Nonaqueous Synthesis and Characterization of a Novel Layered Zirconium Phosphate Templated with Mixed Organic and Inorganic Cations

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A novel layered zirconium phosphate templated with organic diprotonated ethylendiamine and inorganic ammonium cations, $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$, has been synthesized in a nonaqueous medium and characterized by single-crystal and powder X-ray diffractions, thermal analysis, CHN elemental analysis, and infrared spectrum. The compound crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$), with $a = 9.383(3)$ Å, $b = 9.923(3)$ Å, $c = 8.342(2)$ Å, $\alpha = 97.85(2)°$, $\beta = 111.75(2)°$, $\gamma = 113.01(2)°$, and $V = 627.0(4)$ Å^3 ($R = 0.051$ and $R_w = 0.056$). In this compound, the layer consists of eight- and four-membered rings, which are formed by corner-sharing $ZrO_4(OH)_2$ octahedra and PO_4 terahedra. Organic diprotonated ethylendiamine and inorganic ammonium cations lie above and below the eight- and four-membered windows within the layers, respectively. The two template cations are arranged alternately over the layer surface and link adjacent layers through hydrogen bonds of NH_3^+ and NH_4^+ groups.

Introduction

Metal phosphates have been known for a long time and were extensively investigated with respect to crystal structure chemistry, various properties, and many potential applications in a wide area of materials. Some zirconium phosphates, because of their proton conductivity, ion exchange, and catalytic activity, have attracted more attention than others. The study of crystalline zirconium phosphate chemistry started originally from the successful obtaining of α-zirconium phosphate and the establishment of its α-form layered structure by Clearfield and Stynes in 1964.[1] A further development in layered zirconium phosphates, realizing the formula of γ-zirconium phosphate as $ZrPO_4{\cdot}H_2PO_4{\cdot}H_2O$, first discovered by Clearfield et al.,[2] was made in the late 1980s.[3] In the following years, the possibility of relating the properties of zirconium phosphates to their crystal structures and the many potential applications in the fields of ion exchange and intercalation, stimulated a variety of researches into this family of compounds.[4] Moreover, preparations of layered zirconium phosphonates were also attempted for their novel properties, particularly for the potential uses as "molecular recognition", and solid-state gas sensors.[5,6]

Although the study of organically templated zirconium phosphates was conspicuous and some inspiring results were recently achieved, there were still few examples of them. In 1994, a layered zirconium phosphate fluoride was reported by Clearfield et al.[7] A one-dimensional double-stranded polymer $[enH_2]_{1.5}[Zr(PO_4)(HPO_4)F_2]$ was solvothermally synthesized in 1995.[8] In the following year, a zirconium phosphate fluoride containing organic template with a three-dimensional cage structure was obtained for the first time.[9] More recently, a series of zirconium phosphate fluorides were prepared.[10] But up to now, only two low-dimensional zirconium phosphates free from fluoride have been reported: one is one-dimensional $[enH_2]$ $[Zr(HPO_4)_3]$, and the other is a two-dimensional $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$ which is the ion-exchanged analogue of γ-ZrP.[11]

It is known that nonaqueous syntheses have been effectively applied in the preparation of various metal phosphates, including amine-containing aluminum, gallium, indium, zinc, and cobalt phosphates with three-dimensional open-framework structures.[12−16] Moreover, phosphates with a layered or chain structure can also be crystallized from nonaqueous media.[17,18]

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Herein, we describe the nonaqueous synthesis and characterization of a novel two-dimensional zirconium phosphate, $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$, with $[NH_4]^+$ and $[H_3N(CH_2)_2NH_3]^{2+}$ cations as mixed templates, in a $ZrOCl_2-H_3PO_4-H_2N(CH_2)_2NH_2-NH_4F-HO(CH_2)_2OH$ system.

Experimental Section

Synthesis. The title compound was synthesized from a reaction mixture of composition $1.0ZrOCl_2{:}1.2H_3PO_4{:}1.0H_2N(CH_2)_2NH_2{:}4.0NH_4F{:}30HO(CH_2)_2OH$. In a typical synthesis procedure, 3.22 g of $ZrOCl_2{\cdot}8H_2O$ (C. R.) was dissolved in 20 mL of ethylene glycol to form a solution, to which 8 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, and then ethylendiamine 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.

