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Oxyfluorotitanophosphate Cluster $[Ti_{10}P_4O_{16}F_{44}]^{16-}$: Synthesis and Characterization of $K_{16}[Ti_{10}P_4O_{16}F_{44}]$

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One oxyfluorotitanophosphate cluster compound, $K_{16}[Ti_{10}P_4O_{16}F_{44}]$ (**1**), has been synthesized and structurally characterized. As far as we know, it is the first cluster compound for titanophosphate.

Despite having been known for almost 200 years,[1] cluster compounds still attract considerable interest because of their molecular and electronic structural diversity and their significance in catalysis, medicine, and materials science.[2] In particular, the recent enormous expansion of work on metal−organic frameworks[3] and molecular sieves[4] has driven up the level of interest in clusters because they can be considered as the secondary building unit in those compounds.

Since the pioneering work on microporous aluminophosphate materials reported in 1982,[5] metal phosphates have been developed as important molecular sieves.[6,7] Among them, open-framework titanium phosphates (TiPOs) are very valuable because of their anticipated potential in catalysis. Substantial difficulties are encountered in their synthesis[8] despite the existence of many one-dimensional, two-dimensional, and even closely packed three-dimensional TiPOs.[9] It seems highly interesting and potentially very useful to find a way to prepare new open-framework TiPOs. During such efforts, a series of one-dimensional fluorotitanophosphates, $(NH_4)_xK_{4-x}[Ti_2PO_4F_9]$ ($x = 0$, 0.70, 1.00, and 1.25), have been synthesized by us.[10] Here we report the synthesis and structural characterization of a new oxyfluorophosphate cluster compound, $K_{16}[Ti_{10}P_4O_{16}F_{44}]$ (**1**), which is, to our knowledge, the first example of a TiPO cluster compound, which may be potentially useful in the synthesis of new open-framework TiPOs.

Colorless octahedral crystals of **1** were obtained under hydrothermal conditions in Teflon-lined stainless steel autoclaves, starting from acidic suspensions of K_2TiF_6 and phosphoric acid in a molar ratio of 2.0:1.0:7.0 (K/Ti/P). As a typical example, a mixture of 3.00 g (12.5 mmol) of K_2TiF_6 (C.R.) and 6.0 mL (87.6 mmol) of H_3PO_4 (85%, A.R.), together with 3.0 mL of $N_2H_4 \cdot H_2O$ (85%, A.R.), was loaded into a 50-mL Teflon-lined stainless steel autoclave. The autoclave was sealed, heated to 200 °C under autogenous pressure for 5 days, and then cooled to room temperature at a rate of 5 °C/h. About 1.70 g of product (yield 60% based on K_2TiF_6), appearing as octahedral single crystals, was isolated by washing the product with hot distilled water and

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(1) Berzelius, J. J. *Ann. Phys. (Weinheim, Ger.)* **1826**, *6*, 369–380.

(2) (a) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171–198. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed.* **1991**, *30*, 34–48.

(3) (a) Maspoch, D.; Ruiz-Molina, D.; Vecaina, J. *Chem. Soc. Rev.* **2007**, *36*, 770–818. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (c) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.

(4) (a) Zhang, H. X.; Zhang, J.; Zheng, S. T.; Yang, G. Y. *Inorg. Chem.* **2005**, *44*, 1166–1168. (b) Hsu, K. F.; Wang, S. L. *Inorg. Chem.* **2000**, *39*, 1773–1778.

(5) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147.

(6) (a) Yu, J. H.; Xu, R. R. *Acc. Chem. Res.* **2003**, *36*, 481–490. (b) Yu, J. H.; Xu, R. R. *Chem. Soc. Rev.* **2006**, *35*, 593–604.

(7) (a) Wang, Y.; Yu, J. H.; Guo, M.; Xu, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 4089–4092. (b) Yang, G. Y.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 8389–8390.

(8) (a) Poojary, D. M.; Bortun, A. I.; Bortun, L. N.; Clearfield, A. *J. Solid State Chem.* **1997**, *132*, 213–223. (b) Ekambaram, S.; Sevov, S. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 372–375. (c) Ekambaram, S.; Serre, C.; Férey, G.; Sevov, S. C. *Chem. Mater.* **2000**, *12*, 444–449. (d) Fu, Y. L.; Liu, Y. L.; Shi, Z.; Zou, Y. C.; Pang, W. Q. *J. Solid State Chem.* **2001**, *162*, 96–102. (e) Liu, Y. L.; Shi, Z.; Fu, Y. L.; Chen, W.; Li, B. Z.; Hua, J.; Liu, W. Y.; Deng, F.; Pang, W. Q. *Chem. Mater.* **2002**, *14*, 1555–1563. (f) Liu, Y. L.; Shi, Z.; Zhang, L. R.; Fu, Y. L.; Chen, J. S.; Li, B. Z.; Hua, J.; Pang, W. Q. *Chem. Mater.* **2001**, *13*, 2017–2022.

