Inorg. Chem. **2002**, *41*, 2310–2312

Inorganic Chemistry
Communication

Single Crystal Structure Determination of a New Zirconium *N*-Ethylpyridinium Phosphonate: $Zr(O_3PCH_2CH_2NC_5H_5)(F^-)_3$

Lori A. Vermeulen,*,[†] Rasheta Z. Fateen,[†] and Paul D. Robinson[‡]

Department of Chemistry and Biochemistry and Department of Geology,
Southern Illinois University, Carbondale, Illinois 62901

Received November 14, 2001

We describe the structure of a new zirconium *N*-ethylpyridinium phosphonate, $Zr(O_3PCH_2CH_2NC_5H_5)(F^-)_3$, that has been determined by single-crystal X-ray analysis (monoclinic, $P2_1/c$ (No. 14), $a = 12.3634(12)$ Å, $b = 9.3090(17)$ Å, $c = 9.8077(13)$ Å, $\beta = 112.819(8)°$, $V = 1040.4(3)$ Å^3, $Z = 4$). This structure is unlike any other reported zirconium phosphonate. Octahedral coordination about zirconium is completed by three oxygen atoms of three different phosphonate groups and three fluoride ligands. The structure is composed of corrugated infinite layers of these Zr octahedra that corner share their three oxygen atoms with the phosphonate tetrahedra. The appended cationic pyridinium groups lie between the inorganic sheets and are charge-balanced by the $[Zr(O_3P–)_3F_3]^-$ octahedra. This structure represents a new example of the structure-directing influence of cationic organic ligands on the zirconium phosphonate framework.

Zirconium phosphates and phosphonates have become materials of intense interest primarily because of their desirable properties of high thermal stability and structural versatility that make them potentially useful in such areas as optoelectronics, catalysis, and separations.[1] Zirconium phosphate is known to exist in two common forms: α zirconium phosphate (α-ZrP, $Zr(HPO_4)_2{\cdot}H_2O$)[2] and γ zirconium phosphate (γ-ZrP, $Zr(PO_4)(H_2PO_4){\cdot}2H_2O$).[3] These two phases both consist of infinite two-dimensional inorganic layers but differ in the manner in which the phosphate groups are bonded to the zirconium ions within the layers. A variety of phosphonates have been prepared possessing the α structure where the interlamellar OH group is simply replaced by an organic moiety.[4] In addition, porous and pillared materials have been prepared from γ-ZrP by topotactic exchange of H_2PO_4 groups with organic phosphonates.[5] In most cases, because single crystals of the zirconium phosphonates are difficult to obtain, structure determination is based upon evaluation of the powder pattern.[6−11] In only a few cases, new structures differing from the α and γ types have been observed.[8,10,12] Here, we report the single-crystal X-ray structure determination of a new zirconium *N*-ethylpyridinium phosphonate, $(Zr(O_3PCH_2CH_2NC_5H_5)(F^-)_3$, Zr(PYR), that exhibits features unlike those of any previously reported zirconium phosphonates.

The starting phosphonate, *N*-ethylphosphonatopyridinium chloride (PYR)[13] was treated with Zr(IV) and HF to obtain transparent, single crystals.[14] The structure of Zr(PYR)[15] is unlike that of the usual α or γ zirconium phosphonates.

---

* To whom correspondence should be addressed. E-mail: vermeulen@chem.siu.edu.

[†] Department of Chemistry and Biochemistry.

[‡] Department of Geology.

(1) For a recent comprehensive review, see: Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1998; Vol. 47, p 371.

(2) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431. Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(3) Poojary, D. M.; Shpeizer, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1995**, 111.

(4) Alberti, G.; Costantino, U. In *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic: New York, 1982; p 147. Dines, M. B.; Di Giacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.

(5) Alberti, G.; Murcia-Mascaros, S.; Vivani, R. *J. Am. Chem. Soc.* **1998**, *120*, 9291. Alberti, G.; Giontella, E.; Murcia-Mascaros, S. *Inorg. Chem.* **1998**, *37*, 4672. Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801. Alberti, G.; Bartocci, M.; Santarelli, M.; Vivani, R. *Inorg. Chem.* **1997**, *36*, 3574. Alberti, G.; Giontella, E.; Murcia-Mascaros, S. *Inorg. Chem.* **1997**, *36*, 2844. Alberti, G.; Casciola, M.; Costantino, U.; Vivani, R. *Adv. Mater.* **1996**, *8*, 291.