X-ray Structure Determination. A transparent prismatic crystal having approximate dimensions of $0.2 \times 0.1 \times 0.08$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator.

The data were collected using the ω-2θ scan technique to a maximum 2θ value of 90.0°. Of the 10 755 reflections which were collected, 10 337 were unique; equivalent reflections were merged. The intensities of three representative reflections were measured after every 500 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied and resulted in transmission factors ranging from 0.88 to 1.00. The data were also corrected for Lorentz and polarization effects.

The crystal structure was solved by direct methods and expanded by Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the TEXSAN[19] crystallographic software package. Further details of crystal data are summarized in Table 1. The coordinates and anisotropic temperature factors are given in Table 2, and selected bond lengths and angles are shown in Tables 3 and 4.

X-ray Powder Diffraction. X-ray powder diffraction (XRD) patterns were taken on a RINT 1200 Rigaku X-ray diffractometer, using Ni-filtered Cu Kα radiation. XRD patterns at high temperatures were measured up to 1000 °C in air.

Thermal Analysis. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out by using a Rigaku Thermoflex TAS 200 thermal analysis system with a heating rate of 5 °C/min over 20−1000 °C temperature range.

Infrared Spectrum. Infrared absorption spectra (IR) were recorded on a JASCO FT/IR-410 spectrometer using transparent KBr pellets: 1−2 mg of the sample was crushed and mixed with 300 mg KBr.

Table 1. Crystal Data and Structure Refinement for $[NH_4]_2[H_3N(CH_2)_2NH_3]_2\ [Zr_3(OH)_6(PO_4)_4]$

empirical formula	$H_{34}Zr_3P_4O_{22}N_6C_4$
formula weight	915.91
crystal system	triclinic
space group	$P\bar{1}$ (#2)
lattice parameters	
a (Å)	9.383(3)
b (Å)	9.923(3)
c (Å)	8.342(2)
α (deg)	97.85(2)
β (deg)	111.75(2)
γ (deg)	113.01(2)
V (Å$^{3)}$	627.0(4)
Z value	1
D_{calcd} (g/cm^3)	2.426
radiation	Mo Kα ($\lambda = 0.71069$ Å)
μ (cm^{-1})	15.6
no. of reflections measured	total: 10755 unique: 10 337 ($R_{int} = 0.066$)
no. observations ($I > 3.00\sigma(I)$)	4242
no. variables	179
reflection/parameter ratio	23.7
residuals: R; R_w	0.051; 0.056
goodness of fit indicator	1.63

$R = \Sigma||F_o| - |F_c||/\Sigma|F_c| = 0.051$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2} = 0.056$.

Table 2. Atomic Coordinates and B_{eq} for $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$

atom	site	x	y	z	$B_{eq}{}^a$
Zr(1)	1a	0.0000	0.0000	0.0000	0.76(1)
Zr(2)	2i	0.77767(6)	0.49472(5)	0.12717(6)	0.782(8)
P(1)	2i	0.3909(2)	0.3180(1)	0.1368(2)	1.01(2)
P(2)	2i	0.8277(2)	0.2397(1)	0.8354(2)	0.94(2)
O(1)	2i	0.3194(5)	0.4318(4)	0.0909(5)	1.51(7)
O(2)	2i	0.5245(5)	0.3370(4)	0.0629(5)	1.66(7)
O(3)	2i	0.0822(4)	0.1026(4)	0.2661(4)	1.10(6)
O(4)	2i	0.2386(5)	0.1519(4)	0.0263(5)	1.66(7)
O(5)	2i	0.9076(6)	0.1538(5)	0.9470(6)	2.4(1)
O(6)	2i	0.9633(5)	0.3510(5)	0.7897(6)	1.99(8)
O(7)	2i	0.4688(5)	0.3440(5)	0.3382(5)	1.88(7)
O(8)	2i	0.6617(5)	0.1279(5)	0.6616(6)	2.30(8)
O(9)	2i	0.2288(5)	0.3515(4)	0.6999(5)	1.25(6)
O(10)	2i	0.1421(5)	0.5939(4)	0.6750(5)	1.19(6)
O(11)	2i	0.2152(6)	0.6653(5)	0.0471(6)	2.25(9)
N(1)	2i	0.3713(7)	0.1717(6)	0.6065(7)	2.2(1)
N(2)	2i	0.3854(7)	0.8760(6)	0.6815(7)	2.2(1)
N(3)	2i	0.2025(6)	0.4422(6)	0.3800(6)	1.89(9)
C(1)	2i	0.322(1)	0.9707(8)	0.7613(10)	2.8(2)
C(2)	2i	0.2391(8)	0.0391(8)	0.6273(9)	2.5(1)

