Single-crystal structure of coordination polymer \([\text{Nd}_2(C_8H_5NO_4)_3 \cdot 4\text{H}_2\text{O}]\)  

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Abstract The single-crystal structure of the coordination polymer \([\text{Nd}_2(C_8H_5NO_4)_3 \cdot 4\text{H}_2\text{O}]\), with rhombic-channels is reported in this paper. There are two crystallographically independent Nd(III) ions, and each Nd(III) ion is in the eight-coordinated environment. Seven of eight oxygen atoms are from six 5-aminoisophthalic acid ligands, the other oxygen atom is given by coordination water. Carboxyl groups link two Nd(III) ions using \(\eta^1\) and \(\eta^2\) modes. Two carboxyl groups from ligands chelate Nd(III) ion to form four-membered rings. Crystal data: Triclinic, space group \(P\overline{1}\), \(a = 1.03680(5)\) nm, \(b = 1.66934(15)\) nm, \(c = 0.88221(14)\) nm, \(\alpha = 99.754(2)^{\circ}\), \(\beta = 111.169(4)^{\circ}\), \(\gamma = 85.400(4)^{\circ}\). Some ligands linking metal Nd(III) ions parallel to \(ab\) plane form molecular ladders, and the others linking molecular ladders result in rhombus channels along \(c\)-axis. These coordinated water molecules and amino groups are pendent in the channels.

Keywords: coordination polymer; channels; X-ray single-crystal structure.

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Rapid progress is now being made in the design and synthesis of coordination polymers with unique topological structures\(^6\)\(^7\)\(^8\)\(^9\). Lots of interesting topological structures such as chain-like\(^{[6]}\), ladder-like\(^{[5]}\), grid-like\(^{[6]}\), brick-like\(^{[10]}\), comb-like structures\(^{[11]}\), etc., have been reported. In recent years, preliminary applications of coordination polymers to chemistry and material science, such as molecular sieve, catalysis, nonlinear optical properties, magnetic materials, biotic sensors, etc., are also achieved. For the design of ideal topological structures, however, it requires rational selection from various organic ligands and metal ions in order to obtain the expected topological structure by means of assembly, thus making its realization somewhat difficult and challenging.

5-aminoisophthalic acid is a rigid ligand with various functional groups including carboxyl, and the symmetry is \(C_{2v}\). In the self-assembly process, the carboxyl tends to provide multiform coordination modes, which is of benefit to the design and assembly of the coordination polymers with novel structures, and the rigid framework of benzene could provide supports for the poly-dimensional structure. Moreover, being an independent group, NH\(_2\) creates condition for the formation of hydrogen bond. In the present study, a three-dimensional coordination polymer with rhombic channels, \([\text{Nd}_2(C_8H_5NO_4)_3 \cdot 4\text{H}_2\text{O}]\), is synthesized by using Nd\(^{3+}\) as the metal ion center and 5-aminoisophthalic acid as ligand, along with its single crystal structure reported.

The hydrothermal method has been proved extremely effective for the growth of the single crystal of coordination polymer although there are many techniques such as volatilization, diffusion, infiltration, etc\(^{[12]}\)\(^{[13]}\), can be used. Previously we have already obtained several ideal products in our lab by using the hydrothermal method and so have in this experiment.

1 Experimental

(i) Materials. Regents: 5-aminoisophthalic carboxylic acid, NaOH, Nd\(_2\)O\(_3\). All the regents were purchased from Aldrich or similar companies and were used directly in the present experiment without further purification except that Nd\(_2\)O\(_3\) was previously reacted with HNO\(_3\) to prepare Nd(NO\(_3\))\(_3\).

(ii) Synthesis. To 20 mL of distilled water were added a mixture of 53.7 mg of 5-aminoisophthalic acid and 12.0 mg of NaOH. After been heated to boiling, the aqueous solution was cooled and introduced into a Teflon-lined digestion bomb with a capacity of 40 mL, 99.0 mg of Nd(NO\(_3\))\(_3\) were added, and the digestion bomb was then sealed. After maintaining the temperature at 152°C for 48 h, the digestion bomb was cooled to room temperature. Complexes\(^7\) suitable for X-ray diffraction were obtained after washing the product by distilled water.

