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Luminescent Lanthanide Oxalatophosphites with a 3D Framework Structure: $[Ln(H_2O)(C_2O_4)_{0.5}(HPO_3)]\cdot H_2O$ (Ln = Pr, Nd, and Sm−Lu)

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Many reports are concerned with the synthesis of organic−inorganic hybrid compounds by incorporating organic ligands such as oxalate, 4,4′-bipyridine, and isonicotinate into the structures of inorganic metal phosphates because of their interesting structural chemistry and potential applications.[1–12] The underlying idea is to combine the robustness of inorganic phosphate frameworks with the versatility and chemical flexibility of organic ligands. Oxalate was found to be a good candidate, and a large number of oxalatophosphates of transition metals and main group elements with interesting structures have been synthesized. Recently, the pseudotetrahedral phosphite group, HPO_3^{2-}, has been employed as a building unit to replace the tetrahedral phosphate group, which gives rise to a new class of organic−inorganic hybrid compounds.[13–15] Although a good number of oxalatophosphites of transition metals have been synthesized, the corresponding lanthanides have not been reported. Lanthanide complexes have received great attention because of interesting luminescence properties and a wide range of applications.[16–20] Recently, we synthesized the first examples of lanthanide oxalate-methylphosphonate, $Na[M_3(H_2O)_4(C_2O_4)_4(CH_3PO_3)]\cdot 2H_2O$ (M = Nd and Pr) that have a novel 3D framework structure built of a discrete MO_9 polyhedron and a tetramer of edge- and face-sharing MO_9 polyhedra, in addition to a methylphosphonate group and six distinct oxalate units.[21] Following the successful synthesis of the neodymium and praseodymium oxalatophosphonates, we report in this paper a series of lanthanide oxalatophosphites: $[Ln(H_2O)(C_2O_4)_{0.5}(HPO_3)]\cdot H_2O$ (Ln = Pr, Nd, Sm−Lu). The 12 compounds are isostructural and feature a 3D architecture in which 2D layers of $[Ln(H_2O)(HPO_3)]^+$ are pillared by oxalate ligands. The synthesis, structural characterization, thermal stability, guest desorption−sorption, luminescence, and catalytic properties have been studied.

Hydrothermal reactions were performed in a Teflon lined, 23 mL autoclave at 150 °C for 3 d followed by slow cooling to room temperature at 6 °C h^{-1}. Block crystals of $[Ln(H_2O)(C_2O_4)_{0.5}(HPO_3)]\cdot H_2O$ (Ln = Pr (**1**), Nd (**2**), Sm (**3**), Eu (**4**), Gd (**5**), Tb (**6**), Dy (**7**), and Ho (**8**)) were obtained by heating a mixture of $Ln(NO_3)_3\cdot xH_2O$ (0.5 mmol), $H_2C_2O_4\cdot 2H_2O$ (10 mmol), H_3PO_3 (10 mmol), 1,4-diazabicyclo[2.2.2]octane (dabco) (2 mmol), and H_2O (10 mL), while the Er (**9**), Tm (**10**), Yb (**11**), and Lu (**12**) analogues were obtained from a mixture of $Ln(NO_3)_3\cdot xH_2O$ (0.25 mmol), $H_2C_2O_4\cdot 2H_2O$ (2 mmol), H_3PO_3 (0.69 mmol), 2,2′-bipyridine (2 mmol), and H_2O (10 mL). These 12 compounds are isostructural, as indicated by either powder or single-crystal X-ray diffraction (see Table S1 and Figure S1 in the Supporting Information). Energy-dispersive X-ray fluorescence spectroscopy analysis of several crystals of compound **4** confirms the presence of Eu and P. Elemental analysis results of **4** are consistent with the formula [Anal. Found (calcd): C, 3.71 (3.85); H, 1.76 (1.62)]. Thermogravimetric analysis measurements on **4** in flowing O_2 showed three steps of weight loss in the range from 40 to 900 °C (Figure S2a, Supporting Information). The first and the second steps correspond to the loss of one lattice water molecule (calcd: 5.77%) and one coordination water molecule, respectively. The final decomposition product is $EuPO_4$, as indicated by powder X-ray diffraction. The total observed weight loss of 20.12% is close to the calculated value of 20.85%. To determine the thermal stability, a sample of **4** was heated in air to 150 and 300 °C and kept there for 1 h for each temperature, followed by powder X-ray diffraction study. The results showed that the sructure was retained at 150 °C and decomposed at 300 °C. To study guest desorption−sorption properties, a sample of **4** which had been heated at 150 °C for 1 h on a TG analyzer was exposed to air at room temperature for 1 day and then heated to 150

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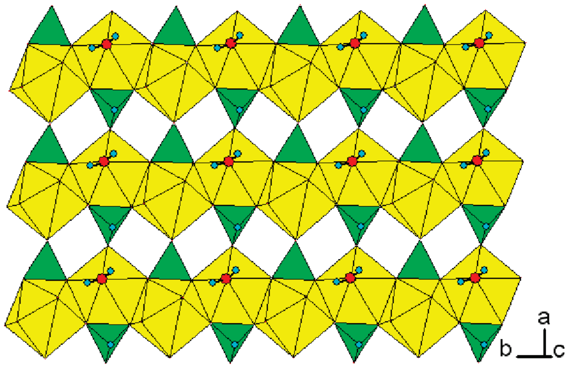

Figure 1. Section of an inorganic layer of europium phosphite in **4**. The yellow and green polyhedra are EuO_8 polyhedra and HPO_3 pseudotetrahedra, respectively. Red circles, water oxygen atoms; blue circles, H atoms.

