Syntheses and Structure of a Novel Layered Lanthanide–Zinc Coordination Polymer: $[LaZn(HIDA)(IDA)_2{\cdot}0.5H_2O]_n$

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The hydrothermal reactions of La_2O_3, $Zn(CH_3COO)_2{\cdot}2H_2O$, iminodiacetic acid ($H_2IDA$), and H_2O resulted in the formation of a novel coordination polymers $[LaZn(HIDA)(IDA)_2{\cdot}0.5H_2O]_n$. X-ray diffraction analyses confirms that in complexe **1** La ions are lined through sharing the O atoms of IDA ligands which the octahedron-coordinated Zn ions are beside alternately to form a 1-D zigzag inorganic chain. And then a 2-D layered coordination polymer is constructed by helix bridging protonated HIDA ligands.

Recently, studies on the syntheses, structures, and properties of lanthanide-transition metal complexes are of current great interest, not only because they possess abundant structures, but also because there are potential applications to magnetic materials,[1–3] La-doped semiconductor technology,[4] luminescent properties,[5] sensitive luminescent sensors,[6] and fiber optical materials[7] in recent rapidly developing fields. However, the structures of Ln–Zn coordination polymer are more less reported than other lanthanide-transition metal complexes.[8] Iminodiacetic acid, a derivative of glycine, was selected as the ligand in this investigation, because it has more coordinated atoms and coordinated patterns.[2,9] A series of Ln–Cu, Ln–Ni coordination polymers have been synthesized by conventional methods and structurally characterized, but till now as far as we know, no Ln–Zn coordination polymers with H_2IDA ligands have been reported. Herein we report the preparation and structure of a novel layered lanthanide heterometallic complexe containing d-block element zinc, $[LaZn(HIDA)(IDA)_2{\cdot}0.5H_2O]_n$.[1]

The compound **1** was prepared under hydrothermal conditions: heating a mixture of La_2O_3 (0.0815 g, 0.25 mmol), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.1098 g, 0.5 mmol) H_2IDA (0.133 g, 1 mmol) and 14mL H_2O in a 25mL stainless-steel reactor with Teflon liner at 160 °C for 72 h resulted in colorless crystals of **1**. Yield: 65% based on the La. Anal. Found: C, 23.58; H, 2.72; N, 6.53%. Calcd. For $C_{12}H_{17}LaN_3O_{12.5}Zn$ (607.61): C, 23.71; H, 2.83; N, 6.92%. IR (KBr): 3470 (m), 3299 (m), 1663 (m), 1581 (s), 1436 (s), 1294 (s), 1128 (m), 1025 (m), 913 (m), 726(m), 627 (m), 533 cm^{-1} (m).

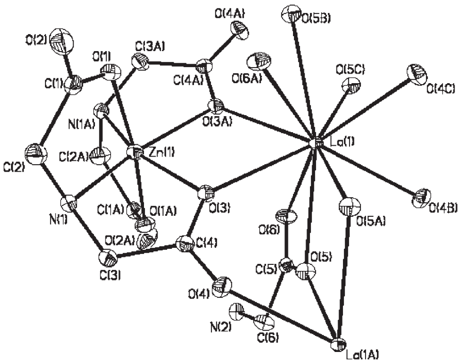
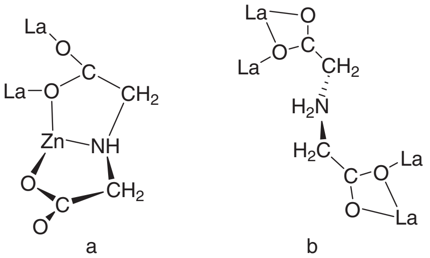


Figure 1. The coordination environment of complex **1**.



Scheme 1. The coordination mode of H_2IDA ligands in **1**.

A crystallographic analysis[10] of **1** exhibited a 2-D structure and the coordination environment is shown in Figure 1. Each Zn center is coordinated by a nitrogen and two oxygen atoms from a IDA ligand to form two five-membered chelating rings, which shows the typical *fac*-NO + O (apical) tridentate coordinated mode[11] as in Scheme 1a. At the same time the Zn ion further coordinated by the other same IDA ligand to form an octahedral geometry. The Zn1–N1 bond length is 2.137(3) Å, whereas the Zn1–O1 and Zn1–O3 bond distances are 2.092(3) and 2.126(3) Å. Each La^{3+} ion coordinated with ten oxygen atoms from eight different IDA ligands. The La–O bonds range from 2.439(3) Å to 2.781(3) Å and the ranges of the O–La–O angles from 47.20(7)° to 164.80(11)°. The adjacent La(III) is linked through the IDA ligand by two different types of IDA ligands in both the coordination mode and the available mode. One is the double O atoms (O3, O4) of a carboxylic group of IDA ligand, the separation of two La ions is 4.305 Å. Both the two deca-coordinate La and octa-coordinatd Zn and deca-coordinate La are connected together via an edge-sharing mode. The other one is the single O atom bridging mode, as it is shown in Scheme 1b, using the O5 from a carboxylic group of HIDA ligand whose N atom is protonated. The Zn and La ions are linked by sharing the O atoms of the carboxylic group of IDA ligand to form a 1-D zigzag inorganic chain and octahedron-coordinated Zn ions are beside the 1-D chain, alternately. The separations of Zn and La and the adjacent La ions are 3.815 and 4.305 Å, respectively. The HIDA ligand shows a helix bridging mode, as it is shown in Figure 2, to makes a 1-D inorganic chain extending further into a