(iii) Measurement. The single-crystal structure of the coordination polymer was measured by a RIPDAKU as6s four-circle diffractometer.

2 Results and discussions

The light brown filmy single crystal of the coordination polymer \([\text{Nd}_2(C_8H_5NO_4)_3 \cdot 4\text{H}_2\text{O}]\) is stable in air and insoluble in water and common solvents such as ethanol, ether, and N,N-dimethyle formamide. Infrared spectroscopy of the solid complex distilled by KBr pellets was measured within the frequency range of 4000—400 cm\(^{-1}\) (Fig. 1). There are strong absorption peaks at 3648, 3392, 3264 and 3190 cm\(^{-1}\), due to stretching vibration of N—N and O—H of the ligand. The stretching vibration of carboxyl also results in the strong absorption peaks at 1626 and 3190 cm\(^{-1}\).
Fig. 1. IR spectrum of [Nd₂(C₆H₄NO₄)₃ • 4H₂O]ₙ single crystal.

The data on the single crystal structure of the coordination polymer, [Nd₂(C₆H₄NO₄)₃ • 4H₂O]₀, are as follows: molecular weight, 894.91; crystal system, triclinic; space group, P1; a = 1.03680(5) nm, b = 1.66934(15) nm, c = 0.88221(8) nm, α = 99.754(2)°, β = 111.169(4)°, γ = 85.400(4)°; V = 1.4029(2) nm³; Z = 2; ρcalc = 2.118 Mg/m³; final R[w] = 0.0265, wR₂ = 0.0608. The selected data on the bond lengths and bond angles of the single crystal are listed in Table 1.

As shown in Fig. 2, there are two crystallographically independent Nd³⁺ ions, either of which is in the eight-coordinated environment. For Nd¹⁺, seven of eight coordinating oxygen atoms surrounding the ion come from six different 5-aminoisophthalic acid ligands, and the other one from the coordinating water molecule. The Nd¹⁺ and a chelating ligand form a four-membered ring with the least coordination angle θO₃3Nd₁O₃4 = 49.19(8)°. The bond length of Nd—O ranges from 0.2372(3) to 0.2751(3) nm and its average bond length is 0.2481 nm. Behaving as Nd²⁺, Nd³⁺ is chelated by the carboxyl (O₁₄—C₁₈—O₁₃), which results in another four-membered ring. The least coordination angle is θO₁₃Nd₂O₁₄ = 48.99(9)° and the bond length ranges from 0.23483(3) to 0.2769(3) nm with an average value of 0.2462 nm. A comparison of the results obtained above shows that the data on the Nd¹⁺ and that on the Nd²⁺ are very close to each other, which results from the similar coordination environment. The ions center Nd¹⁺ and Nd³⁺ are connected with each other by three carboxyl using the θ¹ and θ³ mode. Using the rare earth metal as ion center often leads into high coordination number, but here we only got 8 other than 9—12. This may attribute to the steric hindrance of the organic ligand in the coordination polymer.

Being a kind of ligand with various functional groups, 5-aminoisophthalic acids can react with Nd³⁺ to construct a three-dimensional coordination polymer with rhombic channels [Nd₂(C₆H₄NO₄)₃ • 4H₂O]₀ (as shown in Fig. 3). Despite of the different coordination environments for two types of Nd³⁺ ions, each ligand coordinates with metal ions in the same way, i.e. one of two carboxyls in a ligand chelates one Nd³⁺ and bridges another Nd³⁺; another carboxyl bridges two Nd³⁺ ions. The group NH₂ behaves an independent one and does not act in the coordination process. Some ligands linking metal Nd³⁺ ions parallel to ab plane form molecular ladders, and the others linking molecular ladders result in rhombic channels along c-axis. The coordinated water molecules and the NH₂ group suspend in the channels and thus make the channels valuable. The active NH₂ groups and coordinated water molecules may pull the free water molecules around the channels through hydrogen bonds so that the channels are endowed with water-absorbing capacity. This work is under further research.