Non-aqueous Synthesis and Structure of a Novel Monodimensional Zirconium Phosphate: $[NH_4]_3[Zr(OH)_2(PO_4)(HPO_4)]$

Dan Wang,*†# Ranbo Yu, Takahiro Takei, Nobuhiro Kumada, Nobukazu Kinomura, Ayumu Onda,† Koji Kajiyoshi,† and Kazumichi Yanagisawa†

Institute of Inorganic Synthesis, Faculty of Engineering, Yamanashi University, Miyamae-Cho 7, Kofu 400-8511

†*Laboratory of Hydrothermal Chemistry, Faculty of Science Kochi University, 2-5-1 Akebono-Cho, Kochi 780-8520*

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A novel one-dimensional zirconium phosphate inorganic polymer, $[NH_4]_3[Zr(OH)_2(PO_4)(HPO_4)]$ has been synthesized in $(HOCH_2CH_2)_2O$ medium with F^- ions in presence, and structurally characterized. The compound consists of macroanionic chains of $[ZrP_2O_{10}H_3]^{3-}$ separated by NH_4^+ cations.

Zirconium 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.[1,2] Since the fluoride ion mineralizer was introduced into the synthesis of zirconium phosphates, zirconium phosphates with novel structures have been developed rapidly. In 1994, Clearfield et al. reported a layered zirconium phosphate fluoride.[3] A one-dimensional double-stranded polymer $[enH_2]_{1.5}[Zr(PO_4)(HPO_4)F_2]$ was solvothermally synthesized in 1995.[4] In the following years, a series of zirconium phosphate fluorides were prepared.[5,6] But up to now, only three low-dimensional zirconium phosphates free from fluoride element have been reported, one is one-dimensional $[enH_2][Zr(HPO_4)_3]$,[7] one is two-dimensional $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$,[7] and the other is tow-dimensional $[NH_4]_2[enH_2]_2[Zr_3(OH)_6(PO_4)_4]$.[8]

It is known that non-aqueous synthesis has been effectively applied in the preparation of various metal phosphates.[4,9,10] In the present work, by using diethylene glycol ($(HOCH_2CH_2)_2O$) as the reaction medium and F^- ions as the mineralizer, the predominantly non-aqueous synthesis of a novel one-dimensional zirconium phosphate, $[NH_4]_3[Zr(OH)_2(PO_4)(HPO_4)]$ has been achieved.

The title compound was synthesized from a reaction mixture with the composition of $1.0ZrOCl_2{\cdot}8H_2O : 1.2H_3PO_4 : 1.0H_2N(CH_2)_2NH_2 : 4.0NH_4F : 30.0(HOCH_2CH_2)_2O$. In a typical synthetic procedure, $ZrOCl_2{\cdot}8H_2O$ (C.R.) was dissolved in diethylene glycol to form a solution, to which phosphoric acid (85%) was added, then the mixture gelled. Ammonium fluoride was added to the gel to form a sol under stirring with a glass stick, and then ethylenediamine was added dropwise to the sol under vigorous stirring. After stirred with a magnetic stirrer for 2 h, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave to a fill fraction of 60%, and heated at 180 °C for 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 Zr/P ratio of 1 : 1.96. Elemental analysis indicates that the C, H, and N contents are 0, 4.3, and 11.3 wt%, respectively, corresponding to an empirical molar ratio H : N = 5.3 : 1.0. These analytical results are in good agreement with the calculated value for the formula $[NH_4]_3[Zr(OH)_2(PO_4)(HPO_4)]$.

A suitable transparent needle-like crystal was selected for single-crystal X-ray analysis.[11] The compound crystallizes in the triclinic system, space group $P1$, with the lattice parameter $a = 8.1432(8)$ Å, $b = 12.718(2)$ Å, $c = 5.2463(6)$ Å, $\alpha = 91.85(1)°$, $\beta = 92.16(1)°$, $\gamma = 74.25(1)°$, $V = 522.4(1)$ Å^3, $Z = 2$. The atomic coordinates are listed in Table 1.

