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Adjusting the structures of lanthanide(III) complexes by variation of the metal sources: From a 2D $(3^2.4)(3^4.4^3.5^2.6^5.7)$ layer to an unusual 3D $(4^{12}.6^3)(4^9.6^6)$ **nia** network

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ABSTRACT

A novel coordination polymer $[La(L)(H_2O)]_n$ (1) has been prepared by hydrothermal reaction of 5-hydroxyisophthalic acid (H₃L) with La(NO₃)₃·6H₂O, which exhibits an unusual three-dimensional (3D) (6,6)-connected **nia** net with Point (Schläfli) symbol of $(4^{12}.6^3)(4^9.6^6)$. Meanwhile, a two-dimensional (2D) (3,6)-connected (3².4)(3⁴.4³.5².6⁵.7) coordination network { $[Ho_2(HL)_3(H_2O)_2] \cdot H_2O$ }_n (S1) was also obtained with partially deprotonated HL²⁻ ligand. Comparison of the structural differences between 1 and S1 suggests that the different metal sources play an important role in the construction of such coordination networks.

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The construction of coordination polymers based on assembly of metal atoms and multifunctional organic ligands has been extensively studied in recent years owing to their intriguing topologies and potential applications as functional materials [1,2]. In comparison with the d-block transition metal (TM) ions, lanthanide atoms have higher coordination numbers and more flexible coordination spheres, which make it even more difficult to control the structures. In addition, according to the hard-soft acid-base theory, the lanthanide atoms have high affinity for oxygen donor atoms [3]. In general, multicarboxylate ligands are usually employed in the construction of lanthanide polymeric complexes [4]. Among them, 5-hydroxyisophthalic acid (H₃L), as a carboxylate derivative, has attracted much interest based on the following considerations: (1) it has two carboxyl groups which may exhibit diverse coordination modes; (2) the hydroxyl group may provide the additional binding site and connect metal atoms to generate more complicated structures incorporation with the carboxyl groups; and (3) the carboxyl and hydroxyl groups are good candidates for hydrogen bonds to construct supramolecular structures with higher dimensionality. Thus far, several lanthanide coordination polymers constructed by using H₃L have been reported [5–9]. For example, Li and co-workers have hydrothermally synthesized a series of 2D lanthanide layered structures, {[Ln(HL)(H₂- O_{5}] $\cdot 0.5HL \cdot H_{2}O_{n}$ (Ln = Eu, Gd, Tb, Dy, and Er), which exhibited the helical cation chains with organic ligands as templates [5]. Also, Yan, et al. [6,7] and Huang, et al. [8] have successfully obtained a series of another 2D lanthanide networks, namely $\{[Ln(HL)(H_2L)(H_2O)_2] \cdot 2H_2O\}_n \cdot (Ln = La, Ln)$

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Tb, Er, Sm for Yan, et al. and Nd for Huang, et al.), which comprise 1D Ln–O–C–O–Ln chains. By the reaction of La(ClO₄)₃·6H₂O with H₃L in the presence of NaOH and K₂C₂O₄·6H₂O, Si, et al. isolated a complicated 3D structure with coordinated oxalic ions, {[La₂(ox)(HL)₂(H₂-O)₄]·2H₂O}_n (ox = oxalate) [9]. Thus, further efforts are required to provide more information on the coordination behavior of H₃L, in order to design and prepare new crystalline materials with such types of organic ligands.

In this work, a 3D (6,6)-connected **nia** lanthanide network $[La(L)(H_2O)]_n$ (1) was obtained by the reaction of H_3L with $La(NO_3)_3$ ·6- H_2O under hydrothermal condition. Moreover, a 2D (3,6)-connected (3².4)(3⁴.4³.5².6⁵.7) coordination polymer { $[Ho_2(HL)_3(H_2O)_2] \cdot H_2O]_n$ (**S1**) was synthesized in this research by changing the metal source. Herein, we report the syntheses, crystal/topological structures, and properties of **1** and **S1**.

Complexes 1 and S1 were obtained by the hydrothermal reaction of H_3L with $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La for 1 and Ho for S1) in the presence of NaOH [10]. The compositions were confirmed by elementary analysis and IR spectra, and the phase purities of the bulk samples for luminescent/thermal measurements were identified by powder X-ray diffraction (PXRD) (please see Fig. S6 in the Supplementary material).

The structure of **1** has a very complicated 3D coordination framework [11]. The asymmetric unit consists of one La(III) atom, one L^{3-} ligand, and one coordinated water molecule. Each La(III) atom is nine-coordinated and shows a distorted tricapped trigonal prism coordination geometry (see Fig. 1) finished by eight carboxylate O atoms (O1, O2, O2A, O5B, O4C, O3D, O4D, and O5E) from six distinct L^{3-} ligands and one O_{water} atom (here O6). The La–O bond distances and the bond angles around each La(III) atom are in the ranges from

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Fig. 1. View of the local coordination environment of La(III) in **1**. The atoms labeled with the suffixes A, B, C, D, and E are generated by the symmetry operations (x, -y + 1/2, z + 1/2), (-x+2, y+1/2, -z+3/2), (x+1, -y+1/2, z+1/2), (x+1, y, z), and (-x+2, -y, -z+2), respectively.