[a] $B_{eq} = {}^8/_3\pi[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 3. Bond Lengths (Å) for $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$

Zr(1)−O(3)	2.015(3) × 2	P(1)−O(2)	1.551(4)
Zr(1)−O(4)	2.059(4) × 2	P(1)−O(4)	1.541(4)
Zr(1)−O(5)	2.052(4) × 2	P(1)−O(7)	1.500(4)
Zr(2)−O(1)	2.079(4)	P(2)−O(5)	1.534(4)
Zr(2)−O(2)	2.074(4)	P(2)−O(6)	1.536(4)
Zr(2)−O(6)	2.070(4)	P(2)−O(8)	1.515(4)
Zr(2)−O(9)	1.987(3)	P(2)−O(11)	1.532(4)
Zr(2)−O(10)	2.014(3)	N(1)−C(2)	1.498(8)
Zr(2)−O(11)	2.041(4)	N(2)−C(1)	1.497(8)
P(1)−O(1)	1.547(4)	C(1)−C(2)	1.513(9)

Results and Discussion

Synthesis. The crystalline products with high purity and yield were obtained from a typical composition with molar ratio $1.0ZrOCl_2{:}1.2H_3PO_4{:}1.0H_2N(CH_2)_2NH_2{:}4.0NH_4F{:}30HO(CH_2)_2OH$ at 180 °C for 3 days. Although the product crystallized with good crystallinity during the first day, the yield is rather low. Temperature lower

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Table 4. Bond Angles (deg) for $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$

O(3)−Zr(1)−O(3)	180.0	O(3)−Zr(1)−O(4)	89.8(1)
O(3)−Zr(1)−O(4)	90.2(1)	O(3)−Zr(1)−O(5)	86.9(2)
O(3)−Zr(1)−O(5)	93.1(2)	O(3)−Zr(1)−O(4)	90.2(1)
O(3)−Zr(1)−O(4)	89.8(1)	O(3)−Zr(1)−O(5)	93.1(2)
O(3)−Zr(1)−O(5)	86.9(2)	O(4)−Zr(1)−O(4)	180.0
O(4)−Zr(1)−O(5)	91.1(2)	O(4)−Zr(1)−O(5)	88.9(2)
O(4)−Zr(1)−O(5)	89.9(2)	O(4)−Zr(1)−O(5)	91.1(2)
O(5)−Zr(1)−O(5)	180.0	O(1)−Zr(2)−O(2)	90.0(2)
O(1)−Zr(2)−O(6)	94.3(2)	O(1)−Zr(2)−O(9)	93.0(1)
O(1)−Zr(2)−O(10)	175.4(1)	O(1)−Zr(2)−O(11)	88.0(2)
O(2)−Zr(2)−O(6)	175.6(2)	O(2)−Zr(2)−O(9)	89.4(2)
O(2)−Zr(2)−O(10)	86.7(1)	O(2)−Zr(2)−O(11)	90.3(2)
O(6)−Zr(2)−O(9)	89.4(2)	O(6)−Zr(2)−O(10)	89.0(1)
O(6)−Zr(2)−O(11)	90.8(2)	O(9)−Zr(2)−O(10)	90.2(1)
O(6)−Zr(2)−O(11)	179.0(2)	O(10)−Zr(2)−O(11)	88.8(2)
O(1)−P(1)−O(2)	108.6(2)	O(1)−P(1)−O(4)	107.8(2)
O(1)−P(1)−O(7)	110.8(2)	O(2)−P(1)−O(4)	105.4(2)
O(2)−P(1)−O(7)	112.4(2)	O(4)−P(1)−O(7)	111.7(2)
O(5)−P(2)−O(6)	108.8(2)	O(5)−P(2)−O(8)	111.5(3)
O(5)−P(2)−O(11)	108.4(3)	O(6)−P(2)−O(8)	110.3(2)
O(6)−P(2)−O(11)	108.7(2)	O(8)−P(2)−O(11)	109.0(2)
Zr(2)−O(1)−P(1)	139.9(2)	Zr(2)−O(2)−P(1)	138.6(2)
Zr(1)−O(4)−P(1)	141.4(2)	Zr(1)−O(5)−P(2)	158.1(3)
Zr(2)−O(6)−P(2)	148.1(3)	Zr(2)−O(11)−P(2)	168.6(3)
N(2)−C(1)−C(2)	111.4(5)	N(1)−C(2)−C(1)	112.7(5)