Table 1. Atomic coordinates and temperature factors

Atom	x	y	z	B_{eq}
Zr(1)	0.287(3)	0.626(3)	0.061(3)	1.11(2)
Zr(2)	0.871(3)	0.083(3)	−0.421(3)	0.60(2)
P(1)	0.682(3)	0.980(3)	0.070(3)	0.84(4)
P(2)	0.189(3)	0.477(3)	−0.442(3)	0.29(3)
P(3)	0.971(3)	0.234(3)	0.079(3)	2.29(8)
P(4)	0.496(3)	0.722(3)	0.565(3)	1.39(5)
O(1)	0.411(4)	0.717(3)	0.291(4)	1.7(1)
O(2)	0.165(4)	0.532(3)	−0.174(4)	1.9(2)
O(3)	0.007(4)	0.166(3)	−0.174(4)	0.8(1)
O(4)	0.192(4)	0.567(3)	0.357(4)	1.5(1)
O(5)	0.652(4)	0.204(3)	−0.440(4)	1.4(2)
O(6)	0.791(3)	0.016(3)	−0.120(4)	1.4(1)
O(7)	0.498(4)	0.507(3)	0.067(4)	1.6(2)
O(8)	0.038(3)	0.432(3)	−0.514(4)	1.3(1)
O(9)	0.072(4)	0.741(3)	0.064(4)	1.3(1)
O(10)	0.354(3)	0.381(3)	−0.433(4)	0.86(9)
O(11)	0.087(4)	0.951(3)	−0.420(4)	1.3(1)
O(12)	0.770(4)	0.982(3)	−0.671(4)	0.9(1)
O(13)	0.381(4)	0.688(4)	−0.235(4)	3.5(3)
O(14)	0.502(4)	0.057(3)	0.072(4)	1.5(1)
O(15)	0.680(3)	0.860(3)	0.018(4)	0.58(7)
O(16)	0.812(4)	0.319(4)	0.084(4)	4.1(2)
O(17)	0.963(4)	0.153(3)	−0.722(4)	2.4(2)
O(18)	0.129(4)	0.277(4)	0.154(4)	2.9(3)
O(19)	0.513(4)	0.833(3)	0.642(4)	2.4(2)
O(20)	0.675(4)	0.641(3)	0.582(4)	2.3(2)
N(1)	0.685(4)	0.417(3)	−0.432(4)	1.0(1)
N(2)	0.490(4)	0.290(4)	0.064(4)	2.9(3)
N(3)	0.256(4)	0.937(3)	0.080(4)	1.7(2)
N(4)	0.913(4)	0.774(4)	0.566(5)	2.9(3)
N(5)	0.830(4)	0.550(3)	0.064(4)	1.9(2)
N(6)	0.349(4)	0.130(4)	0.568(5)	3.5(3)

Up to now, only two one-dimensional zirconium phosphates have been reported. The simple models of one-dimensional chain of zirconium phosphates showing different polyhedra linkages are given schematically in Figure 1. Figure 1a shows the double-stranded chain of zirconium phosphate fluoride $[enH_2]_{1.5}[Zr(PO_4)(HPO_4)F_2]$,[4] Figure 1b shows the triple-bridge chain of $[enH_2][Zr(HPO_4)_3]$.[7] The chain type of the title compound is given in Figure 1c. This chain represents another fundamental chain type for zirconium phosphates, which is similar to that ($[AlP_2O_8H]^{2-}$) of one-dimensional aluminum phosphate.[12] In these macroanionic chains (empirical formula $[ZrP_2O_{10}H_3]^{3-}$), each Zr-centered octehedra connect with four phosphorus-centered tetrahedra via corner sharing. NH_4^+ cations are accommodated among

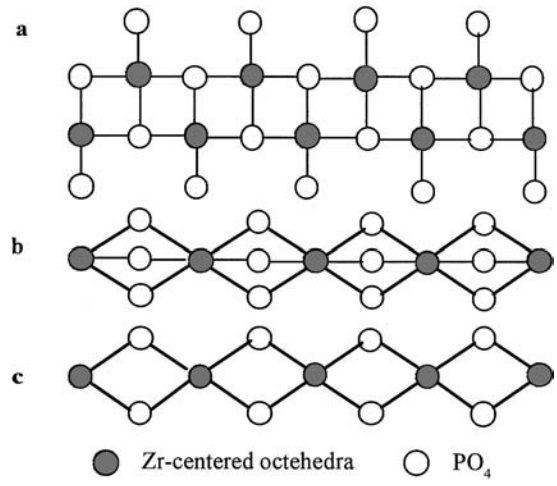

Figure 1. Chain structures for 1-D zirconium phosphates: (a) Double-Stranded chain for $[Zr(PO_4)(HPO_4)F_2]^{3-}$; (b) Triple-bridged chain for $[Zr(HPO_4)_3]^{2-}$; (c) Double-bridged chain for $[Zr(OH)_2(PO_4)(HPO_4)]^{3-}$.

