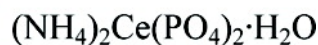
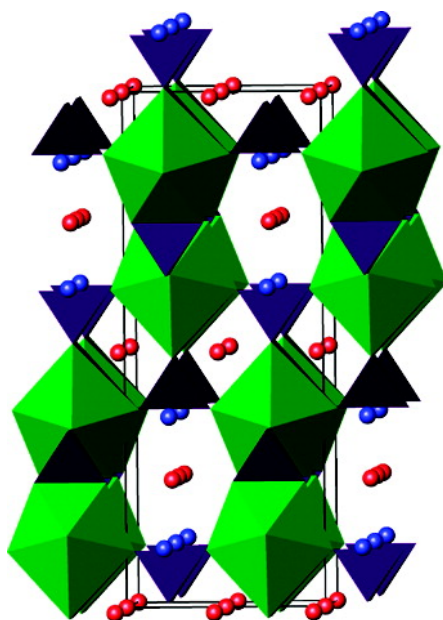


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## Crystal Structure of a Cerium(IV) Bis(phosphate) Derivative

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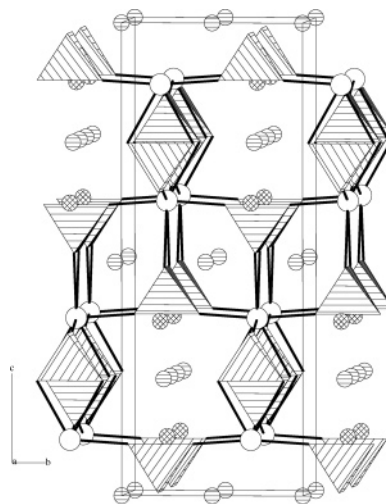
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Since 1975, the year in which Herman and Clearfield<sup>1</sup> published the first synthesis of a crystalline cerium(IV) phosphate with a P/Ce molar ratio equal to 2, three decades of fruitless attempts to ascertain the structure of a cerium(IV) bis(phosphate) have elapsed. The first structure of a cerium(IV) phosphate,  $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})_{0.5}$ , has only very recently been published.<sup>2</sup> In said paper, the authors duly point out that compared with zirconium and titanium phosphates, which are well-documented materials, cerium(IV) phosphates appear to be much more complex, with P/Ce ratios ranging between 1:1 and 3:1, in contrast with the two well-characterized layered structures of the other tetravalent metals:<sup>3–6</sup>  $\text{M}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\alpha$ -MP) and  $\text{M}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  ( $\gamma$ -MP), when  $\text{M} = \text{Ti}, \text{Zr}$ . Despite efforts and evidence that the structures do not correspond to the  $\alpha$ - or  $\gamma$ -MP types,<sup>7</sup> all the structures of CeP with P/Ce = 2 have remained unknown until now, including a monohydrated ammonium cerium(IV) bis(phosphate),  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , hydrothermally synthesized from the  $\text{CeO}_2\text{--NH}_3\text{--P}_2\text{O}_5\text{--H}_2\text{O}$  system.<sup>8</sup>

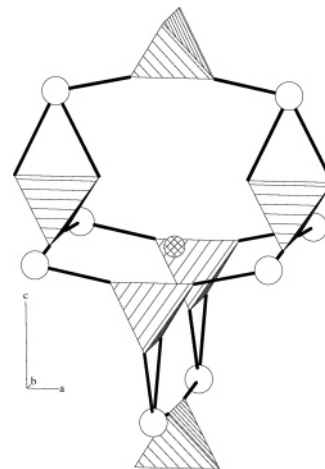
In this work, microcrystals of  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  were hydrothermally obtained from a  $\text{CeO}_2\text{--CO}(\text{NH}_2)_2\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$  system. The structure was solved by X-ray powder diffraction. The compound was found initially to be tetragonal with a strong cell elongation along the  $c$ -axis, consistent with the elongated octahedral habit of crystallites. The structure was solved with the space group  $I4_1/amd$  (No. 141) but after considering the presence of structural disorder the final refinement was made in the orthorhombic space group  $Imma$  (No. 74) with the following final unit cell parameters:  $a = 6.8940(9)$ ,  $b = 6.8860(9)$ ,  $c = 17.723(2)$  Å,  $V = 841.3(2)$  Å<sup>3</sup>.

This structure bears absolutely no resemblance to the  $(\text{NH}_4)_2\text{Zr}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ <sup>9</sup> nor to the  $\alpha$ - or  $\gamma$ -ZrP structures.<sup>3,4</sup> It consists of  $\text{CeO}_8$  distorted dodecahedra and  $\text{PO}_4$  tetrahedra joined together to form a three-dimensional framework. Each cerium is joined to four phosphate groups by vertex sharing in the  $ab$  plane and with two phosphate groups by edge sharing in the  $[0\ 0\ 1]$  and  $[0\ 0\ -1]$  directions. This framework possesses small four-sided and larger six-sided tunnels in the  $[1\ 0\ 0]$  and  $[0\ 1\ 0]$  quasi-equivalent directions (Figure 1). Ammonium ions and water molecules are situated inside the larger tunnels. These perpendicular tunnels are displaced along the  $[0\ 0\ 1]$  direction in such a way that they are interconnected by windows generating cavities in which water molecules reside (Figure 2) and additional channels along the  $[1\ -1\ 1]$ ,  $[-1\ 1\ 1]$ ,  $[1\ 1\ 1]$ , and  $[1\ 1\ -1]$  directions where both ammonium and water molecules are simultaneously enclosed (Figure 3) forming a three-dimensional tunnel network. This fact is consistent with the ionic conductivity measurements previously reported for this compound.<sup>8</sup>

