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A series of lanthanide organic–inorganic hybrid frameworks with unusual trinodal topology: Syntheses, structures and magnetic properties

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ABSTRACT

Five isomorphous lanthanide–organic frameworks based on 3-carboxymethoxy phenyl acrylic acid (H_2L), $[LnL(HCOO)(H_2O)]_n$ (Ln = La(**1**), Ce(**2**), Pr(**3**), Nd(**4**), Y(**5**)), have been hydrothermally synthesized. X-ray structural analysis reveals that these complexes are rare organic–inorganic hybrid frameworks with unusual (3, 4, 7)-connected $(4^2.6)\ (4^4.6^2)\ (4^9.6^8.8^4)$ topology. Moreover, the magnetic properties of **2** and **3** were also investigated and suggested that the thermal depopulation of the crystal-field energy levels of the multiplet, and the antiferromagnetic interactions between Ln^{3+} ions.

Lanthanide–organic frameworks (LnOFs), also known as lanthanide coordination polymers (LCPs), have attracted much attention not only because of the use as functional materials for potential applications in optical, magnetic and catalytic fields [1], but also because of their fascinating topological architectures. Since the early days, the topological study of the coordination polymers has been investigated, with the fundamental contributions by J. V. Smith [2] and M. O'Keeffe [3], and the continuous research on this subject has generated serious different novel approaches [4], which is very useful for rationalization and categorization of the topological nets. The analysis of topology is often a difficult task, nonetheless, it is necessary to rational designed synthesis of coordination polymers, and especially, give the perspective to establish useful relationships between structure and properties.

Compared with the design of MOFs with transition metal ions, the rational design of LnOFs is more challenging and difficult because of the variable and high coordination numbers and flexible coordination geometry of lanthanide ions. In order to synthesize LnOFs with desirable structures and properties, several strategies have been developed, such as the related "reticular synthesis" method proposed by Yaghi et al. [5], and the net-based approach proposed by Robson and Hoskins [6]. Both methods are very helpful for the design of coordination frameworks.

The carboxylate ligands, which usually adopt binding mode as various as terminal monodentate, chelating bidentate, bridging bidentate and bridging tridentate et al. [7], have been proven to play a significant role in coordination chemistry. A series of LnOFs with different dimensionality and topologies have been synthesized from multicarboxylate ligands [8], because they have strong capability of coordination such as 1,4-benzene-dicarboxylate [9], 4,4′-biphenyl-dicarboxylate [10] and 1,3,5-benzene-tricarboxylate [11].

On the basis of above consideration, we designed and synthesized a dicarboxylate 3-carboxymethoxy phenyl acrylic acid (H_2L) as ligand. Because of the flexibility of H_2L, it can meet the requirement of the coordination conformation. In this communication, five isostructural lanthanide-organic frameworks based on the H_2L ligand have been synthesized under hydrothermal conditions, namely, $[LnL(HCOO)(H_2O)]_n$ (Ln = La(**1**), Ce(**2**), Pr(**3**), Nd(**4**), Y(**5**)). They present rare 3D organic–inorganic hybrid frameworks with unique (3,4,7)-connected trinodal topology. Moreover, the magnetic properties of complexes **2** and **3** have been investigated.

Complexes **1**–**5** were hydrothermally synthesized at 120 °C by the reaction of $Ln(NO_3)_3 \cdot 6H_2O$ with H_2L [12] in 1:4 DMF/H_2O mixed solvent [13]. Single-crystal X-ray crystallographic studies show that these complexes crystallize in monoclinic space group $P2_1/c$ and are isomorphous. Only the structure of **1** is described in detail. An ORTEP view of complex **1** is shown in Fig. 1a. The asymmetric unit contains one La^{3+} ion, one formate anion, one L^{2-} ligand and one coordinated water molecule. Each La^{3+} atom is nine-coordinated by five carboxylate oxygen atoms from four L^{2-} ligands (O3, O2#1, O4#3, O4#4, O5#4), one

