

complex **6** was isolated from preparative-scale reactions between equimolar amounts of reactants at 20 °C. It is intensely soluble in hexane (ca. 1 g/mL), from which it can be crystallized at -80 °C. Tellurolysis of the remaining methyl group with a second equivalent of the tellurol is slow at room temperature, but on warming to 50 °C for 3 h, the maroon bis-tellurolate **7** is produced in high yield.

We are now probing the reactivity of these compounds and attempting to extend the tellurolysis approach to a wider variety of main-group and transition-metal tellurolates.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and the Department of Education for a fellowship (to P.J.B.).

**Supplementary Material Available:** Spectroscopic and analytical data for new compounds (1 page). Ordering information is given on any current masthead page.

### Synthesis and Crystal Structure of a Spherical Polyoxyvanadium Organophosphonate Anion: $[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8]^{4-}$

G. Huan,<sup>\*1a</sup> V. W. Day,<sup>1b</sup> A. J. Jacobson,<sup>1a</sup> and D. P. Goshorn<sup>1a</sup>

*Exxon Research & Engineering Company  
Annandale, New Jersey 08801  
Crystallitics Company, Lincoln, Nebraska 68501*

*Received December 10, 1990*

Several polyoxovanadates have recently been shown to form inclusion compounds with neutral molecules, for example,  $[\text{V}_{12}\text{O}_{36}(\text{CH}_3\text{CN})]^{4-}$ ,<sup>2</sup>  $[\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})]^{12-}$ ,<sup>3</sup>  $[\text{As}_6\text{V}_{15}\text{O}_{42}(\text{H}_2\text{O})]^{6-}$ ,<sup>4</sup> and  $[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ ,<sup>5</sup> and with anions in  $[\text{H}_9\text{V}_{18}\text{O}_{42}(\text{VO}_4)]^{6-}$ ,  $[\text{V}_{18}\text{O}_{42}(\text{SO}_4)]^{8-}$ ,  $[\text{H}_4\text{V}_{18}\text{O}_{42}(\text{X})]^{9-}$  (X = Cl, Br, I), and  $[\text{V}_{15}\text{O}_{36}(\text{Y})]^{6-}$  (Y = Cl, Br, CO<sub>3</sub>).<sup>6-8</sup> In one case,  $[\text{V}_{12}\text{O}_{36}(\text{CH}_3\text{CN})]^{4-}$ ,<sup>2</sup> the inclusion process is reversible, and consequently this compound can be considered a molecular analogue of the microporous oxides. Very recently, a vanadium organophosphonate anion,  $[\text{H}_6(\text{VO}_2)_{16}(\text{CH}_3\text{PO}_3)_8]^{8-}$ , which includes a tetramethylammonium cation, has been reported.<sup>9</sup> In this communication, the synthesis and structure of a new vanadium organophosphonate,  $[\text{N}(\text{C}_3\text{H}_7)_4]_4[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8] \cdot 1.48\text{H}_2\text{O}$  (**1**), containing a large spherical anion,  $[\text{V}_{12}\text{P}_8\text{O}_{48}]$ , analogous to the  $[\text{V}_{18}\text{O}_{42}]$  systems is described.

Blue, parallelepiped crystals of **1** were prepared in ~70% yield by hydrothermal reaction of  $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$  (0.952 g),  $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$  (0.434 g), and tetra-*n*-propylammonium hydroxide (8.2 g, 1 M in  $\text{H}_2\text{O}$ ) at 200 °C for 2 days.<sup>10</sup>

(1) (a) Exxon Research & Engineering Company. (b) Crystallitics Company.

(2) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959.

(3) Johnson, G. K.; Schlemper, E. O. *J. Am. Chem. Soc.* **1978**, *100*, 3645.

(4) Müller, A.; Döring, J. *Angew. Chem.* **1988**, *100*, 1789; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1721.

(5) Huan, G.; Greaney, M. A.; Jacobson, A. J. *J. Chem. Soc., Chem Commun.*, in press.

