Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 6335–6337 **6335**
DOI: 10.1021/ic9006394

Synthesis of Novel Organic−Inorganic Hybrid Compounds: Lanthanide Phosphites Incorporating a Squarate Ligand

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Received April 1, 2009

The first examples of metal phosphite incorporating a squarate anion as a ligand have been synthesized by a hydrothermal method. Their structures contain zigzag chains of edge-sharing LnO_8 (Ln = Sm, Eu, and Gd) square antiprisms connected by phosphite groups to form 2D layers, which are pillared by squarate ligands into a 3D framework. The photoluminescence properties of the Eu compound have also been studied.

A great deal of attention has been devoted to the synthesis of metal phosphates incorporating multifunctional organic ligands because of their interesting structural chemistry and potential applications in catalysis, adsorption, and ion exchange.[1,2] The ligands 4,4′-bipyridine and oxalate are the most common organic species used for the synthesis of these organic−inorganic hybrid compounds. The pseudotetrahedral phosphite group, HPO_3^{2-}, has also been employed as a building unit instead of the tetrahedral phosphate to generate a new class of organic−inorganic hybrids.[3] For example, we reported the first examples of lanthanide oxalatophosphites, $[Ln(H_2O)(C_2O_4)_{0.5}(HPO_3)]\cdot H_2O$ (Ln = Pr, Nd, and Sm−Lu).[4] The structures of these 12 compounds consist of 2D layers of lanthanide phosphites, which are pillared through oxalate ligands to form a 3D framework. Recently, we have been interested in extending our studies to incorporate larger carbon oxo anions such as squarate ($C_4O_4^{2-}$) and croconate ($C_5O_5^{2-}$) into the inorganic phosphate or phosphite frameworks. The squarate dianion is a monocyclic carbon oxo anion with aromaticity. Many squarate-based compounds possessing structural features for interesting zeolitic, luminescent, and magnetic properties have been reported.[5] The squarate anion may be engaged in a variety of binding modes, and bite-angle considerations show that it can only chelate large cations. Previously, we synthesized a vanadium squarate, $[\{V(OH)(C_4O_4)\}_2]\cdot 4H_2O$, whose 3D framework contains dimers of edge-sharing $V^{III}O_6$ octahedra linked by squarate anions in μ_2 and μ_4 binding modes.[6] To our knowledge, there are no reports about this anion association with metal phosphate or phosphite except that Yang and Mao reported a manganese(II) squaratodiphosphonate, $\{Mn[NH(CH_2PO_3H)_2](H_2O)_2\}_2$-$\{Mn(C_4O_4)(H_2O)_4\}\cdot(C_4H_2O_4)$ and a copper(I) squaratophosphonate, $Cu_3(H_3L)(bipy)_2\cdot 2H_2O$ ($H_5L = C_4HO_3N$-$(CH_2PO_3H_2)_2$), in which the new ligand squaratoiminodiphosphonate was formed by the condensation reaction between one C═O group of squaric acid and the amino group of $NH(CH_2PO_3H_2)_2$.[7] Herein, we report the first examples of metal squaratophosphite, $[Ln(H_2O)(C_4O_4)_{0.5}(HPO_3)]$ (Ln = Sm, Eu, and Gd), whose 3D frameworks contain inorganic sheets of lanthanide phosphites pillared by squarate ligands. We report their synthesis, structural characterization, and luminescence properties.

Colorless block crystals of $[Ln(H_2O)(C_4O_4)_{0.5}(HPO_3)]$ (Ln = Sm, Eu, and Gd) were obtained by heating a mixture of $Ln(NO_3)_3\cdot xH_2O$ (0.3 mmol), H_3PO_3 (7.5 mmol), squaric acid (0.5 mmol), and H_2O (10 mL) in a Teflon-lined, 23-mL autoclave at 150 °C for 3 days. The products were monophasic, and the yields were 62%, 54%, and 59% for the Sm (**1**), Eu (**2**), and Gd (**3**) compounds, respectively. Suitable

