal La^{3+} ions owing to O-η^2 and the other carboxylate anion bridges another two metal La^{3+} ions to construct 2-D layers parallel to *ac* plane (Fig. 2). The ligands (not shown), whose benzene ring is parallel to *b*-axis, connect layers to furnish channels along *b*-axis via carboxyl groups. Amino groups and coordination waters were pendant in these channels. There are interactions of hydrogen bonds (N(1)–H(11)···O(2)#7 = 3.136(4) Å, O(7)–H(14)···O(4)#5 = 2.867(3) Å, and O(7)–H(15)···N(1)#8 = 2.826(4) Å) among amino groups, coordination waters and oxygen atoms of carboxylate anions. These channels would be hydrophilic. Further studies about this property are in progress.

The thermogravimetric analysis was done in nitrogen to study the thermal stability of this compound. The result shows

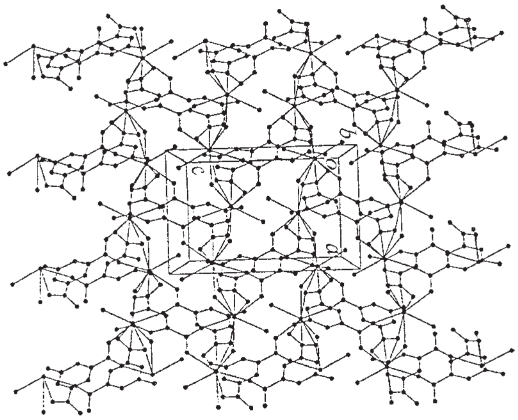

Figure 2. Perspective view of **1** along the *b* axis.

that 4.0% weight loss from 230 °C to 240 °C due to the removal of coordination water (cal: 4.2%). The IR spectrum of the dehydrated sample showed no changes. The XRD patterns are slightly changed from the original in the positions and the intensities of some lines. It means that the channel-structures don't change when coordination waters are dehydrated. And from 440 °C to 880 °C the weight loss 57.40% was equivalent to loss of organic ligands (cal: 57.44%) again. The decomposed product was La_2O_3 particle that was determined by XRD.

The EPR spectrum of the compound showed no signal except for the signal at 3420G ($g = 2.0037$) due to DPPH ($g = 2.0037$). It fully corresponds to the d^0 La (III) configuration.

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14 Crystal data for $[La(C_8H_5NO_4)_{1.5}(H_2O)]$: $C_{12}H_{9.5}LaN_{1.5}O_7$, $M = 425.62$, Orthorhombic, space group $P\ bcn$, $a = 12.2746(3)$, $b = 8.0820(2)$, $c = 25.7209(8)$ Å. $Z = 8$, $V = 2551.7(9)$ Å^3, $D_{calcd} = 2.216\ g\,cm^{-3}$, Crystal size $0.45 \times 0.30 \times 0.08\ mm^3$, λ (Mo Kα) = 0.71073 Å, $T = 293(2)$ K, $\mu = 3.386\ mm^{-1}$, $3.02° < 2\theta < 27.48°$, $R_1\ [I > 2\sigma(I)] = 0.0214$, $wR_2\ [I > 2\sigma(I)] = 0.0345$, wR2 (all data) $= 0.0357$, GOF $= 0.824$. Deposited in CCDC 175780.