

## A Novel Layered Zirconium Phosphate $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$ Synthesized through Non-aqueous Route

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A novel layered zirconium phosphate  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  has been synthesized by using nonaqueous method in an ethylene glycol medium. The as-synthesized product was further characterized by means of single-crystal and powder X-ray diffractions, TG-DTA, CHN elemental analysis, and IR. The compound consists of macroanionic layers of  $[\text{ZrPO}_7\text{H}_3]^{2-}$  separated by  $\text{NH}_4^+$  cations.

The study of crystalline zirconium phosphate chemistry started originally from the successful obtaining of  $\alpha$ -zirconium phosphate and the establishment of  $\alpha$ -form layered structure by Clearfield and Stynes in 1964.<sup>1</sup> In recent years, zirconium phosphates attracted considerable research attentions because of crystal structure chemistry, various properties, and many potential applications.<sup>2</sup> Today we know that it is possible to obtain a large number of zirconium phosphates with layered structure.<sup>3</sup> Opportunities in designing new zirconium phosphates with low-dimensional structures were achieved by employing organic templates and fluoride anion mineralizer in hydrothermal synthesis systems.<sup>4,5</sup> But up to now, only four low-dimensional zirconium phosphates free from fluorine element have been reported.<sup>5-8</sup>

Recently, nonaqueous synthesis as an effective method was proposed. It is known that nonaqueous synthesis has been applied in the preparation of various metal phosphates with open-framework, layered, and chain structures.<sup>9</sup> However, besides two zirconium phosphates with layered and chain structures we reported,<sup>7,8</sup> only one chain zirconium phosphate has been crystallized from nonaqueous media.<sup>5</sup> In the present work, by using ethylene glycol as the reaction medium, in the presence of  $\text{NH}_4\text{F}$  as the mineralizer, the predominantly nonaqueous synthesis of a novel layered zirconium phosphate,  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  has been achieved.

The pure crystalline  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  was prepared from the starting compositions of 1.0  $\text{ZrOCl}_2$  : 1.2  $\text{H}_3\text{PO}_4$  : 1.0  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  ( $n = 3-6$ ) : 4.0  $\text{NH}_4\text{F}$  : 30  $\text{HO}(\text{CH}_2)_2\text{OH}$ , which is similar to that for layered zirconium phosphate  $[\text{NH}_4]_2[\text{enH}_2]_2[\text{Zr}_3(\text{OH})_6(\text{PO}_4)_4]$  we have reported.<sup>6</sup> But in this synthesis, long-chain organic diamines, such as  $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$ ,  $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$ ,  $\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$ , and  $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$  were used to take the place of  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ . In a typical synthesis procedure, 3.22 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (C.R.) was dissolved in 20 ml of ethylene glycol to form a solution, to which 8.0 ml of phosphoric acid (85%) was added, and then the mixture gelled. Ammonium fluoride (1.48 g) was added to the gel to form a sol under stirring with a glass stick, then a suitable amount of selected

diamine was added dropwise to the sol under vigorous stirring. The reaction mixture was stirred with a magnetic stirrer for 120 min and then was transferred into a Teflon-lined stainless steel autoclave to a fill fraction of 60%. The crystallization was carried out under autogenous pressure at 160–190 °C for 3–6 days. The colorless crystalline product was filtered and washed with deionized water and ethanol, and then dried in air at ambient temperature. ICP analysis gave the  $\text{Zr}/\text{P}$  ratio of 1 : 0.98. Elemental analysis indicates that the H, and N contents are 3.58, and 9.01 wt%, respectively, corresponding to an empirical molar ratio  $\text{H} : \text{N} = 11.12 : 2.00$ . The analysis results are in good agreement with the calculated value ( $\text{H} : \text{N} = 11 : 2$ ) for the formula  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$ .

A suitable transparent prismatic crystal was selected for single-crystal X-ray analysis.<sup>10</sup> The compound crystallizes in the monoclinic system, space group  $P2_1/n$  (No. 14), with the lattice parameter  $a = 7.661(2)$  Å,  $b = 9.699(2)$  Å,  $c = 10.473(2)$  Å,  $\beta = 95.16(2)$  °,  $V = 775.1(3)$  Å<sup>3</sup>,  $Z = 4$ .

The structure of  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  is based on a sheet of zirconium-centered octahedra and phosphorus-centered tetrahedral (Figure 1). The structure consists of macroanionic  $[\text{ZrPO}_7\text{H}_3]^{2-}$  sheets separated by inorganic ammonium cations (Figure 2a).  $\text{ZrO}_3(\text{OH})_3$  octahedra link up with  $\text{PO}_4$  tetrahedra via corner-sharing in a strictly alternating manner to give rise to an infinite layer (Figure 2b). Three vertices of the  $\text{ZrO}_3(\text{OH})_3$

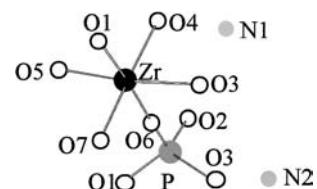


Figure 1. Asymmetric unit of the title compound with atoms labeled.