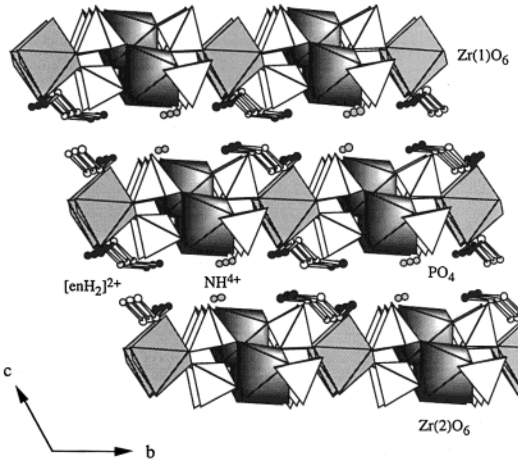

Figure 1. View parallel to plane of layer.

than 150 °C did not give the product. The mineralizer, NH_4F, was found to be an important factor that affected the synthesis of the product. When excess NH_4F was used, no crystallization of the product could be achieved, and when less NH_4F was used, impurity was synthesized simultaneously. Several kinds of diamines such as 1,3-diaminnopropane, 1,4-diaminnobutane, 1,6-diaminnohexane, and 1,7-diaminnoheptane were used as the templates, but all of them gave another novel layered zirconium phosphate, in which only NH_4^+ cations resided between the layers, and no diamines were included.

Crystal Structure. The structure consists of macroanionic $[Zr_3P_4O_{22}H_6]^{6-}$ sheets separated by organic diprotonated ethylendiamine and inorganic ammonium cations (Figure 1). The sheet lying in the crystallographic *ab* plane is built up from corner-sharing $ZrO_4(OH)_2$ octahedra and PO_4 tetrahedra (Figure 2). Whereas four vertexes of the $ZrO_4(OH)_2$ octahedron are shared by adjacent PO_4 units, three vertexes of the PO_4 tetrahedron are linked to adjacent $ZrO_4(OH)_2$ units, with those remaining corresponding to the P=O group, leading to a P/Zr ratio of 4/3.

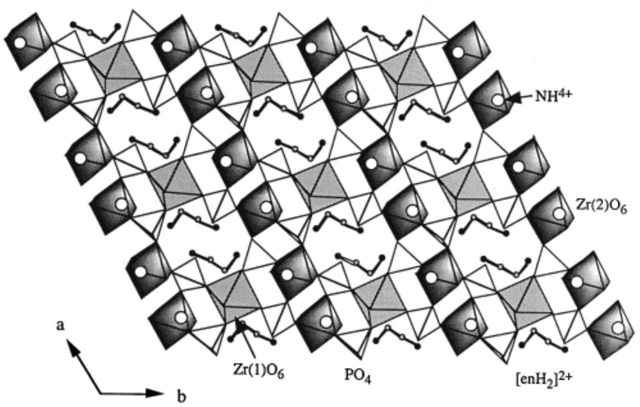

Figure 2. View normal to the plane of layer showing location of templates.