(9) (a) Yang, S. H.; Li, G. B.; You, L. P.; Tao, J. L.; Loong, C. K.; Tian, S. J.; Liao, F. H.; Lin, J. H. *Chem. Mater.* **2007**, *19*, 942–947. (b) Sorokina, N. I.; Voronkova, V. I. *Cryst. Rep.* **2007**, *52*, 80–93.

(10) Yang, S. H.; Li, G. B.; Li, L.; Tian, S. J.; Liao, F. H.; Xiong, M.; Lin, J. H. *Inorg. Chem.* **2007**, *46*, 11431–11436.

10.1021/ic702214g CCC: $40.75

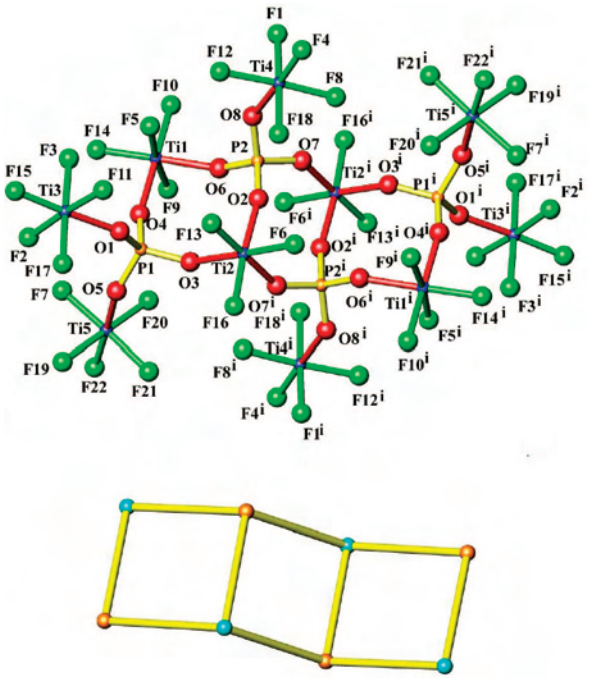

Figure 1. Cluster anion presented in **1** (top) and the corresponding topological linkage (bottom). The P, Ti, O, and F atoms are shown as orange, blue, red, and green spheres, respectively. Symmetry code: (i) $1 - x$, $-y$, $1 - z$.

dried at ambient temperature. **1** is stable and insoluble in water and in most organic solvents.

Single-crystal X-ray analysis revealed that **1** crystallizes in the monoclinic space group $P2_1/n$,[11] with 8 K, 5 Ti, 2 P, 8 O, and 22 F atoms in the asymmetric unit, which comprises half of the large oxyfluorotitanophosphate cluster $[Ti_{10}P_4O_{16}F_{44}]^{16-}$, with the other half being related through a center of symmetry, as shown in Figure 1. The $[Ti_{10}P_4O_{16}F_{44}]^{16-}$ cluster consists of four PO_4 tetrahedra, two TiO_3F_3 octahedra, two TiO_2F_4 octahedra, and six $TiOF_5$ octahedra. The range of bond lengths is 1.518–1.543 Å for P–O, 1.917–1.982 Å for Ti−O, and 1.800–1.878 Å for Ti−F, in good correspondence with the reported values for similar compounds such as $Na_5TiP_2O_9F$, $K_3Ti_3P_5O_{20}$, and TiF_4.[12] In the solid-state ^{31}P NMR spectrum (Figure 2), two separate resonances of similar intensity were observed in the upfield region at $\delta = -21.8$ and -26.0 ppm, suggesting the presence of two magnetically non-equivalent P atoms in the asymmetric unit,[13] which corresponds to the two crystallographically distinct P

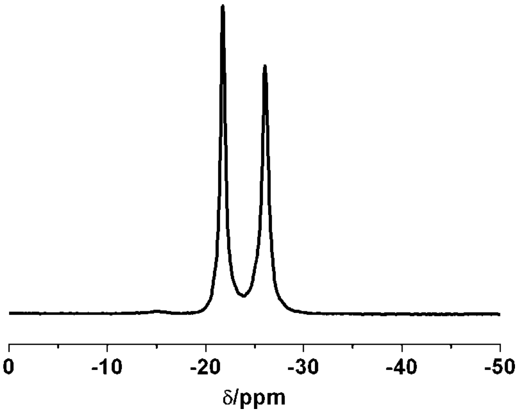

Figure 2. Solid-state ^{31}P NMR spectrum of **1**.