(6) Müller, A.; Döring, J.; Bögge, H.; Krickmeyer, E. *Chimia* **1988**, *42*, 300.

(7) Müller, A.; Krickmeyer, E.; Penk, M.; Walberg, H.-J.; Bögge, H. *Angew. Chem.* **1987**, *99*, 1060; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1045.

(8) Müller, A.; Penk, M.; Rohlfing, R.; Krickmeyer, E.; Döring, J. *Angew. Chem.* **1990**, *102*, 927; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 926.

(9) Huan, G.; Jacobson, A. J.; Day, V. W. *Angew. Chem.*, in press.

X-ray structural analysis<sup>11</sup> of **1** revealed the presence of discrete  $\text{TPA}^+$  (tetra-*n*-propylammonium) cations and disordered water molecules of crystallization in the lattice and inside the two crystallographically independent  $[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8]^{4-}$  anions per asymmetric unit (Figure 1). Each anion possesses rigorous crystallographic  $C_{7-}$  symmetry and consists of six condensed vanadium-oxygen dimers covalently connected by eight  $\text{PO}_3\text{C}$  tetrahedra through corner-sharing oxygen atoms. Vanadium atoms are square-pyramidally coordinated by one doubly bonded terminal oxygen atom, two doubly bridging V-(OH)-V hydroxyl oxygens, and two doubly bridging V-O-P oxygen atoms. Each  $\text{VO}_5$  unit shares one of its edges to form an  $\text{O}_2\text{-VO-(OH)}_2\text{-V-O-O}_2$  dimer, and each  $\text{C}_6\text{H}_5\text{PO}_3$  unit is bonded to three vanadium oxygen dimers. The protons of each dimer are positioned favorably to form hydrogen bonds which stabilize the anion structure (Figure 1). The phenyl groups, as well as the terminal (vanadyl) oxygen atoms, protrude from the surface of the "ball" forming a hydrophobic shell. Disordered water molecules were found at four partial occupancy (0.13-0.15) sites inside each anion. Each of these water molecules ( $\text{O}_{3w}$ ,  $\text{O}_{4w}$ ,  $\text{O}_{5w}$ , and  $\text{O}_{6w}$ ) appears to be weakly coordinated to the vanadium atoms of a  $\text{O}_2\text{-VO-(O-H)}_2\text{-VO-O}_2$  dimer at bridging sites as shown in Figure 2. The V-O distances and V-O-V angles for these water molecules have ranges of 2.85 (6)-3.37 (6) Å and 57 (6)-60 (6)°, respectively, and the O=V-O(water) angles range from 162 (1)° to 178 (1)°. Since the  $\text{O}_{3w}\cdots\text{O}_{4w}$  and  $\text{O}_{5w}\cdots\text{O}_{6w}$  distances are 2.49 and 2.53 Å, respectively, and each water molecule has a V-O(water) $\cdots$ O(water) angle in the range 102-123°, the included water molecules may exist as hydrogen-bonded and weakly complexed pairs. The 12 vanadium and eight phosphorus atoms of each anion are located at the vertices of a pentagonal dodecahedron (Figure 2); each of its 12 faces is a distorted pentagon consisting of three vanadium atoms and two phosphorus atoms. The V $\cdots$ V and P $\cdots$ V separations have ranges of 3.082 (2)-3.106 (1) Å and 3.295 (2)-3.352 (1) Å, respectively.

Magnetic susceptibility data of **1** measured from 7 to 300 K show a broad maximum at 50 K indicating antiferromagnetic exchange interactions between the  $\text{d}^1$  V(IV) ions in the dimers. Similar behavior is observed for the layered compounds  $\text{VO-(HPO}_4)_0.5\text{H}_2\text{O}$ ,  $(\text{VO})_2\text{P}_2\text{O}_7$ ,  $\text{VOSeO}_3\text{H}_2\text{O}$ , and  $\text{VOSeO}_3$ ,<sup>12-15</sup> which contain similar structural units.