In the *ab* plane, the $ZrO_4(OH)_2$ octahedra link up with the PO_4 tetrahedra in a strictly alternating manner to give rise to an infinite layer. The layer consists of eight- and four-membered rings. There is only one crystallographically distinct eight-membered ring, nearly circular in shape with O···O distances varying between 6.43 and 7.65 Å. The eight-membered rings connect each other through common $ZrO_4(OH)_2$ octahedra and four-membered rings along the *a* and *b* axis, respectively. The organic diprotonated ethylendiamine and inorganic ammonium cations are located in the interlaminar region of the structure and lie alternately over the layer surface (Figure 1). The organic diprotonated ethylendiamine cations occupy positions close to the eight-membered ring windows, there being two cations above and below a layer for each window. On the other hand, inorganic ammonium cations situate closely to $Zr(2)O_4(OH)_2$ octahedra and the corresponding four-membered ring windows (Figure 2). It is unusual that the structure consists of mixed organic and inorganic template cations to balance the framework charge. In a previous report, NH_4^+ as one of two interlayer cations was considered to have arisen from the fragmentation of the reactive organic template.[18] However, as to the title compound, it is inferred that the NH_4^+ is offered by the NH_4F of the reaction mixture. Some other syntheses, such as those using HF or KF instead of NH_4F, had also been attempted, and no title compound was crystallized. These results further confirmed our inference.

For each PO_4 tetrahedron, three of its coordinating oxygen atoms bridge to Zr atoms with P−O bond lengths in the range 1.532(4)−1.551(4) Å. Normally, the terminal P−OH bond length is about 1.59 Å, and the terminal P=O is about 1.50 Å due to enhanced d−p π-bonding.[11] Therefore, the remaining P−O linkages with lengths of 1.500(4)−1.515(4) Å, namely, P(1)−O(7) and P(2)−O(8), may be considered as P=O double bonds. These distances can also be compared with those of the terminal P=O groups in $H_3PO_4 \cdot 0.5H_2O$ of 1.485 and 1.495 Å,[20] and in some $AlPO_4$-*n* phases.[21] In addition, the presence of P=O bonds can also be learned from the difference of bond angles about phosphorus. As expected from elementary VSEPR (valence shell electron-pair repul-

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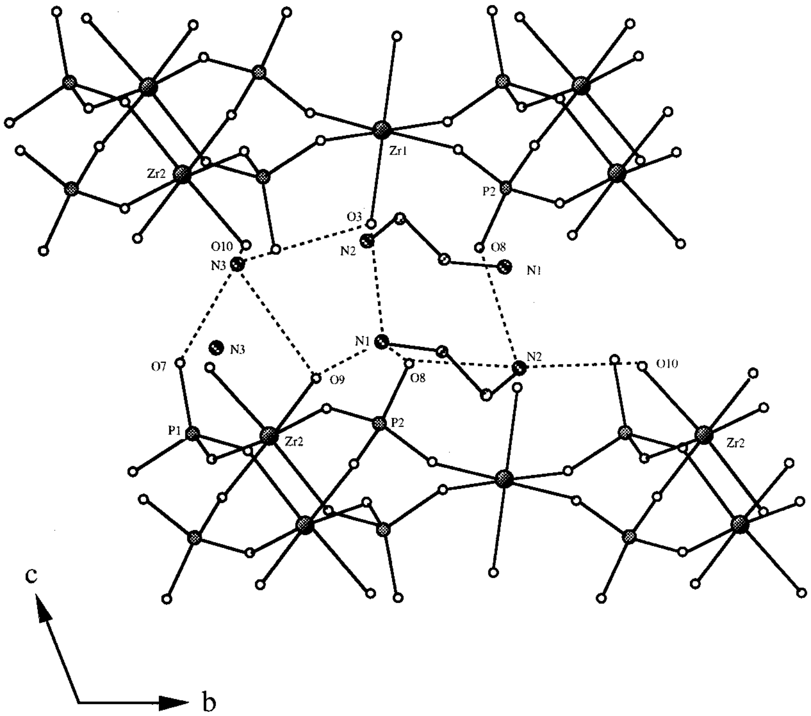

Figure 3. View parallel to plane of layers showing interlayer hydrogen bonding.

sion) theory,[22] all of the O−P−O angles with varying values between 105.4(2)−108.8(2)° are less than the O−P═O angles in the range 109.0(2)−112.4(2)°.

The environments of the two Zr sites are topologically different. Although both of the $ZrO_4(OH)_2$ octahedra link to four PO_4 tetrahedra, their forms of connection are different as shown in Figure 2. For $Zr(1)O_4(OH)_2$ octahedra, the bridging Zr(1)−O bond lengths are similar to each other, with an average of 2.056 Å and with corresponding O−Zr(1)−O angles very close to those of a regular octahedron. Whereas for Zr(2) the bridging Zr(2)−O distances vary between 2.041(4)−2.079(4) Å with a larger average value of 2.066 Å, the O−Zr(2)−O angles deviate from a regular octahedron slightly. The terminal Zr−O bond lengths for Zr(1)−O(3) (2.015(3) Å) and Zr(2)−O(7), O(9) (average value of 2.001 Å) are relatively shorter and may be considered as Zr−OH linkages.