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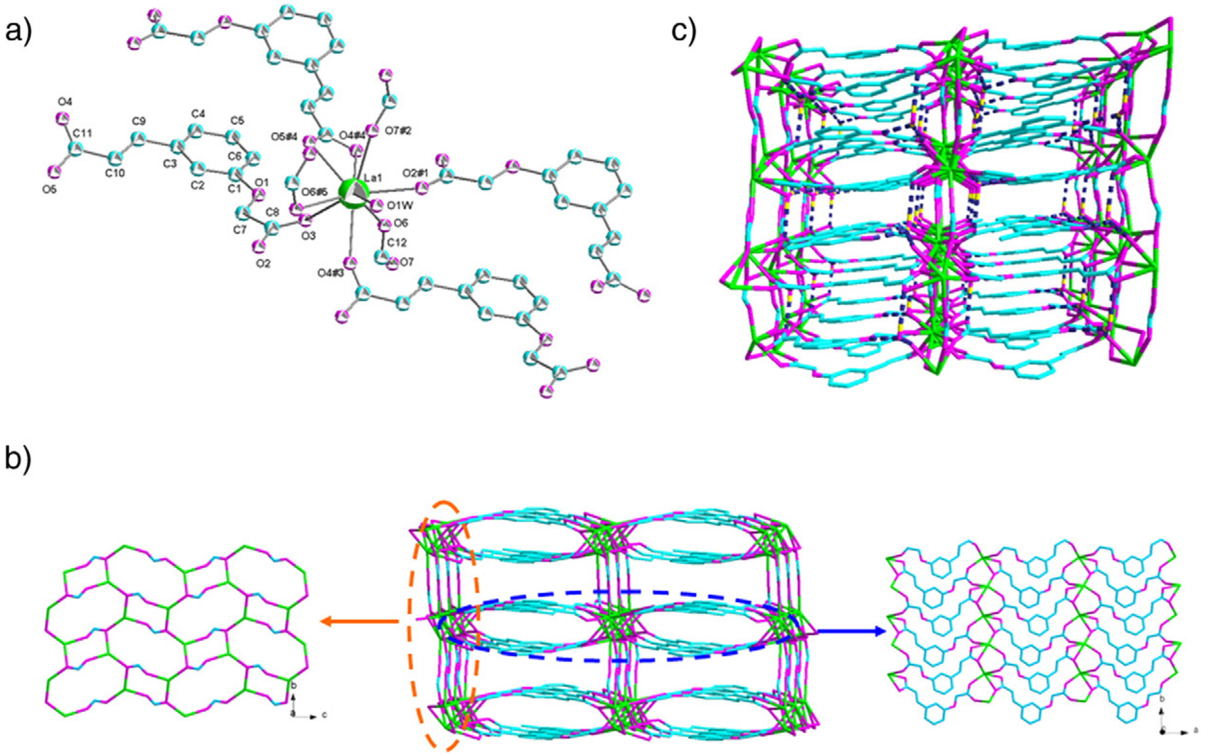

Fig. 1. (a) View of the coordination environment of the La center in **1** (symmetry codes: #1 −x + 1,y + 1/2,−z + 3/2; #2 x,−y + 1/2,z − 1/2; #3 x − 1,y,z; #4 −x + 2,y + 1/2,−z + 3/2; #5 −x + 1,y − 1/2,−z + 3/2). (b) Schematic representation of 3D pillar-layer organic—inorganic hybrid framework. (c) The 3D network showing the hydrogen-bonding interactions.

coordinated water molecule(O1W) and three formate anions (O6, O6#5, O7#2), featuring a distorted monocapped square antiprismatic geometry [14]. The average La – O length is 2.579 (2) Å, while the corresponding average Ln – O length are 2.551 (1) Å for **2**, 2.533 (2) Å for **3**, and 2.520 (2) Å for **4**, respectively. It is obvious that the bond lengths around the Ln ions gradually decrease with decreasing radii of

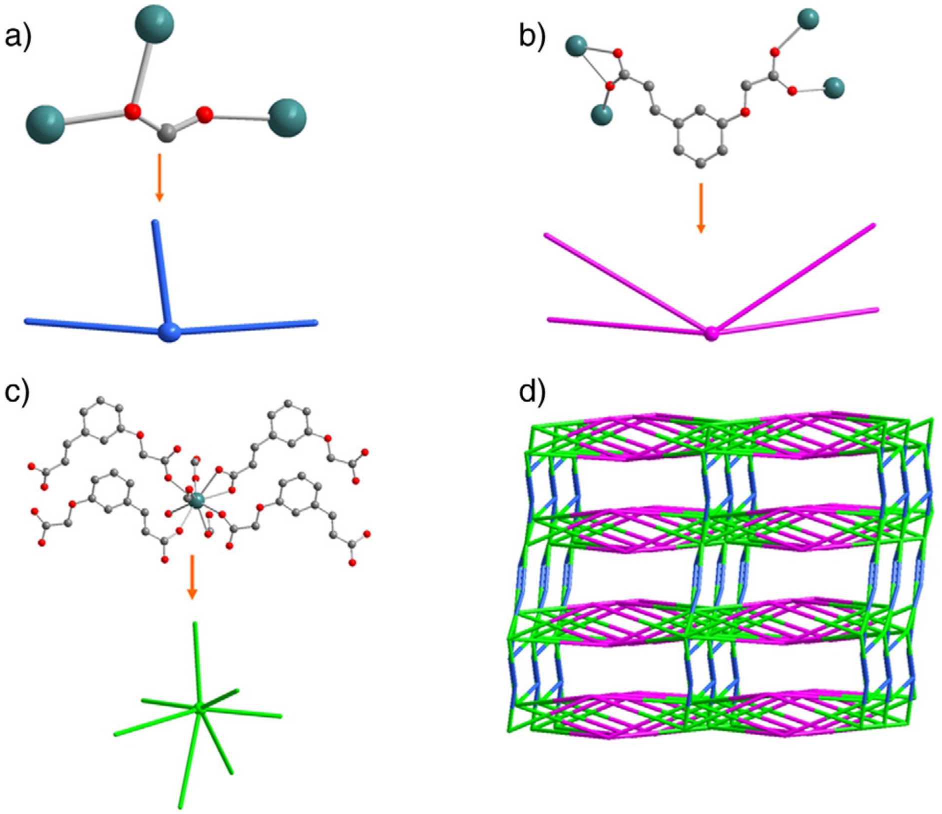

Fig. 2. (a) View of the 3-connected methanoic anions. (b) View of the 4-connected L ligand. (c) View of the 7-connected La center. (d) The (3,4,7)-connected trinodal net with the point symbol of $(4^2.6)$ $(4^4.6^2)$ $(4^9.6^8.8^4)$.