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crystals of **2** and **3** were selected for single-crystal X-ray diffraction. The crystals of **1** in the reaction product were too small to be used for indexing and intensity data collection. These three compounds are isostructural, as indicated by either single-crystal[8] or powder X-ray diffraction (see Figure S1 in the Supporting Information). Elemental analysis results are consistent with the formula. Anal. Found (calcd) for **1**: C, 7.42 (7.89), H, 1.06 (0.99). Anal. Found (calcd) for **2**: C, 7.62 (7.85), H, 0.94 (0.99). Anal. Found (calcd) for **3**: C, 7.43 (7.71), H, 1.01 (0.97). Energy-dispersive X-ray fluorescence spectroscopy analysis of several crystals of **2** confirms the presence of Eu and P. Thermogravimetric analysis (TGA) measurements in flowing O_2 at 5 °C min^{-1} showed three steps of weight loss in the range from 40 to 920 °C (Figure S2 in the Supporting Information). The first step between 40 and 240 °C is attributed to the loss of one coordination water molecule (obsd, 6.0%; calcd, 5.89%). The final decomposition product is $EuPO_4$, as indicated by powder X-ray diffraction (JCPDS-18-0506). The observed total weight loss of 18.45% from 40 to 920 °C is close to the value of 19.29% calculated according to the equation $Eu(H_2O)(C_4O_4)_{0.5}(HPO_3) + {}^7/_4O_2 \rightarrow EuPO_4 + 2CO_2 + {}^3/_2H_2O$. Powder X-ray diffraction studies of a sample of **2** that had been heated at 250 and 500 °C for 1 h in air and then cooled to room temperature revealed that the compound changed to a different crystalline material at 250 °C and decomposed to poorly diffracting material at 500 °C (Figure S3 in the Supporting Information).

The three compounds are isostructural; therefore, only the structure of **2** is discussed. All atoms are in general positions except that P(1), P(2), O(1), O(4), H(1), and H(2) lie in mirror planes. The structure is constructed from a EuO_8 polyhedron in the geometry of a distorted square antiprism, two phosphite pseudotetrahedra, and a planar squarate ligand. A water molecule coordinates to the Eu^{3+} cation. Each EuO_8 square antiprism shares two edges with two others to form zigzag infinite chains along the *b* axis, which are further connected by $HP(1)O_3$ groups to form layers in the *bc* plane. Each $HP(2)O_3$ group is bonded to four Eu atoms through three μ_3-O atoms by sharing its two edges with two EuO_8 polyhedra and two corners with another two EuO_8 polyhedra; namely, each $HP(2)O_3$ group is a bidentate ligand to two Eu^{3+} cations and a monodentate ligand to another two Eu^{3+} cations (Figures 1 and S4 in the Supporting Information). To our knowledge, the coordination mode of $HP(2)O_3$ is observed for the first time. Neighboring sheets of europium phosphite are linked through bridging squarate ligands to form a 3D framework (Figures 2 and S5 in the Supporting Information). Recently, a mangananese squaratodiphosphonate and a copper squaratophosphonate have been reported.[7] The Mn compound is composed of two types of 1D chains, which are a 1D manganese diphosphonate chain and a 1D manganese squarate chain. The Cu compound, which has a 2D layer structure, is formed by 4,4′-bipyridine and squaratoiminodiphosphonate ligands. The structures of the title compounds are unique in that both squarate and phosphite ligands are bonded to the same metal ion. They are also the first examples of 3D architectures in which 2D layers of metal phosphites are pillared by squarate ligands, although a large number of related compounds containing oxalate or 4,4′-bipyridine pillars have been reported.

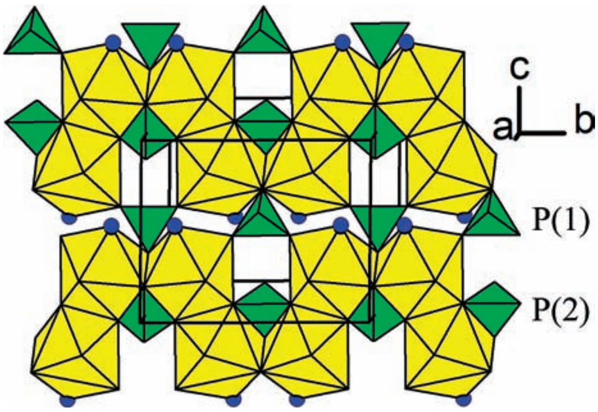

Figure 1. Section of an inorganic layer of europium phosphite in **2**. The yellow and green polyhedra are EuO_8 square antiprisms and HPO_3 pseudotetrahedra, respectively. Blue circles are coordination water O atoms.