Although from the discussion above, a formulation of the compound as $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$ is reasonable, the locations of the hydrogen atoms in the structure are not definitive. However, the possible hydrogen sites can be estimated by bond valence calculations.[23] O(7) and O(8) hydrogen bond to NH_4^+ and $[H_3N(CH_2)_2NH_3]^{2+}$, respectively, resulting in their lower valence sums as presented in Table 5. Similarly, the much lower valence sums for O(3), O(9), and O(10) indicate the linkages of these oxygen atoms to terminal hydrogen atoms, as well as the hydrogen bond to hydrogen atoms of NH_4^+ and $[H_3N(CH_2)_2NH_3]^{2+}$ cations. The calculated results agree well with the formula above, and according to it, a possible network of hydrogen bonding involving the diprotonated ethylendiamine and ammonium cations, by which $[Zr_3P_4O_{22}H_6]^{6-}$ sheets are held together, can be estimated as shown in Figure 3. At one end of the diprotonated ethylendiamine dication, N(1) forms one hydrogen bond to the O(3) atom of the Zr(1)−OH group in the layer above and two hydrogen bonds to O(8) and O(9) atoms of the P(2)═O and Zr(2)−OH groups in the layer below, respectively, whereas the other nitrogen of the ethylendiamine dication, N(2) forms two hydrogen bonds to O(10) and O(8) of the Zr(2)−OH and P(2)═O groups in the layer below and one to O(8) of the P(2)═O group in the layer above. The hydrogen bond distances are in the range 2.72−2.89 Å. The ammonium cation forms two hydrogen bonds to O(7) and O(9) of the P(1)═O and Zr(2)−OH groups in the layer below and two to the Zr(1)−OH and Zr(2)−OH in the layer above with N(3)−H···O distances varying between 2.77and 2.98 Å.

Table 5. Bond Valence Sum of Atoms in $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$

atom	bond valence sum	atom	bond valence sum
Zr(1)	4.523	O(5)	1.939
Zr(2)	4.513	O(6)	1.900
P(1)	4.833	O(7)	1.327
P(2)	4.896	O(8)	1.274
O(1)	1.848	O(9)	0.874
O(2)	1.845	O(10)	0.812
O(3)	0.810	O(11)	1.970
O(4)	1.904		

Elemental analysis indicates that the C, H, and N contents are 5.16, 3.58, and 9.01 wt %, respectively, corresponding to an empirical molar ratio C:H:N = 1.00:8.33:1.50. The analysis results are in good agreement with the calculated value (C:H:N = 1.00:8.50:1.50) for the formula $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$.

Thermal Properties. Thermogravimetric curve of this compound in air from room temperature to 1000 °C is shown in Figure 4. The observed total weight loss of 28.20% agrees well with the calculated value of 28.46% according to eq 1. From the XRD patterns of the

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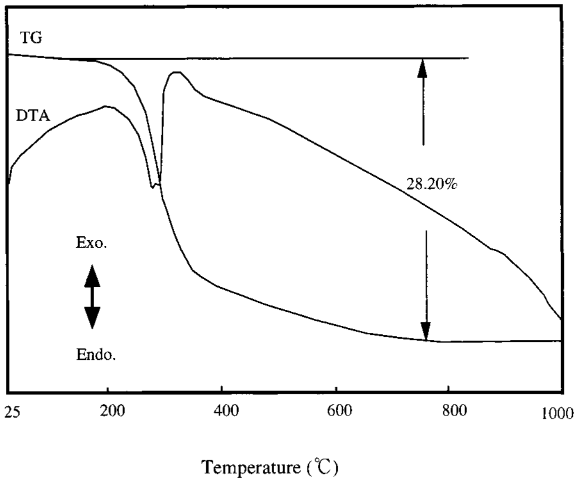

Figure 4. Thermal analysis curves of $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$.

