The First Organically Templated Layered Cerium Phosphate-Hydrogen Sulfate: $[enH_2]_{0.5}[Ce^{III}(PO_4)(HSO_4)(OH_2)]$

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A novel organically templated layered cerium phosphate-hydrogen sulfate $[enH_2]_{0.5}[Ce^{III}(PO_4)(HSO_4)(OH_2)]$ has been hydrothermally synthesized. The product was further characterized by means of single-crystal and powder X-ray diffractions, TG-DTA, CHN elemental analysis, SEM, and IR. Its unique layered structure possesses cerium-centered polyhedral CeO_9 as a new basic building unit. The diprotonated ethylenediamine cations contact adjacent layers via hydrogen bonds to compensate the charge of the inorganic framework.

Lanthanide materials with potential applications as ion exchanger, moisture sensor, fluorescence material, and ion conductor, have attracted considerable research attentions.[1] Synthesis of novel lanthanide materials with layered or open-framework structures is of great interest because of the high coordination numbers, a variety of coordination geometries, and existence of changeable oxidation states of lanthanide elements, which would give new materials with novel framework architectures and some potential properties such as catalysis, ion exchange, intercalation, and magnetism as well.[2]

Hydrothermal methods have proved to be invaluable for the synthesis of almost all kinds of recently important materials,[3] in particular layered and porous materials with novel structures.[4] Synthesis of lanthanide materials by using soft chemistry method was explored early.[5] However, so far except for the two novel open-framework cerium materials, cerium oxyfluoride, YU-1[6] and cerium phosphate fluoride,[7] and one microporous cerium silicate,[8] no formation of new lanthanide containing material has been reported in hydrothermal systems. Although hydrothermal synthesis has already given a great deal of organically templated layered compounds, lanthanide material has not been observed. In the present work, a novel organically templated layered cerium phosphate sulfate, $[enH_2]_{0.5}[Ce^{III}(PO_4)(HSO_4)(OH_2)]$, has been hydrothermally crystallized. Its unique layered structure possesses cerium-centered polyhedral CeO_9 as a new basic building unit. The ethylenediamine cations contact both the adjacent layers via hydrogen bonds to compensate charge of the inorganic framework.

The title compound was synthesized hydrothermally from a starting composition of 1.0 $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 4H_2O$/3.0 H_3PO_4/4.0 $H_2N(CH_2)_2NH_2$/8.0 H_2SO_4/240 H_2O. This mixture was sealed in Teflon-lined stainless steel autoclaves and heated at 110 °C for 4 days. The cream colored crystalline product was filtered and washed with deionized water, and then dried in air at ambient temperature. Although fluoride ion was proved to be the effective mineralizer for crystallization of open-framework cerium materials in our previous research, we did not employed it in this synthesis because of its high activity for combination with metal atoms and probable obstruction for organic species incorporation. As the acidity of the reaction system is always the dominant factor for product crystallization, we tried to increase the acidity of the synthesis system and decrease the synthesis temperature, so as to stabilize the protonated organic amine and further incorporate it into the structure of the product. ICP analysis gave the Ce/P/S ratio of 1 : 0.96 : 0.98. Elemental analysis indicated that the C, N, and H contents are 3.23%, 3.85%, and 1.35%, corresponding to a molar ratio C : N : H = 1.00 : 1.02 : 5.02. These results are in accordance with the formula of $[enH_2]_{0.5}[Ce^{III}(PO_4)(HSO_4)(OH_2)]$ for the title compound. Thermogravimetric analysis in air revealed the title compound could be stable up to ca. 260 °C.

A prismatic crystal with approximate dimensions of $0.25 \times 0.10 \times 0.05\,mm^3$ was selected for single-crystal X-ray analysis.[9] The result indicates that this compound crystallizes in the monoclinic system, space group $P2_1/a$ (No. 14) with the cell parameters of $a = 12.999(5)$, $b = 7.150(4)$, $c = 9.212(5)$ Å, and $\beta = 95.33(4)°$.

The structure of this crystal is based on a network of cerium-centered polyhedral CeO_9, phosphorus-centered tetrahedral PO_4, and sulfur-centered tetrahedral SO_4. The asymmetric unit of it is shown in Figure 1. Without the effect of F^- ions, a new type of basic building unit, CeO_9 polyhedron is formed with the centered cerium atom coordinated by nine oxygen atoms, and completed

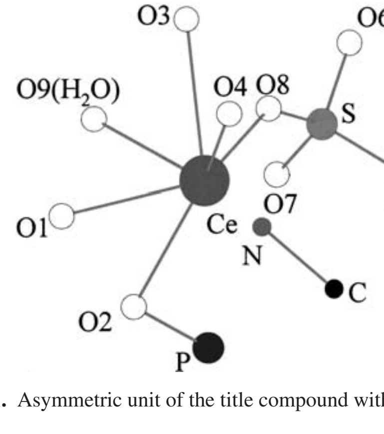

Figure 1. Asymmetric unit of the title compound with atoms labeled.