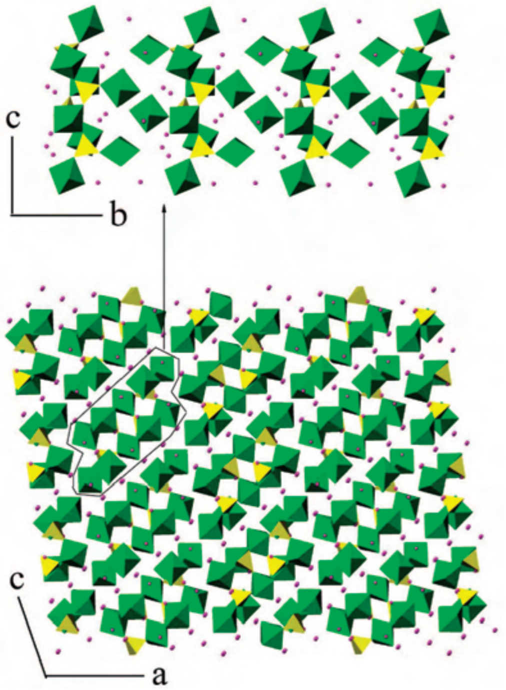

Figure 3. Projections of the structure of **1** along the *a* axis (top) and along the *b* axis (bottom): TiO_xF_{6-x}, green octahedra; PO_4, yellow tetrahedra; K, small red sphere.

atoms in the asymmetric unit of **1**. Two PO_4 tetrahedra and two TiO_3F_3 octahedra are connected by vertex sharing to form a single four ring (S4R), as shown in Figure 1. This S4R further connects to two groups of vertex-sharing PO_4 tetrahedra and a TiO_2F_4 octahedron with common O atoms at both sides. Such a linkage has been observed in the three-dimensional compound $NaZnPO_4 \cdot H_2O$, the layer compound $[Zn_2(HPO_3)_2(C_{14}H_{14}N_4)] \cdot 0.4H_2O$, and $Zn_{2-x}Co_x(HPO_4)_3 \cdot C_3N_2H_{12}$.[14]

Compound **1** is constructed from discrete $[Ti_{10}P_4O_{16}F_{44}]^{16-}$ clusters with the K^+ counterions disposed around the clusters as shown in the view onto the *ac* and *bc* planes (Figure 3). Thermogravimetric analysis−differential scanning calorimetry−mass spectrometry (TGA−DSC−MS) measurements and X-ray

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(11) Crystal data for **1**: $K_{16}[Ti_{10}P_4O_{16}F_{44}]$, $M_r = 2320.48$, 0.10 × 0.07 × 0.05 mm, colorless octahedron, monoclinic, space group $P2_1/n$, $a = 10.295(2)$ Å, $b = 10.848(2)$ Å, $c = 24.727(5)$ Å, $\beta = 98.36(3)°$, $V = 2732(1)$ Å^3, $Z = 2$, $T = 298(2)$ K, λ(Mo Kα) = 0.710 73 Å, $\rho_{calcd} = 2.821$ g cm^{-3}, 5388 reflections collected, 5088 unique ($R_{int} = 0.0495$), $R(F) = 0.060$ and $wR_2 = 0.148$ using 3283 reflections with $I > 2\sigma(I)$. Further details of the crystal structure determination can be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax, (49) 7247 808 666; e-mail, crysdata@fiz-karlsruhe.de] on quoting the depository number CSD-418414.

(12) (a) Golubev, A. M.; Andrianov, V. I.; Sigarev, S. E.; Timofeeva, V. A. *Kristallografiya* **1988**, *33*, 1104–1107. (b) Nagornyi, P. G.; Kapshuk, A. A. *Zh. Neorg. Khim.* **1993**, *38*, 11–13. (c) Bialowons, H.; Mueller, M.; Mueller, B. G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1227–1231.

(13) Murugavel, R.; Kuppuswamy, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 7022–7026.

(14) (a) Fan, J.; Slebodnick, C.; Troya, D.; Angel, R.; Hanson, B. E. *Inorg. Chem.* **2005**, *44*, 2719–2727. (b) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Broach, R. W.; Bedard, R. A. *Chem. Mater.* **1996**, *8*, 145–151. (c) Liu, Y. L.; Na, L. Y.; Zhu, G. S.; Xiao, F. S.; Pang, W. Q.; Xu, R. R. *J. Solid State Chem.* **2000**, *149*, 107–112.

diffraction studies have demonstrated that compound **1** is stable up to 400 °C under an argon atmosphere (see the Supporting Information).

