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Synthesis, structure and properties of three-dimensional organic–inorganic hybrids based on α-metatungstate

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ABSTRACT

Four new organic–inorganic hybrids with three-dimensional (3D) framework based on the α-metatungstate clusters $[H_2W_{12}O_{40}]^{6-}$, $(NH_4)_2[Ln_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot nH_2O$ (Ln = Ce^{III} (**1**), $n = 9$; Pr^{III} (**2**), $n = 12$; Nd^{III} (**3**), $n = 11$; Sm^{III} (**4**), $n = 10$; L = 2-pyrazinecarboxylate), have been conventionally synthesized and structurally characterized by single-crystal X-ray diffraction analyses, elemental analyses, IR spectra and thermal gravimetric analyses. Single-crystal X-ray diffraction analyses reveal these compounds are isostructural with a *P2(1)/c* space group. And L ligand connects two kinds of Ln^{3+} ions in a tridentate chelating-bridging coordination mode, resulting in two sorts of infinite one-dimensional (1D) zigzag chains. $[H_2W_{12}O_{40}]^{6-}$ cluster acting as a pentadentate linker connects five Ln^{3+} ions from three zigzag chains through its five terminal oxygen atoms, forming a complicated 3D framework structure with a novel $(3^2 4^1 5^2 6^1)(3^2 4^2 5^3 6^3)(3^1 4^3 5^3 6^1 7^2)$ topology. In compounds **1**–**4**, there exist S-type channels with maximum length of ca. 12.563 Å and minimum length of ca. 3.888 Å along the *a*-axis direction. In addition, solid-state luminescence properties of compounds **1**, **2**, **4** and 2-pyrazinecarboxylic acid (HL) have been studied at room temperature.

1. Introduction

Organic–inorganic hybrid materials based on polyoxometalates (POMs) not only possess intriguing structures and novel topologies but also are good functional materials in view of their potential applications in some fields like electronic, magnetic, catalytic, sorption and optical materials and they have attracted an extensive attention of chemists worldwide lately [1–7]. The design and synthesis of organic–inorganic hybrid materials based on various available POMs with high-dimensional structures are still a challenging and interesting project. It is noteworthy that a series of factors may influence on the construction of the high-dimensional hybrid materials. Among the factors, the selection of POMs, metal ions and organic ligands must be taken into account seriously. It is well known that POMs are commonly considered as favorable inorganic building unit [8]. In the huge family of the POMs, α-metatungstate cluster $[H_2W_{12}O_{40}]^{6-}$ (abbreviated to W_{12}) captures our attention because its higher negative charge density on the cluster surface is helpful to form more interesting and high-dimensional structures. However, there are not many high-dimensional organic–inorganic hybrid compounds based on W_{12} clusters reported to date [9–12]. So it will be a judicious choice to synthesize high-dimensional organic–inorganic hybrid compounds based on W_{12} clusters. In the sight of metal ions, lanthanide cations are good candidates due to the following reasons: (i) lanthanide cations are prone to form high-dimensional and unusual architectures because of their higher coordination number, more flexible coordination geometry and stronger oxophile ability [13–16]; (ii) lanthanide materials are generally provided with strong magnetic interactions between lanthanide ions and good optical property which make some of them be applied to manufacture [17,18]. In addition, concerning to various organic ligands, aromatic carboxylate ligands containing N atoms are mostly popularly investigated [19–23]. 2-Pyrazinecarboxylic acid (abbreviated as HL), a remarkable multidentate ligand, has the potential ability to form high-dimensional structures owing to its flexible coordination modes and excellent coordination ability [24–27]. On the other hand, it can display interesting luminescence property [28–30]. As far as we know, reported compounds based on POMs and 2-pyrazinecarboxylic acid are a few till now [31–34] and those reports are all with regard to transition metal.

Based on the above mentioned points, we have employed 2-pyrazinecarboxylic acid, $Ln(NO_3)_3\cdot 6H_2O$ and $(NH_4)_6[H_2W_{12}O_{40}]\cdot 3H_2O$ to construct the high-dimensional organic–inorganic hybrid materials. Herein, we report the synthesis, characterization, and crystal structures, as well as luminescent properties of the compounds, $(NH_4)_2[Ln_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot nH_2O$ (Ln = Ce^{III} (**1**), $n = 9$; Pr^{III}

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(**2**), $n = 12$; Nd^{III} (**3**), $n = 11$; Sm^{III} (**4**), $n = 10$; L = 2-pyrazinecarboxylate). To our best knowledge, compounds **1**–**4** are the first examples of organic–inorganic hybrid compounds based on 2-pyrazinecarboxylic acid, lanthanide cations and W_{12} clusters.