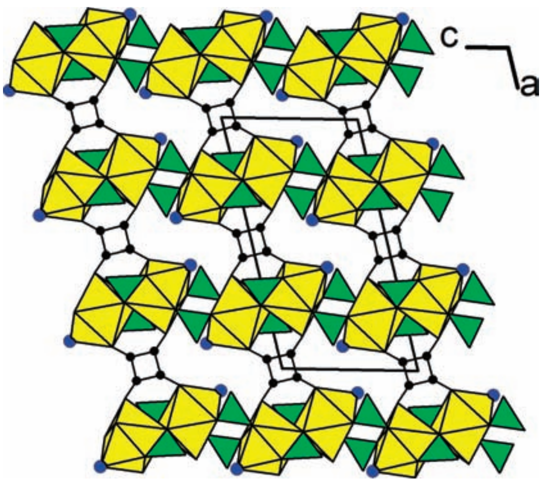

Figure 2. Structure of **2** viewed along the *b* axis. Color code: black circles, C atoms; blue circles, coordination water O atoms.

The room temperature emission spectrum of **2** recorded at 391 nm excitation exhibits characteristic bands of the Eu^{3+} ion at 580, 591, 612, 650, and 700 nm, which 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 (Figure S6 in the Supporting Information). Only one ${}^5D_0 \rightarrow {}^7F_0$ transition was observed in the spectrum. 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) transiton, which is also consistent with the structure analysis result that the Eu^{3+} site lacks inversion symmetry.

In summary, we have synthesized and structurally characterized three novel lanthanide phosphites incorporating squarate ligands. Their structures contain 2D layers

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(8) Crystal data for $[Eu(H_2O)(C_4O_4)_{0.5}(HPO_3)]$ (**2**): crystal of dimensions $0.2 \times 0.1 \times 0.1$ mm^3, $T = 293$ K, monoclinic, space group $C2/m$, $Z = 8$, $M_r = 305.97$, $a = 15.430(3)$ Å, $b = 10.224(2)$ Å, $c = 8.1616(16)$ Å, $\beta = 104.61(3)°$, $V = 1245.9(4)$ $Å^3$, $D_{calc} = 3.262$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 10.292$ mm^{-1}, 1479 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 54.96°$, $R_{int} = 0.0485$), GOF = 1.130, $\Delta\rho_{max} = 1.29$ e $Å^{-3}$, $\Delta\rho_{min} = -1.77$ e $Å^{-3}$, R1 = 0.0249, wR2 = 0.0680. Crystal data for $[Gd(H_2O)(C_4O_4)_{0.5}(HPO_3)]$ (**3**): crystal of dimensions $0.15 \times 0.1 \times 0.1$ mm^3, $T = 293$ K, monoclinic, space group $C2/m$, $Z = 8$, $M_r = 311.26$, $a = 15.392(3)$ Å, $b = 10.196(2)$ Å, $c = 8.1580(16)$ Å, $\beta = 104.70(3)°$, $V = 1238.4(4)$ $Å^3$, $D_{calc} = 3.339$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 10.937$ mm^{-1}, 1498 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 54.96°$, $R_{int} = 0.0649$), GOF = 1.106, $\Delta\rho_{max} = 1.01$ e $Å^{-3}$, $\Delta\rho_{min} = -1.04$ e $Å^{-3}$, R1 = 0.0198, wR2 = 0.0461. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-H atoms.

of lanthanide phosphite, which are pillared through $C_4O_4^{2-}$ to form a 3D framework. Our previous attempts to synthesize some first-row d-block metal squaratophosphites or phosphates were unsuccessful because the squarate anion can only chelate large cations. The title compounds are the first examples of a new class of inorganic–organic hybrids. There is potential for further exploration. For example, it would be interesting to synthesize an organically templated lanthanide squaratophosphite/phosphate and to incorporate a second metal into the framework. It is likely that many novel structures exist. Further research on this theme is in progress.

Acknowledgment. We thank the National Science Council for support and Dr. Y.-S. Wen at the Institute of Chemistry, Academia Sinica, for X-ray data collection.

Supporting Information Available: Crystallographic data in CIF format, X-ray powder patterns, a TGA curve, an ORTEP diagram, and a luminescence spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.