As far as we know, $K_{16}[Ti_{10}P_4O_{16}F_{44}]$ is the first TiPO cluster compound, although there were many reports describing aluminum and zinc phosphate clusters.[15,16] The appearance of such a compound may benefit from the use of K_2TiF_6 as the source of titanium in hydrothermal synthesis. Comparatively, several fluorotitanophosphates have been reported in the literature; their structure varied from three dimensions to two dimensions without the use of K_2TiF_6 as the source of titanium. For example, the compounds $Ti_2F(PO_4)_2{\cdot}2H_2O$[17] and $Na_3[Ti_2P_2O_{10}F]$[9a] were three-dimensional where the F atoms were bridging bonded (Ti−F−Ti) and were synthesized using $TiCl_3$ and $Ti(SO_4)_2$, respectively. The layered fluorotitanophosphates, such as $Ti_2(PO_4)_2F_4{\cdot}N_2C_3H_{12}{\cdot}H_2O$[18a] and $[Ti_3O_2F_2(PO_4)_4]{\cdot}(NH_3(CH_2)_2NH_3)_3{\cdot}(H_2O)_2$[18b] with all the F atoms terminally bonding, were synthesized using hydrous TiO_2 and TiO_2, respectively. One-dimensional TiPO compounds were rare. The first example was $[Ti_3P_6O_{27}]{\cdot}5[NH_3CH_2CH_2NH_3]{\cdot}2H_3O$.[19] Recently, the second example, a series of one-dimensional fluorotitanophosphates $(NH_4)_xK_{4-x}[Ti_2PO_4F_9]$ ($x = 0$, 0.70, 1.00, and 1.25),[10] was reported by our group; these were synthesized using K_2TiF_6. It is expected that more similar compounds will appear when more hydrothermal syntheses are performed with K_2TiF_6 as the source of titanium.

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Supporting Information Available: Experimental section, CIF file, TGA−DSC−MS curves, powder X-ray diffraction patterns at different temperatures, and a discussion on the so-called large cell of compound **1**. This material is available free of charge via the Internet at http://pubs.asc.org.

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(15) (a) Murugavel, R.; Kuppuswamy, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 7022–7026. (b) Azais, T.; Bonhomme, C.; Bonhomme-Coury, L.; Kickelbick, G. *Dalton Trans.* **2003**, 3158–3159. (c) Fujdala, K. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 10133–10134. (d) Yang, Y.; Walawalkar, M. G.; Pinkas, J.; Roesky, H. W. *Angew. Chem.* **1998**, *37*, 96–98. (e) Yang, Y.; Pinkas, J.; Schafer, M.; Roesky, H. W. *Angew. Chem.* **1998**, *37*, 2650–2653.

(16) (a) Harrison, W. T. A.; Hanooman, L. *J. Solid State Chem.* **1997**, *131*, 363–369. (b) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **2000**, *150*, 417–422. (c) Ayi, A. A.; Choudhury, A.; Natarajan, S.; Neeraj, S.; Rao, C. N. R. *J. Mater. Chem.* **2001**, *11*, 1181–1191. (d) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2001**, *34*, 80–87. (e) Natarajan, S.; van Wullen, L.; Klein, W.; Jansen, M. *Inorg. Chem.* **2003**, *42*, 6265–6273. (f) Dan, M.; Udayakumar, D.; Rao, C. N. R. *Chem. Commun.* **2003**, 2212–2213. (g) Natarajan, S. *Solid State Sci.* **2005**, *7*, 1542–1548. (h) Natarajan, S.; Prots, Y.; Ewald, B.; Niewa, R.; Kniep, R. *Z. Anorg. Allg. Chem.* **2006**, *632*, 37–41.

(17) Serre, C.; Guillou, N.; Férey, G. *J. Mater. Chem.* **1999**, *9*, 1185–1189.

(18) (a) Serre, C.; Férey, G. *J. Mater. Chem.* **1999**, *9*, 579–584. (b) Serre, C.; Taulelle, F.; Férey, G. *Chem. Mater.* **2002**, *14*, 998–1003.

(19) Guo, Y. H.; Shi, Z.; Yu, J. H.; Wang, J. D.; Liu, Y. L.; Bai, N.; Pang, W. Q. *Chem. Mater.* **2001**, *13*, 203–207.