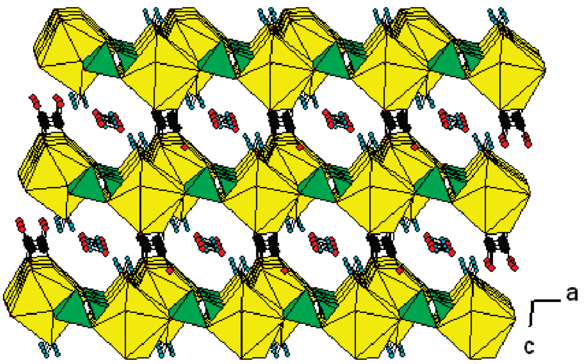

Figure 2. Structure of **4** viewed along the *b* axis. Red circles, water oxygen atoms; blue circles, H atoms; black circles, C atoms.

°C by using the same analyzer (Figure S2b, Supporting Information). The results showed that a dehydrated compound can absorb water reversibly. Further evidence for the stability and persistence of **4** upon release of lattice water was obtained from variable-temperature in situ powder X-ray diffraction (Figure S3, Supporting Information). The pattern for dehydration at 150 °C shows that the sample remains crystalline after loss of lattice water, and that for rehydration by exposing to air at ambient temperature for 1 d confirms that the integrity of the framework is not affected by the H_2O release. The Eu^{3+} ion in **4** can be partially replaced by Tb^{3+} for forming a mixed-metal compound, as indicated by EDX and luminescence spectroscopy.

The 12 compounds are isostructural; therefore, only the structure of **4** is discussed. All atoms are in general positions. The asymmetric unit contains the following structural elements: one EuO_8 polyhedron, one oxalate unit, one HPO_3 pseudotetrahedron, one lattice−water molecule, and one coordination water molecule. The coordination environments of the Eu atoms and atom labeling scheme are shown in Figure S4, Supporting Information. The Eu^{3+} cations are 8-fold coordinated by oxygen atoms in a geometry of distorted trigonal dodecahedron which is a common structure for eight-coordination. The EuO_8 polyhedra are chelated by HPO_3^{2-} anions, and the two chelating oxygen atoms, O (1) and O (3), bond to adjacent Eu^{3+} ions forming zigzag infinite chains. The remaining oxygen atom of the phosphite group, O(2), bridges a Eu^{3+} ion in another chain to generate 2D layers in the *ab*-plane (Figure 1). A layered cerium phosphite, $[Ce(H_2PO_3)(HPO_3)]\cdot 2H_2O$, was previously reported.[22] There are two different coordination modes of the phosphate groups in the cerium compound: HPO_3^{2-} groups are bridging chelates to link metal atoms to form a layer structure; $H_2PO_3^-$ anions decorate the Ce^{3+} ions above and below each layer. In our compounds, neighboring sheets of metal phosphites are linked through oxalates into a 3D framework with channels that are occupied by lattice water molecules (Figure 2). Extensive hydrogen bonding exists between the lattice water molecules and between aqua molecules and framework oxygen atoms. The Ow···O distances are 2.702 Å for Ow(1)···O(4), 3.081 Å for Ow(2)···O(2), and 3.111 Å for Ow(2)···O(5). The Ow···Ow distances are 2.751 Å for Ow(1)···Ow(2) and 3.174 Å for Ow(2)···Ow(2). It is interesting that the $H_2PO_3^-$ anion in the Ce compound is replaced by bridging oxalate, forming a new family of organic−inorganic hybrid compounds.