2.458(3) to 2.754(3) Å and 49.12(11) to 153.72(12)°, respectively (see Table S1 in the Supplementary material). In **1**, the carboxylate and hydroxyl groups of H_3L ligand are fully deprotonated. The L^{3-} ligand shows the μ_6 -bridging mode (see Scheme 1), which connect six La(III) atoms through one μ_2 -hydroxyl and two μ_2 - η^1 : η^2 chelating/ bridging carboxylate groups. Remarkably, the examples with the hydroxyl group involving in the metal coordination in different forms of H₃L ligands are still rare even though there are a few of coordination polymers constructed by H₃L ligands [12–15]. To the best of our knowledge, only four such polymeric complexes were reported, namely $[Ni(HL)(C_{10}H_{14}N_4O)(H_2O)]_n$ $[C_{10}H_{14}N_4O = 2,2'-bis(1H-imi$ dazolyl)ether] [12], {[CuZn(HL)₂(bipy)(H₂O)] \cdot 1.5H₂O}_n [bipy = 4,4'bipyridyl] [13], $\{18$ -crown[6]·Cs[HL]\}_n [14] and $\{(Me_2NH_2)\}$ $[PbSr(HL)(L)]_n$ [15]. Significantly, complex **1** exhibits the first lanthanide example in which the hydroxyl group of H₃L ligand takes part in the coordination with the metal atoms. Based on the linkage of carboxylater groups in L^{3-} ligands, La(III) atoms are connected to generate an infinite 2D layered motif (see Fig. 2). Moreover, the connections of μ_2 -hydroxyl groups in L^{3-} ligands bridge the 2D motifs mentioned above to lead to the formation of the final 3D network (see Fig. 3). In addition, in **1**, the benzene π planes of L^{3-} ligands do not interact obviously with each other [the closest centroid-centroid separation is 5.223 Å checked and calculated by PLATON procedure, which is very longer than 3.8 Å].

From the viewpoint of topology, both L^{3-} ligand and La(III) atom can be regarded as isolated 6-connectors due to each of them linking six of the other ones. Thus, the overall net of **1** can be reduced as a binodal (6,6)-connected network with the Point (Schläfli) symbol of (4⁹.6⁶)(4¹².6³) calculated by TOPOS program (see Fig. 4) [16], which has been referred by O'Keeffe as an **nia** notation [17].

When we used Ho(NO₃)₃·6H₂O instead of La(NO₃)₃·6H₂O in this research, a 2D (3,6)-connected $(3^2.4)(3^4.4^3.5^2.6^5.7)$ topological net (**S1**) was obtained under the same condition (see Figs. 5 and 6 as



Scheme 1. Coordination mode of L³⁻ ligand in 1.

well as Figs. S1–S3; brief description and discussion of **S1** were shown in the Supplementary material). The results indicate that the more complicated structures can be obtained due to the increase of coordination number of metal atoms with highly connected ligands. Comparison of the structural differences between **1** and **S1** suggests that the different metal sources play an important role in their structural assemblies.

In addition, the solid-state photoluminescent properties of **1** and **S1** were investigated at room temperature, as shown in Fig. S4 in the Supplementary material. The luminescence emission bands with the peak maxima (λ_{max}) were observed at 371 nm (λ_{ex} =341 nm) for **1** and 350 nm (λ_{ex} =280 nm) for **S1**, respectively. To further



Fig. 2. View of the 2D layered motif in 1.



Fig. 3. View of the 3D network in 1. The different layers are highlighted in different colors.



Fig. 4. A schematic representation of the 3D nia topology (blue spheres: La(III) atoms; orange spheres: L^{3-} ligands).

analyze the nature of these emission bands, the photoluminescent properties of the free H₃L have also been investigated under the same experimental conditions. The emission band for free H₃L ligand is attributable to the $\pi^* \rightarrow n$ transitions. The fluorescent behaviors of **1** and **S1** are very similar to that observed for the free H₃L ligand (see Fig. S4 in the Supplementary material), which displays the maximal emission at 364 nm upon excitation at 345 nm. Moreover, the emission mechanism for **1** and **S1** can be properly ascribed to charge-transfer transition between the H₃L ligand and the central Ln(III) ion [18].