(6) Byrd, H.; Clearfield, A.; Poojary, D.; Reis, K. P. *Chem. Mater.* **1996**, *8*, 2239.

(7) Zhang, B.; Poojary, D. M.; Clearfield, A. *Chem. Mater.* **1996**, *8*, 1333.

(8) Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1994**, 2453.

(9) Poojary, D. M.; Zhang, B.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2324.

(10) Poojary, D. M.; Vermeulen, L. A.; Vicenzi, E.; Clearfield, A.; Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1847.

(11) Poojary, M. D.; Hu, H. L.; Campbell, F. L.; Clearfield, A. *Acta Crystallogr.* **1993**, *B49*, 996.

(12) Zhang, B.; Pooojary, D. M.; Clearfield, A. *Inorg. Chem.* **1998**, *37*, 249.

(13) Pyridine (Acros, 7.45 mmol), diethyl 2-bromoethylphosphonate (Acros, 7.46 mmol), and distilled water (12 mL) were combined and refluxed under ambient pressure at 82 °C for 2 days. Concentrated HCl (12 mL) was slowly added, and reflux was resumed for 1 day. The mixture was allowed to cool, and the solvent was evaporated. Water (0.7 mL) was added to barely dissolve the highly viscous yellow residue. 2-Propanol (50 mL) was added to precipitate the product. The product was then recrystallized by dissolving in methanol and adding 2-propanol. ^1H NMR (DMSO, DCl) (ppm) 8.95, 8.52, 8.05, 4.72, 2.36. ^{13}C NMR (DMSO, DCl) (ppm) 146.4, 145.4, 128.6, 56.9, 30.1, 28.4. FTIR KBr (cm^{-1}) 3432, 3125, 3093, 3049, 2933, 2633, 2254, 1635, 1485, 1459, 1385, 1237, 1173, 1074, 964, 942, 825, 782, 762, 733, 677, 645, 594, 489, 436.

10.1021/ic015614z CCC: $22.00

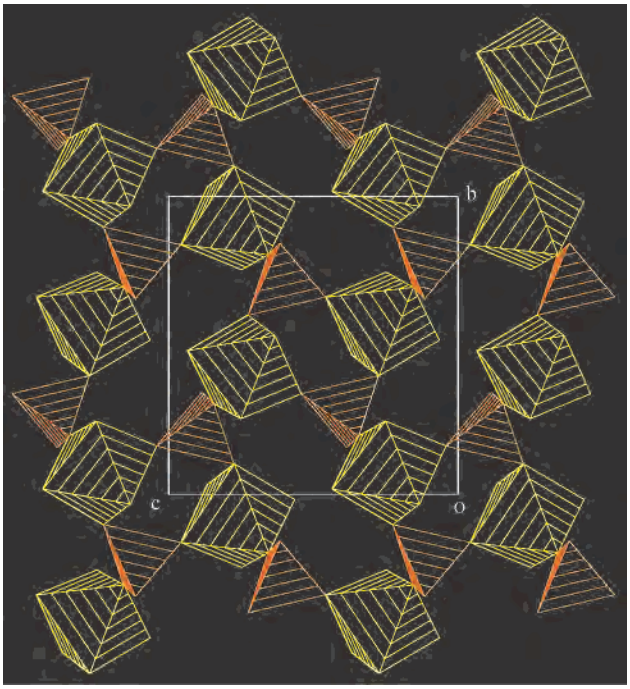

Figure 1. Top view of infinite octahedral/tetrahedral layer of Zr(PYR) as viewed down the *a*-axis.