2. Experimental

2.1. Materials and physical measurements

The lanthanide(III) nitrates were prepared by dissolving corresponding lanthanide oxides in nitric acid and followed by recrystallization and drying. Other chemical reagents were commercially available and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer and that of W, Ce, Pr, Nd, Sm were carried out with a Leaman ICP spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on a Magna-560 spectrophotometer using KBr Pellets. The ammonium–N was determined by ion chromatography (DIONEX 100 with DIONEX CDM-1). TG analyses were performed on a NETZSCH STA 449F3 instrument in N_2 atmosphere with a heating rate of 10 °C min^{-1}. The fluorescent spectra of compounds **1**, **2**, **4** and HL were measured on a F-7000 FL spectrophotometer.

2.2. Syntheses of compounds *1*–*4*

2.2.1. Synthesis of $(NH_4)_2[Ce_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot 9H_2O$ (*1*)

HL (0.0372 g, 0.3 mmol) was dissolved in 10 mL hot water. Then 10 mL water solution of $Ce(NO_3)_3\cdot 6H_2O$ (0.0434 g, 0.1 mmol) was added into the above solution. The mixed solution was kept on stirring for ca. 1 h at about 80 °C. After the mixed solution was cooled to room temperature, $(NH_4)_6[H_2W_{12}O_{40}]\cdot 3H_2O$ (0.1558 g, 0.05 mmol) dissolved in 10 mL mol·L^{-1}water was added into the mixed solution with the appearance of a mass of white insoluble materials. 1.0 mol·L^{-1} HNO_3 solution was added until most of the white insoluble materials disappeared. After stirred for 1 h at room temperature a little insoluble substance was filtered out and the filtrate (pH 1.0) was allowed to evaporate in air at room temperature. After about 10 days, yellow hexagonal crystals were obtained with an about 45% yield (based on Ce). *Anal.* Calc. for **1** ($C_{10}H_{48}N_6O_{60}Ce_2W_{12}$ (3698.94)): C, 3.25; H, 1.31; N, 2.27; Ce, 7.58; W, 59.64. Found: C, 3.18; H, 1.27; N, 2.31; Ce, 7.46; W, 60.36%. IR (solid KBr pellet)/cm^{-1}: 3423.65(s, b), 1613.04(m), 1578.01(m), 1384.03(m), 1183.46(w), 1061.89(w), 933.05(m), 887.23(m), 767.14(s), 420.96(m).

2.2.2. Synthesis of $(NH_4)_2[Pr_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot 12H_2O$ (*2*)

An identical procedure with **1** was followed to prepare **2** except $Ce(NO_3)_3\cdot 6H_2O$ was replaced by $Pr(NO_3)_3\cdot 6H_2O$. After about ten days, green hexagonal crystals of **2** suitable for X-ray diffraction were obtained (about 47% yield based on Pr). *Anal.* Calc. for **2** ($C_{10}H_{54}N_6O_{63}Pr_2W_{12}$ (3754.56)): C, 3.20; H 1.45; N 2.24, Pr, 7.51; W 58.76. Found: C, 3.14; H, 1.38; N, 2.15; Pr, 7.61; W, 59.25%. IR (solid KBr pellet)/cm^{-1}: 3328.63(b), 1610.75(m), 1579.07(m), 1398.67(m), 1183.53(w), 1061.05(w), 933.06(m), 888.25(m), 769.35(s), 422.28(m).

2.2.3. Synthesis of $(NH_4)_2[Nd_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot 11H_2O$ (*3*)

An identical procedure with **1** was followed to prepare **3** except $Ce(NO_3)_3\cdot 6H_2O$ was replaced by $Nd(NO_3)_3\cdot 6H_2O$, After about 10 days, light purple hexagonal crystals of **3** suitable for X-ray diffraction were obtained (about 48% yield based on Nd). *Anal.* Calc. for **3** ($C_{10}H_{52}N_6O_{62}Nd_2W_{12}$ (3743.21)): C, 3.21; H, 1.40; N, 2.25; Nd, 7.71; W, 58.94. Found: C, 3.12; H, 1.34; N, 2.32; Nd, 7.80; W, 59.12%. IR (solid KBr pellet)/cm^{-1}: 3195.82(b), 1611.10(m), 1578.76(m), 1383.09(m), 1183.71(w), 1061.48(w), 933.72(m), 887.33(m), 769.04(s), 422.00(m).