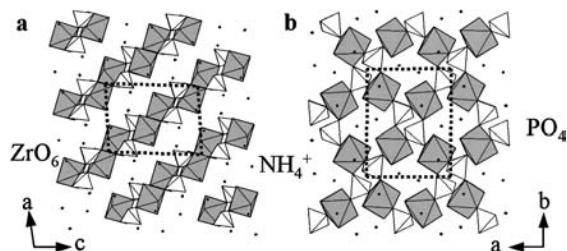
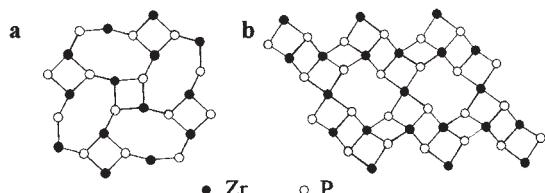


Figure 2. Polyhedral representation of the structure of the compound with unit cell shown as line of dots. (a) view along the b-axis; (b) view along the a-axis.

octahedron are shared by adjacent  $\text{PO}_4$  units, and three vertices of the  $\text{PO}_4$  tetrahedron are linked to adjacent  $\text{ZrO}_3(\text{OH})_3$  units with the remaining corresponding to the  $\text{P}=\text{O}$  linkage, leading to a  $\text{P}/\text{Zr}$  ratio of 1 : 1. Comparing with the structure of another layered zirconium phosphate  $[\text{NH}_4]_2[\text{enH}_2]_2[\text{Zr}_3(\text{OH})_6(\text{PO}_4)_4]$ <sup>7</sup> synthesized under similar conditions, although the title compound also has eight- and four-membered rings in the inorganic sheet, the four-membered rings are surrounded by eight-membered rings, (Figure 3a) which is very different from  $[\text{NH}_4]_2[\text{enH}_2]_2[\text{Zr}_3(\text{OH})_6(\text{PO}_4)_4]$  (Figure 3b). On the other hand, only inorganic ammonium cations are incorporated in the interlayer and lie above and below the windows within the layers. Although some long chain organic diamines have been used as the probable structure-directing agents for the products, the steric effect came from their longer chains made it rather difficult for them to be located near eight-membered windows of the products. On the contrary,  $\text{NH}_4^+$  cation is more competent as the structure-directing agent for the title compound crystallization because of its less steric effect and higher capability of coordinate with the inorganic framework.



**Figure 3.** Different layer structures of (a)  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  and (b)  $[\text{NH}_4]_2[\text{enH}_2]_2[\text{Zr}_3(\text{OH})_6(\text{PO}_4)_4]$ .

For each  $\text{PO}_4$  tetrahedron three of its coordinating oxygen atoms bridge to Zr atoms with P–O bond lengths in the range 1.47(1)–1.53(1) Å. Normally, the terminal P–OH bond length is about 1.59 Å, while the terminal P=O is about 1.50 Å owing to enhanced d–p  $\pi$ -bonding.<sup>7</sup> Therefore, the remaining P–O linkage with length of 1.48(2) Å, namely P(1)–O(7) may be considered as P=O double bond. These distances can also be comparable with those of the terminal P=O groups in  $\text{H}_3\text{PO}_4 \cdot 0.5\text{H}_2\text{O}$  of 1.485 Å and 1.495 Å,<sup>11</sup> and in some  $\text{AlPO}_4\text{-n}$  phases.<sup>12</sup> In addition, the presence of P=O bonds can also be uncovered by the difference of bond angles about phosphorous. As expected from elementary VSEPR (valence shell electron-pair repulsion) theory,<sup>13</sup> all the O–P–O angles with varying values between 106.8(8)–108.9(9)° are less than the O–P=O angles in the range 108(1)–113(1)°.

For  $\text{Zr}(1)\text{O}_3(\text{OH})_3$  octahedra, the bridging  $\text{Zr}(1)\text{–O}$  bond lengths are similar to each other, with an average of 2.06 Å and with the corresponding O–Zr(1)–O angles very close to those of regular octahedron. The terminal Zr–O bond lengths for  $\text{Zr}(1)\text{–O}(3)$  (2.00(1) Å) and  $\text{Zr}(2)\text{–O}(4), \text{O}(6)$  (average value of 1.975 Å) are relatively shorter, and may be considered as Zr–OH linkages. Although the formulation of the compound  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  can be conceivable from the above discussion, the locations of the hydrogen atoms in the structure are not definitive. The bond valences sums of known framework atoms<sup>14</sup> indicated that O(1), O(5), and O(7) might connect with  $\text{NH}_4^+$  cations via hydrogen bond, resulting in their lower valence sums. Similarly, the much lower valence sums for O(3), O(4), and O(6), indicate the linkages of these oxygen atoms to terminal hydrogen atoms, as well as the hydrogen bond to the hydrogen atoms of

$\text{NH}_4^+$  cations.

Thermogravimetric analysis of this compound shows that the  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  undergoes a complicated endothermic decomposition at 200–400 °C, giving a weight loss of ca. 28.15%, which agrees well with the calculated result (28.9%) according to Eq. [1]. At higher temperature, the compound converts via an amorphous into a crystalline phase of  $\text{Zr}_3(\text{PO}_4)_4$ .<sup>15</sup>



In summary, a novel layered zirconium phosphate,  $[\text{NH}_4]_2[\text{Zr}(\text{OH})_3(\text{PO}_4)]$  has been prepared by using nonaqueous synthesis with  $\text{NH}_4\text{F}$  as the mineralizer. In this compound, the inorganic ammonium cations are incorporated in the interlayer and located near the windows within the layers through competition with long-chain organic diamines. Ion-exchange experiments of the title compound indicated interesting results that  $\text{NH}_4^+$  cations could be selectively exchanged by some alkali earth metal cations.

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#### References and Notes

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- 10 Crystal structure determination: fw = 273.29. A colorless prismatic crystal with dimension of 0.30 × 0.25 × 0.25 mm<sup>3</sup> was mounted on a glass fiber. Diffraction data were collected by using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71069$  Å, graphite monochromator). 5954 of the total 6500 collected reflections were unique ( $R_{\text{int}} = 0.022$ ). The final cycle of full-matrix least-squares refinement was based on 1523 observed reflections ( $I > 3.00\sigma(I)$ ) and 101 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.083$ ,  $R_w = 0.120$ .
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