Octahedral coordination about zirconium is completed by three oxygen atoms of three different phosphonate groups and three fluoride ligands. Thus, this material has the unusual composition of Zr/P/F of 1:1:3. The structure is composed of corrugated infinite layers of these Zr octahedra that corner share their three oxygen atoms with the phosphonate tetrahedra. The top view of this infinite octahedral/tetrahedral layer as viewed down the *a*-axis is shown in Figure 1. The detail of the octahedral coordination about the zirconium is shown in Figure 2. The organic pyridinium groups can be seen on either side of the inorganic octahedral/tetrahedral layer as they are linked to the inorganic layer through the C−P bond of the *N*-ethylphosphonatopyridinium group as shown in Figure 3. As can be seen in this view of the structure, the individual layers are not bonded to each other although the pyridinium rings of adjacent layers overlap.

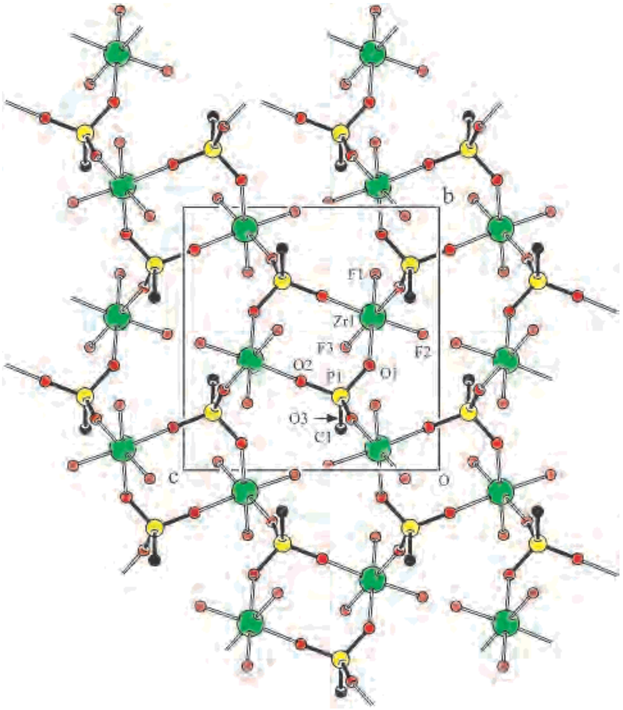

Figure 2. Detailed top view of of infinite octahedral/tetrahedral layer of Zr(PYR) showing zirconium coordination and atom numbering scheme. The organic portion is not shown.

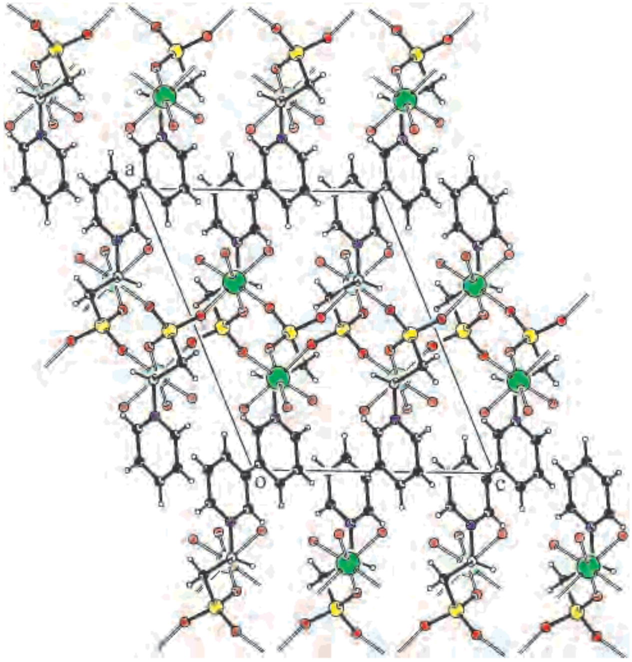

Figure 3. Structure of Zr(PYR) as viewed down the *b*-axis showing the organic ligands in relation to the inorganic layers.