2.2.4. Synthesis of $(NH_4)_2[Sm_2(L)_2(H_2W_{12}O_{40})(H_2O)_7]\cdot 10H_2O$ (*4*)

An identical procedure with **1** was followed to prepare **4** except $Ce(NO_3)_3\cdot 6H_2O$ was replaced by $Sm(NO_3)_3\cdot 6H_2O$. After about 10 days, light yellow hexagonal crystals of **4** suitable for X-ray diffraction were obtained (about 42% yield based on Sm). *Anal.* Calc. for **4** ($C_{10}H_{50}N_6O_{61}Sm_2W_{12}$ (3737.43)): C, 3.21; H, 1.34; N, 2.25; Sm, 8.04; W, 59.03. Found: C, 3.25; H, 1.36; N, 2.19; Sm, 8.11; W, 59.31%. IR (solid KBr pellet)/cm^{-1}: 3327.56(b), 1609.83(m), 1578.87(m), 1398.32(m), 1183.18(w), 1060.85(w), 933.15(m), 888.18(m), 769.23(s), 421.88(m).

Experiments show these new materials possess poor solubility in aqueous and common organic solvent such as methanol, ethanol, ether, acetone, ethyl acetate, and so on.

2.3. X-ray crystallography

The single-crystal X-ray diffraction data of **1** and **3** were collected on an Oxford Diffraction Gemini R CCD with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 293 K. Multi-scans absorption correction was applied. The diffraction data of **2** and **4** were collected on Bruker Smart CCD diffractometer, with Mo Kα monochromatic radiation (λ = 0.71073 Å) at 293 K. Empirical absorption correction was applied. The structures were solved with the direct methods and refined with the full-matrix least-squares methods on F^2 using the SHELXTL-97 crystallographic software package [35,36]. All of the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on carbon atoms were calculated theoretically. Due to poor quality of the diffraction data of **4**, only the cell parameters and structural profile of **4** are given. A summary of the crystallographic data for **1**–**4** and structural refinement for **1**–**3** is provided in Table 1.

3. Results and discussion

3.1. Description of crystal structures

Single-crystal X-ray diffraction analyses reveal that compounds **1**–**4** are isostructural which crystallize in a monoclinic space group *P2(1)/c*. Their unit cell dimensions and volumes are slightly changed according to the changing sequence of Ln^{3+} radii (see Table 1). Herein, the structure of compound **1** is depicted in detail representatively.

As shown in Fig. 1, the asymmetric unit of **1** is composed of one W_{12} cluster, two crystallographically independent L ligands (L1 and L2), two crystallographically unique Ce^{3+} ions (Ce1 and Ce2), seven coordination water molecules, two NH_4^+ ions and nine lattice water molecules.

A remarkable feature of compound **1** is that each W_{12} cluster connects three Ce1 ions and two Ce2 ions (Fig. S1), acting as a pentadentate bridging linker. The cerium atoms linked on W_{12} cluster displays a distorted square pyramidal geometry (Fig. 2a) which is rare in the hybrid compounds based on W_{12} clusters. Like classical Keggin anions, the W_{12} cluster is made of four sets of W_3O_{13} groups consisting of twelve edge-sharing WO_6 octahedra, but the central cavity of W_{12} cluster is occupied by two protons, resulting in the higher charge density on the W_{12} cluster surface. The oxygen atoms of W_{12} clusters can be divided into four groups: four central oxygen atoms, O_a; 12 bridging oxygen atoms from the same W_3O_{13} group, O_c; 12 bridging oxygen atoms from the different W_3O_{13} group, O_b; 12 terminal oxygen atoms, O_t (that linked to Ln^{3+} is labeled as O_t'). As well known, the bond angle of W–O_c–W bonds is about 118° and that of W–O_b–W bonds is about 147° in the $H_2W_{12}O_{40}^{6-}$ anion [37]. However, the W–O_c–W bond angles