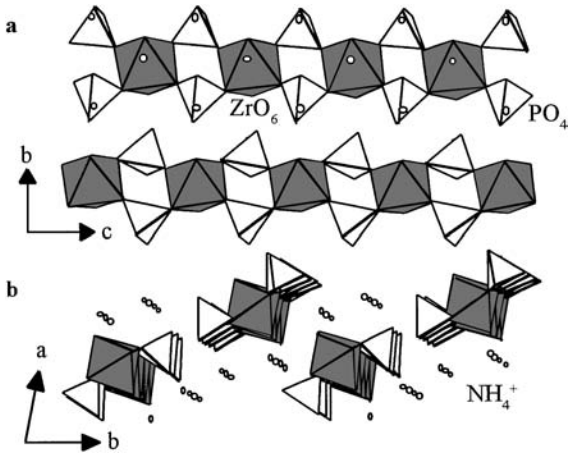

Figure 2. Polyhedral representation of the compound showing the (a) chains along the *c* axis, and (b) locations of NH_4^+ cations.

the chains (Figure 2).

For $Zr(1)O_4(OH)_2$ octahedra, the bridging Zr(1)–O bond lengths vary between 2.01(4)–2.13(2) Å with an average of 2.058 Å, which is comparable with that of the Zr–O groups in $[NH_4]_2[enH_2]_2[Zr_3(OH)_6(PO_4)_4]$ of 2.061 Å.[7] While for Zr(2), the bridging Zr(2)–O distances vary between 2.03(1)–2.12(1) Å with a larger average value of 2.086 Å. These distances can be compared with those of the Zr–O groups in $[enH_2][Zr(HPO_4)_3]$ of 2.068 Å.[8] The terminal Zr–O bond lengths for Zr(1)–O(7) (1.95(1) Å), Zr(1)–O(9) (1.96(1) Å), Zr(2)–O(5) (2.01(1) Å), and Zr(2)–O(11) (2.06(1) Å) (average value of 1.995 Å) are relatively shorter, and may be considered as Zr–OH linkages as compared with average value of 2.001 Å found in the structure of $[NH_4]_2[enH_2]_2$-$[Zr_3(OH)_6(PO_4)_4]$.[8] The average bond length of Zr(1)–O is 2.024 Å, which is a little shorter than that of Zr(2)–O and Zr–O of some known compounds. However, the existences of short Zr–O bonds like Zr(1)–O of the title compound are easily observed in many zirconium phosphates, for example, 2.013 Å for $ZrKH(PO_4)_2$,[13] and 2.00(5) Å for $Zr(NaPO_4)(PO_4)H_2O$.[14] For each phosphor-centered tetrahedron two of its coordinate oxygen bridge to Zr atoms with P–O bond lengths in the range 1.48(2)–1.60(2) Å. Normally, the terminal P–OH bond length is about 1.59 Å, while the terminal P=O is about 1.50 Å due to enhanced d-p π-bonding.[7] Therefore, the remaining P–O linkages with shorter lengths in the range of 1.42(2)–1.55(4) Å, namely P(1)–O(14), P(2)–O(8), P(2)–O(10), P(3)–O(16), P(4)–O(19), and P(4)–O(20) may be considered as P=O double bonds, with an average of 1.50 Å. These distances can also be comparable with those of the terminal P=O groups in $H_3PO_4 \cdot 0.5H_2O$ of 1.485 Å and 1.495 Å,[15] and in some $AlPO_4$-n phases.[16] And the longer P(1)–O(15) (1.58(1) Å) and P(3)–O(18) (1.57(2) Å) may be considered as P–OH bonds. All the O–P–O angles with varying values between 104.0(9) and 113(1)° (average of 108.3°) are less than the O–P=O angles in the range 107(1)–115.4(10)° (average of 110.3°).

In summary, a novel one-dimensional zirconium phosphate, $[NH_4]_3[Zr(OH)_2(PO_4)(HPO_4)]$ has been prepared by using non-aqueous synthesis with F^- ions as the mineralizer. The compound represents a new basic structural type for zirconium phosphate. With NH_4^+ cations located in the interspace among the chains, the title compound might probably have some ion-exchange properties.

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References and Notes

Present address: Catalysis Science Laboratory, Research Institute of Innovative Technology for the Earth, 9-2 Kizugawadai Kizu-Cho Soraku-Gun, Kyoto 619-0292, Japan. E-mail: danwang1@rite.or.jp

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11 The crystal structure for this compound: fw = 555.40. A needle-like crystal with dimension of $0.20 \times 0.05 \times 0.05\,mm^3$ was mounted on a glass fiber. Diffraction data were collected by using molybdenum Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator). 8616 of the total 9017 collected reflections were unique. The final cycle of full-matrix least-squares refinement was based on 4029 observed reflections ($I > 3.00\sigma(I)$) and 290 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.057$, $R_w = 0.061$.

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