The interesting $[Zr(O_3P-)_3F_3]^-$ octahedra that are part of the inorganic layer are formally negatively charged and serve as the counterions to the organic cationic pyridinium groups. In this regard, the structure of Zr(PYR) is reminiscent to that of a zirconium viologen diphosphonate ($Zr_2(O_3PCH_2CH_2$−bipyridinium−$CH_2CH_2PO_3)F_6 \cdot 2H_2O$).[10] The zirconium viologen diphosphonate also contains the unusual Zr/P/F ratio of 1:1:3 and a cationic organic group as well as the interesting $[Zr(O_3P-)_3F_3]^-$ octahedra. However, the Zr(PYR) differs significantly from the zirconium viologen diphosphonate compound in the manner in which the $[Zr(O_3P-)_3F_3]^-$ octahedra are arranged. The zirconium viologen diphosphonate compound has a linear chain structure where the zirconium octahedra form symmetry-related isolated double chains that are linked together by the viologen diphosphonate groups. On the other hand, Zr(PYR) has a true layered

---

(14) *N*-Ethylphosphonatopyridinium chloride (0.8 mmol), zirconyl(IV)-chloride octahydrate (Acros, 0.8 mmol), hydrofluoric acid (Baker, 21 mmol), and distilled water (14 mL) were placed in a 100 mL round-bottom boiling flask. The solution was mixed and was allowed to age under ambient conditions for several months, resulting in the formation of single crystals. FTIR KBr (cm^{-1}) 3431, 3138, 3096, 1635, 1488, 1170, 1070, 818, 783, 679, 558, 501. ^{31}P MAS NMR (ppm) 5.18.

(15) Crystallographic data for $(Zr(O_3PCH_2CH_2NC_5H_5)(F^-)_3$: $M = 334.34$, monoclinic, $P2_1/c$ (No. 14), $a = 12.3634(12)$ Å, $b = 9.3090(17)$ Å, $c = 9.8077(13)$ Å, $\beta = 112.819(8)°$, $V = 1040.4(3)$ Å^3, $Z = 4$, $T = 23$ °C, $\lambda = 0.71069$ Å, $D_{calcd} = 2.134$ g cm^{-3}, $m = 0.1245$ cm^{-1}, refinement on F^2, $R[F^2 > 2\sigma(F^2)] = 0.021$, $R_w(F^2) = 0.051$.

structure where the $[Zr(O_3P-)_3F_3]^-$ octahedra form an infinite two-dimensional inorganic sheet (Figure 1).

There have been only a few zirconium phosphonates prepared that form structures different from the α or γ structure.[8,10,12] These new structures seem to occur when the organic pendant group is either too large to fit into the 24 Å^2 space available in the α structure or when the pendant group is charged and electrostatic interactions become important. This observation demonstrates the structure-directing influence of some organic ligands on the zirconium phosphonate framework. Interestingly, it has been observed that when an additional phosphonate or phosphate is added to the reaction mixture with these particular structure-directing phosphonates, interesting new porous phases can result.[6,7,16] Some of these new phases are crystalline and have well-defined pore sizes and shapes making them reminiscent of zeolites for their potential use in catalysis and separations.[6]

A useful feature of this new zirconium phosphonate concerns the presence of the fluoride ligand that is bonded to zirconium. Because the fluoride ligand is more labile than the phosphonate ligand, zirconium phosphonates with fluoride ligands are reactive toward substitution reactions.[8,12,17] The potential therefore exists to utilize these types of compounds as precursors to other more stable structures that may not be obtainable by the conventional synthetic methods.

In conclusion, the structure reported here reveals a new type of zirconium phosphonate where zirconium octahedra containing fluoride ligands and phosphonate tetrahedra form infinite two-dimensional sheets. The new structure is a further demonstration of the structure-directing properties of organic ligands on the zirconium phosphonate framework. Further work on the exploitation of these new structural features to design materials for use in separations and catalysis is continuing.

Acknowledgment. The authors gratefully acknowledge the Petroleum Research Fund administered by the American Chemical Society and the SIUC Materials Technology Center for support of this work. R.Z.F. acknowledges the Illinois Consortium for Educational Opportunities for a minority student fellowship.

Supporting Information Available: Additional figure and crystallographic data for $Zr(O_3PCH_2CH_2NC_5H_5)(F^-)_3$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC015614Z

---

(16) Vermeulen, L. A.; Thompson, M. E. *Chem. Mater.* **1994**, *6*, 77.
(17) Vermeulen, L. A.; Burgmeyer, S. J. *J. Solid State. Chem.* **1999**, *147*, 520.