Several differences are observed with respect to the only other structurally characterized cerium(IV) phosphate.<sup>2,7</sup> First,  $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})_{0.5}$  can be considered to have a layered structure, whereas the  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  exhibits a clearly three-dimensional network traversed by channels. The cerium atoms are eight-coordinate in both cases, but the environments are different: up to seven  $\text{PO}_4$  groups or six plus one water molecule in the former



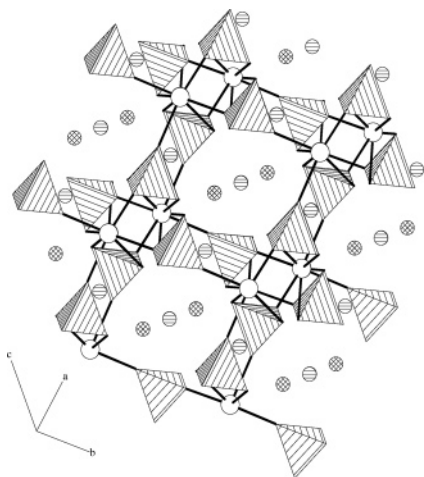
**Figure 1.** Representation of the structure of  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  along the  $a$ -axis with the  $c$ -axis vertical ( $\text{PO}_4$ , tetrahedral; Ce, large empty circles; N, lined circles;  $\text{O}_w$ , doubly lined circles).



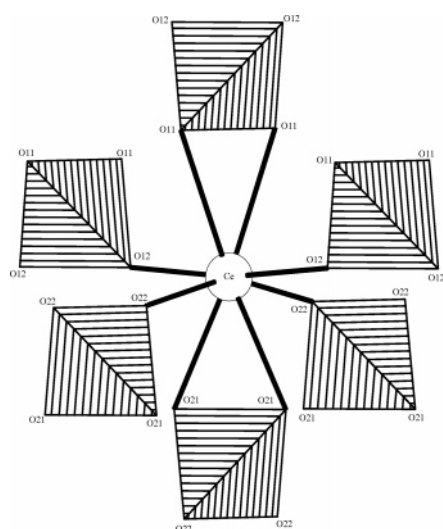
**Figure 2.** View of the framework cavity in which water molecule resides (nitrogen and additional water molecules have been omitted for clarity).

compound, but only six  $\text{PO}_4$  in a very symmetrical fashion in the latter compound. In the structure presented in this paper, the Ce atom is surrounded by eight oxygen atoms at a distance ranging from 2.2 to 2.8 Å, involving four monodentate and two bidentate phosphate groups (Figure 4). This environment could be described as distorted dodecahedra.

The water molecule oxygen is close to four ammonium ion nitrogens, two N1 and two N2, at 2.81 Å in a tetrahedral environment. On the other hand, each ammonium ion is close to two water molecules and four oxygen framework atoms,  $\text{N1} \cdots \text{O11}$  or  $\text{N2} \cdots \text{O21}$  at distances of around 2.80 Å.



**Figure 3.** View along  $[1\ 1\ -1]$  vector of the  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  structure (for symbols, see Figure 1).

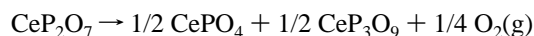
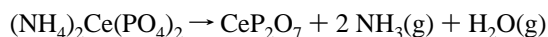
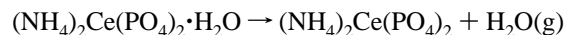


**Figure 4.** Representation of the environment of the cerium atom.

In their paper,<sup>8</sup> Xu et al. do a good job characterizing the novel  $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  compound both chemically and spectroscopically (IR, Raman, impedance). However, the structural parameters published are not satisfactory, and the proposed mechanism for the material thermal decomposition is likewise incorrect.

The TG and DTG data show that the top speed in the release of the crystal water takes place at ca. 130 °C. In two subsequent steps (DTG minima at 310 and 365 °C, respectively), the anhydrous compound is transformed into  $\text{CeP}_2\text{O}_7$  followed by reduction of Ce(IV) to Ce(III) at a temperature (>750 °C) rather low compared to that previously reported.<sup>10</sup> Mass spectrometry analysis (MS) was used to determine the  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{O}_2$  concentration from a

sample of the expelled vapor. The conjunction of TG, DTG, and MS experimental results confirms that the first step is solely related to the release of water. At higher temperatures,  $\text{CeP}_2\text{O}_7$  formation takes place, it being observed that the evacuation of water and ammonia is simultaneous. Finally, oxygen formation is detected as a consequence of the redox process.<sup>11,12</sup> The thermal decomposition may be summarized as:



In conclusion, given the potential applications of cerium(IV) phosphates,<sup>13,14</sup> the structural characterization of the first compound with a P/Ce molar relationship equal to 2 should encourage researchers to search for structural data from related compounds, in particular,  $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$  and  $\text{CeP}_2\text{O}_7$ .

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**Supporting Information Available:** Synthesis, experimental procedures (thermal analysis and powder XRD data), and details on the crystal structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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