2-D layer structure. As shown in Figure 3, the distance of the adjacent inorganic chains is 0.88 nm. At the same time channels can be shown in which guest water molecules are inside. It is noteworthy that the bridging mode of dicarboxylic acid is the first observed for lanthanide-transition metal complexes.

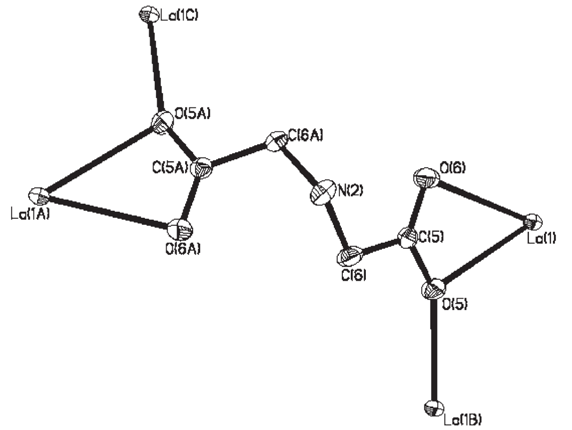


Figure 2. The helix bridging coordination mode of protonated HIDA ligand to La.

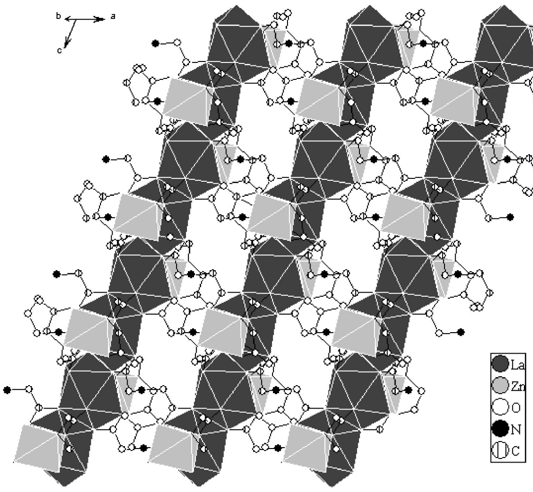


Figure 3. The 2-D layer channel structure of **1** (the water molecules are omitted for clarity).

Under air environment, thermogravimetric analysis (TGA) performed on **1**. In the first step, the uncoordinated H_2O molecule and a part of the ligand were removed in the range 14.7–374 °C. And then all the part of ligands is decomposed in the temperature range 374.21–729.66 °C. The remaining weight of 39.18% corresponds to the percentage (40.20%) of the remaining ZnO and La_2O_3.

In summary, we have synthesized a novel layered channel coordination polymers $[LaZn(HIDA)(IDA)_2{\cdot}0.5H_2O]_n$ through hydrothermal reaction, the organic ligand H_2IDA gave diverse coordination mode, especially an unusual protonated helix bridging mode to link the 1-D zigzag inorganic chain into 2-D layered structure. Further investigation on the other lanthanide–zinc complexes with H_2IDA is in progress so that the diverse coordination number of lanthanide and various configuration of H_2IDA ligand could result in rich structures.

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10 Crystal data for **1**: $C_{12}H_{16}N_3O_{12.5}LaZn$ (293K). $M_r = 606.58$, monoclinic, space group $C2/c$, $a = 9.680(3)$ Å, $b = 24.168(12)$ Å, $c = 8.579(3)$ Å, $\beta = 114.54(2)^\circ$, $V = 1825.8(12)$ Å^3, $Z = 4$, $D_c = 2.207$ g/cm^3, $\mu = 3.642$ mm^{-1}, $F(000) = 1200$, $T = 293(2)$ K. 5127 reflections measured ($2.46^\circ < \theta < 24.99^\circ$, $\lambda = 0.71073$ Å), 1614 unique ($R_{\mathrm{int}} = 0.0433$), $R_1[I > 2\sigma(I)] = 0.0240$, wR_2 (all data) $= 0.0625$ and $S = 1.034$. Deposited in CCDC 225488.

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