by a water molecule O(9)(H_2O). It is different from the other two cerium-centered basic building units, CeO_6F_2 and CeO_4F_4, formed in open-framework structures that we prepared.[6,7] The higher acidity of the reaction system might be the probable reason for the formation of polyhedron with Ce(III) as the center atom. The structure consists of macroanionic $[Ce(PO_4)(HSO_4)(OH_2)]^-$ sheets separated by diprotonated ethylenediamine cations. Along the *b* axis of the structure, there are corrugated chains linked by CeO_9 polyhedra via bridge oxygen atoms (Figure 2a). These chains are further connected via PO_4 groups to create the two-dimensional sheets (Figure 2b). The sulfur-centered tetrahedral SO_4 groups stick to surface of the sheets, and link to CeO_9 polyhedra via corner sharing. The macroanionic sheets were separated by organic diprotonated ethylenediamine cations. In the planes vertical to the *c* axis, there are two kinds of four-ring windows contain two CeO_9 polyhedra and two PO_4 tetrahedra with diagonal varied between 4.28 to 4.82 Å, and 4.18 to 4.68 Å (Figure 2b). The ethylenediamine cations are located near the larger four-ring windows to balance the framework negative charge and direct the windows structure. In our previous studies, ammonium cation was observed also to have template effect and often compete with organic species to direct the framework structures.[4,6,7] For the title compound synthesis, the acid system might be advantageous to enhance the competition ability of ethylenediamine cations.

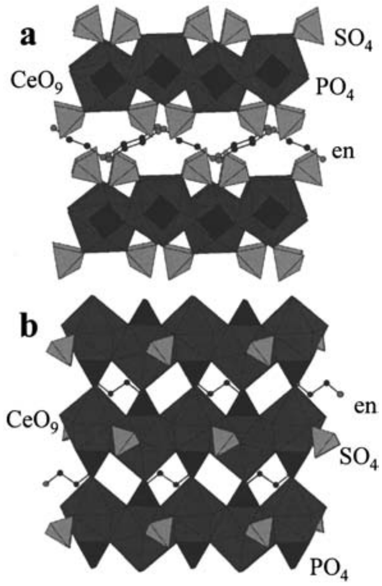

Figure 2. Polyhedral representation of the title compound showing the (a) arrangement of organic template between the adjacent layers and (b) layer structure and location of the template.

The Ce–O distances vary in the range from 2.422 to 2.646 Å, which is comparable with those for cerium atoms in $Ce^{III}(PO_4)$(2.336–2.658 Å).[10] All of the four coordination oxygen atoms of the PO_4 tetrahedron bridge to cerium atoms and have an average bond length of 1.505 Å. For sulfur-centered tetrahedron, S atom shares two of its coordination oxygen atoms with cerium atoms and has S–O distances of 1.496 and 1.480 Å, respectively. Of the remaining S–O linkages, the shorter one (1.458(3) Å), S–O(7) might be considered as S=O double bond, and the longer one (1.469(3) Å), S–O(6) might be the S–O–H bond. The possible hydrogen sites can be estimated by bond valence calculations,[11] the calculated results agree well with the formula above.

In summary, a novel organically templated layered cerium phosphate sulfate with new type of basic building unit, CeO_9, has been synthesized under hydrothermal conditions. This work illustrates that the acidity of the synthesis system might be a dominant factor that influences the incorporation of organic amine template into the structure, and further reveals the possibility of formation of organically templated layered or open-framework materials with wide topological range based on novel units. The synthesis of novel materials via correct controlling of organic templates and reaction conditions are in process. With $[enH_2]^{2+}$ cations located in the interspace between the layers, the title compound might probably have some interesting ion-exchange properties.

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9 Crystal structure data were collected by using a prismatic crystal with dimension of $0.25 \times 0.10 \times 0.05\,mm^3$ by using molybdenum Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator). The space group $P2_1/a$ could be assigned uniquely after a careful inspection of all reciprocal lattice points for which $2\theta < 90°$. 7712 of the total 4257 collected reflections were unique. The final cycle of full-matrix least-squares refinement was based on 5624 observed reflections ($I > 3.00\sigma(I)$) and 128 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.049$, $R_w = 0.084$. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallorgraphic Data Center as supplementary publication to CCDC 170372. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (UK); Tel: (+44)1223-336-408, Fax: (+44)1223-336-033, e-mail: deposit@ccdc.cam.ac.uk.
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