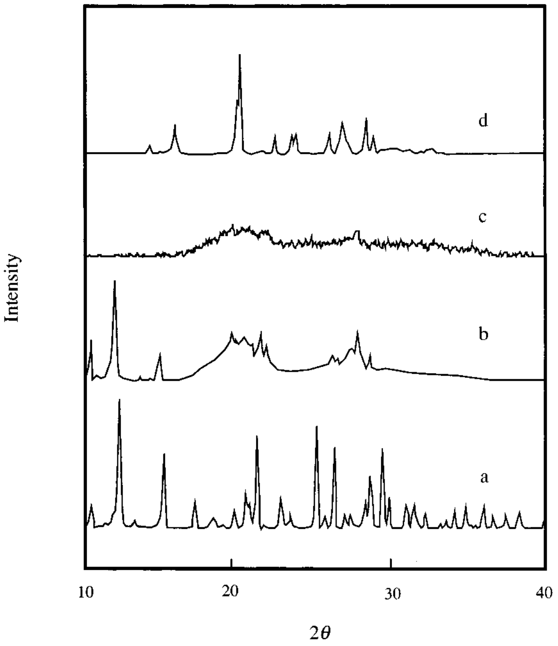

Figure 5. XRD patterns of the products at different temperatures: (a) 25 °C, $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$; (b) 350 °C, $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$ in lower crystallinity; (c) 400 °C, amorphous; (d) 1000 °C, $Zr_3(PO_4)_4$.

products at high temperatures shown in Figure 5, it was found that the compound is stable up to 350 °C. Above 400 °C, the compound became amorphous and finally crystallized with XRD pattern given in Figure 5d, which agrees well with that reported in powder diffraction file for $Zr_3(PO_4)_4$.[24]

$$[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4] \rightarrow Zr_3(PO_4)_4 + 2H_2N(CH_2)_2NH_2\uparrow + 2NH_3\uparrow + 6H_2O\uparrow \quad (1)$$

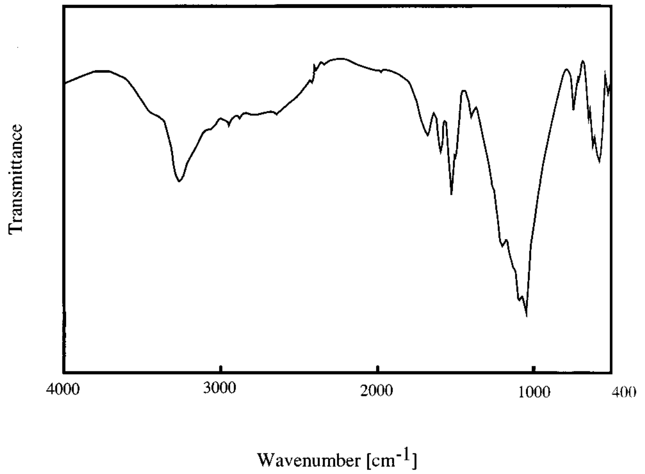

Figure 6. IR spectra of $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$.

Infrared Spectrum. On the basis of the framework vibration model for microporous aluminophosphates,[25,26] the absorption bands for this compound are assigned as follows: 1112, 1005, and 969 cm^{-1} are associated with the stretching vibrations of PO_4 units, and the bands at 648, 547, 515, and 475 cm^{-1} correspond to bending vibrations of PO_4 groups. Bands arising from the template cations $[NH_4]^+$ and $[H_3N(CH_2)_2NH_3]^{2+}$ are also seen. The bands at 1611 and 1516 cm^{-1} may be due to δ_{N-H} of the $-NH_3^+$ or NH_4^+, and the bands at 1454 and 1379 cm^{-1} are assigned to stretching vibration of $-CH_2-$ groups. The broad band at 3259 cm^{-1} is due to Zr−OH groups (Figure 6).

Conclusions

The successful preparation of the novel two-dimensional layered zirconium phosphate $[NH_4]_2[H_3N(CH_2)_2NH_3]_2[Zr_3(OH)_6(PO_4)_4]$ further revealed the advantages of nonaqueous methods in synthesis of metal phosphates, as well as enriching the structural chemistry of zirconium phosphate. Because there are two kinds of cations, $[H_3N(CH_2)_2NH_3]^{2+}$ and $[NH_4]^+$, lying between the layers of the title compound. Therefore, the ion exchange properties of this compound are worthy of investigation.

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