The excitation and emission spectra were recorded at room temperature. Compounds **4**, **5**, and **6** showed red, blue, and green luminescence, respectively. The emission spectrum of **4** excited at 392 nm exhibits the characteristic bands of Eu^{3+} ion in the visible region (Figure S5, Supporting Information). These emission bands at about 580, 593, 611, 654, and 698 nm can be assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively.[23] The presence of one $^5D_0 \rightarrow {}^7F_0$ line indicates the existence of one Eu^{3+} local environment, and this is consistent with the crystallographic results. The integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ (ED) transition is much larger than that of the $^5D_0 \rightarrow {}^7F_1$ (MD) transition, indicating that the Eu^{3+} site lacks inversion symmetry. The Eu^{3+} ion is located at the center of a distorted trigonal dodecahedron, which naturally does not have an inversion symmetry center. The excitation spectrum of **4** monitored within the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ (611 nm) transition displays sharp lines assigned to $^7F \rightarrow {}^5D$, $^7F \rightarrow {}^5L$, and $^7F \rightarrow {}^5G$ transitions (Figure S6, Supporting Information). Under excitation of 370 nm, compound **6** exhibits the characteristic emission bands of the Tb^{3+} ion at about 488 ($^5D_4 \rightarrow {}^7F_6$), 546 ($^5D_4 \rightarrow {}^7F_5$), 582 ($^5D_4 \rightarrow {}^7F_5$), and 622 nm ($^5D_4 \rightarrow {}^7F_3$)[24] (Figure S7, Supporting Information). The excitation spectrum of **6** was monitored within the Tb^{3+} $5D_4 \rightarrow {}^7F_5$ (547 nm) transition. The broadband between 250 and 300 nm can be attributed to the spin-forbidden interconfiguration $4f^8 \rightarrow 4f^75d^1$ transition, and the lines between 300 and 500 nm can be assigned to $^7F \rightarrow {}^5D_0$, $^7F \rightarrow {}^5L_{10}$, and $^7F \rightarrow {}^5G$ intraconfiguration forbidden $4f^8 \rightarrow 4f^8$ transition of the Tb^{3+} ion (Figure S8, Supporting Information). Compound **5** displays a broad blue fluorescent emission band at about 398 nm under excitation at 250 nm (Figure S9, Supporting Information). The metal-centered electronic levels of Gd^{3+} (about 31 000 cm^{-1}) are normally above the ligand-centered electronic levels of organic molecules. Therefore, the blue fluorescent

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emission is ascribed to a ligand-centered (LC) fluorescence, which is similar to the spectrum of $[Gd_3(C_2O_4)(Me_2NHCH_2PO_3)(H_2O)_6]\cdot 6H_2O$.[25]

Biginelli reaction, which is a one-pot cyclocondensation of aldehyde, 1,3-ketoester, and urea or thiourea, is one of the very useful multicomponent reactions in organic synthesis.[26] It has been disclosed that lanthandie triflates can efficiently catalyze the Biginelli reaction under mild conditions.[27] Recently, Bao et al. reported that a coordination polymer, Gd-notp ($notpH_6$ = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid)), is also an effective catalyst for the Biginelli reaction.[28] Therefore, we explored the Biginelli reaction using $[Gd(H_2O)(C_2O_4)_{0.5}(HPO_3)]\cdot H_2O$ (**5**) as a catalyst. A mixture of benzaldehyde (0.5 mmol), ethyl acetoacetate (0.5 mmol), urea (0.6 mmol), compound **5** (0.05 mmol), and methanol (2 mL) was stirred at room temperature for 1−3 d, then water (5 mL) was added, and the product was extracted with ethyl acetate (3 × 5 mL). The organic layer was dried with anhydrous $MgSO_4$ and evaporated, and then the residue was purified by prepared TLC (ether/ethyl acetate = 3:1) to afford 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydro-pyrimidin-2(1*H*)-one. The isolated yields for stirring for 1, 2, and 3 d are 26% (34 mg), 47% (61 mg), and 52% (68 mg), respectively. The cyclocondensation reaction product was not obtained in the absence of **5**. The isolated yields are lower than those when lanthanide triflates are used as catalysts (>80%)[27] and are comparable to that when the Gd-notp compound was used (60%).[28] The product was characterized by ^1H NMR and fast atom bombardment (FAB) mass spectrometry. ^1H NMR (300 MHz, DMSO, TMS): 9.19 (s, 1H; NH), 7.74 (s, 1H; NH), 7.35−7.31 (m, 2H; Ar−H), 7.26−7.21 (m, 3H; Ar−H), 5.14 (s, 1H; CH), 4.01−3.94 (q, J = 7.2 Hz, 2H; $-OCH_2-$), 2.24 (s, 3H; $-CH_3$), 1.11−1.07 ppm (t, J = 7.2 Hz, 3H; $-CH_3$); FAB-MS: m/z 261.1 $[M + H]^+$.

In summary, we have synthesized a series of lanthanide oxalatophosphites by a hydrothermal method. Their structures consist of 2D layers of lanthanide phosphites, which are pillared through $C_2O_4^{2-}$ to form a 3D framework. Compounds **4**, **5**, and **6** showed red, blue, and green luminescence, respectively. Preliminary studies on the catalytic properties of compound **5** show that it can be a catalyst for the Biginelli reaction. They are the first examples of lanthanide oxalatophosphite. Recently, we have synthesized another series of lanthanide oxalatophosphites with a 3D honeycomb structure by using an ionic liquid as the solvent. Different synthetic techniques allow us to explore new materials with interesting structural chemistry and photophysical properties. The structure of the title compounds can allow simultaneous incorporation of a second (or even a third) type of lanthanide ion in the framework and, therefore, the fine-tuning of their photoluminescence properties. Further research on this system is in progress.

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Supporting Information Available: Crystallographic data in CIF format and X-ray powder patterns, a plot of coordination environments of Eu atoms, TGA curve, and luminescent spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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