Thermogravimetric (TG) analyses were performed to explore the thermal stability of **1** and **S1** under a nitrogen atmosphere by heating the corresponding complexes from room temperature to at least 800 °C with a heating rate of 10 °C min⁻¹ (see Fig. S5 in the Supplementary material). The TGA curve exhibits that 1 features two stages of weight loss, the first weight loss of 5.36% between 274 and 324 °C (peaking at 303 °C), corresponding to the loss of one water molecule (calcd: 5.54%). Then, the sample remains largely unchanged until the decomposition occurs at the temperature of ca. 620 °C. Finally, complex 1 starts to quickly decompose with one sharp step of weight loss (peaking at 731 °C). The final residue is not characterized because its weight loss does not stop until heating ends at 900 °C. The TGA curve for **S1** shows a first weight loss of 5.85% in the range of 130–174 °C (peaking at 154 °C), corresponding to the loss of coordinated free water molecules (calcd: 5.91%). The residue keeps thermally stable from 157 to 428 °C, and then shows a continuous weight loss of 39.41% from 430 to 900 °C (peaking at 447 and 593 °C), revealing the decomposition of the coordination framework.



Fig. 5. View of the local coordination environment of Ho(III) atoms in **S1**. The atoms labeled with the suffixes A, B, and C are generated by the symmetry operations (-x, y + 1/2, -z + 1/2), (-x + 1, -y + 1, -z + 1), and (x, -y + 3/2, z + 1/2), respectively.



Fig. 6. A schematic representation of the 2D network in **S1** with $(3^2.4)(3^4.4^3.5^2.6^5.7)$ topology (blue spheres: [Ho2] binuclear units; orange spheres: HL²⁻ ligands with hydroxyl O10).

In summary, two new lanthanide coordination polymers have been prepared under hydrothermal conditions by employing 5hydroxyisophthalic acid (H₃L) ligand, which exhibited (6,6)-connected 3D **nia** net with Point (Schläfli) symbol of $(4^{12}.6^3)(4^9.6^6)$ (1) and (3,6)-connected 2D ($3^2.4$)($3^4.4^3.5^2.6^5.7$) net (**S1**), respectively. Especially, the La(III) complex **1** provides the first example of lanthanide architecture which the hydroxyl group of H₃L involving in the coordination. The present finding promotes us to make a further systemic study on the coordination chemistry of 5-hydroxyisophthalic acid, which may enrich the design and synthesis of crystalline materials based on such versatile multidentate building blocks.

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Appendix A. Supplementary material

CCDC 853405 and 853406 contain the supplementary crystallographic data for $[La(L)(H_2O)]_n$ (1) and $\{[Ho_2(HL)_3(H_2O)_2]\cdot H_2O\}_n$ (S1), respectively. These 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.12.025.

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mmol, 0.092 g). After cooling to room temperature, suitable crystals of **S1** were obtained in yield 40%. Anal. calcd for $C_{24}H_{18}Ho_2O_{18}$: C, 31.19; H, 1.96%. Found: C, 31.23; H, 1.92%. IR (KBr pellet, cm⁻¹): 3384 (br), 2976 (w), 2362 (w), 1630 (w), 1572 (m), 1537 (m), 1484 (w), 14589 (m), 1396 (s), 1308 (w), 1269 (s), 1224 (m), 1181 (m), 1130 (m), 1089 (w), 1048 (s), 1003 (s), 980 (s), 943 (w), 886 (m), 782 (s), 720 (s), 671 (w), 579 (w).

- [11] The data were collected on a Bruker Smart 1000 CCD area-detector diffractometer at 294(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. The structure was solved by direct method using SHELXS-97 and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program. Crystal data for **1**, C₃H₅LaO₆, M = 336.03, Monoclinic, space group P2₁/c, a = 9.9715(5) Å, b = 11.7086(6) Å, c = 7.3056(3) Å, β $= 91.439(4)^{\circ}$, V = 852.68(7) Å³, Z = 4, $D_c = 2.618$ Mg m⁻³, μ (Mo-Ka) = 5.015mm⁻¹, F(000) = 632, T = 294(2) K, $R_{int} = 0.0264$, final $R_1 = 0.0245$, $wR_2 =$ 0.0505 [for selected data with $I > 2\sigma(I)$], GOF = 1.129 for all data. Crystal data for **S1**, C₂₄H₁₈Ho₂O₁₈, M = 924.24. Monoclinic, space group P2₁/c, a =10.7636(11) Å, b = 14.3485(13) Å, c = 17.528(2) Å, $\beta = 102.116(11)^{\circ}$, V =2646.7(5) Å³, Z = 4, $D_c = 2.319$ Mg m⁻³, μ (Mo-Ka) = 6.026 mm⁻¹, F(000)= 1760, T = 294(2) K, $R_{int} = 0.0565$, final $R_1 = 0.0578$, $wR_2 = 0.1628$ [for selected data with $I > 2\sigma(I)$], GOF = 1.069 for all data.
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