The  $[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8]^{4-}$  cage is a new type of spherical anion structure which resembles the previously reported  $[\text{V}_{18}\text{O}_{42}]$  systems in having sufficient internal volume for the inclusion of

(10) Anal. Calcd for  $\text{C}_{96}\text{H}_{167}\text{N}_8\text{V}_{12}\text{P}_8\text{O}_{49.5}$ : C, 38.08; H, 5.56; N, 1.85; V, 20.19; P, 8.18. Found: C, 37.81; H, 5.47; N, 1.80; V, 20.21; P, 8.52. **1** is only slightly soluble in water but dissolves in mineral acids. Redox titration of **1** in sulfuric acid solution gave an average vanadium oxidation state of  $4.00 \pm 0.02$ . IR (solid/KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 1130 (vs), 1110 (vs), 1030 (vs), 1010 (vs), 990 (vs), 905 (s), 755 (m), 715 (s), 690 (s), 590 (m), 540 (s), 510 (s).

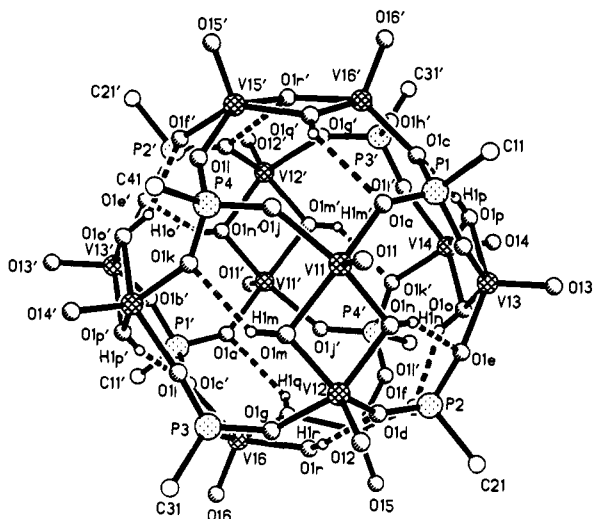
(11) **1**: triclinic, space group  $P\bar{1}$  (No. 2) with  $a = 16.038$  (3) Å,  $b = 16.782$  (3) Å,  $c = 29.345$  (5) Å,  $\alpha = 86.04$  (2)°,  $\beta = 82.45$  (2)°,  $\gamma = 63.41$  (2)°,  $V = 7002$  (2) Å<sup>3</sup>, and  $Z = 2$  ( $d_{\text{calc}} = 1.436$  g  $\text{cm}^{-3}$ ;  $\mu_{\text{Mo K}\alpha} = 0.90$   $\text{mm}^{-1}$ ). A total of 19 255 independent reflections having  $2\theta < 45.8^\circ$  were collected on a Nicolet autodiffractometer using  $\omega$  scans and graphite-monochromated Mo K $\alpha$  radiation. The structure was solved by using SHELXTL-Plus direct method techniques, and the resulting structural parameters have been refined by using counterweighted block-diagonal least-squares techniques to  $R_1$  (unweighted, based on  $F$ ) = 0.053 and  $R_2$  (weighted, based on  $F$ ) = 0.066 for 11 988 independent reflections having  $2\theta < 45.8^\circ$  and  $I > 3\sigma(I)$ . These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms (except  $\text{C}_{4a1}\text{-C}_{4b4}$  and  $\text{O}_{2w}\text{-O}_{6w}$ , which were isotropically refined) and isotropic thermal parameters for all anion hydrogen atoms. Hydroxyl hydrogen atoms  $\text{H}_{1m}\text{-H}_{1r}$  and  $\text{H}_{2m}\text{-H}_{2r}$  on anions 1 and 2 were located from a difference Fourier map and refined as independent isotropic atoms. The remaining (phenyl) hydrogen atoms on the anions were fixed at idealized  $\text{sp}^2$ -hybridized positions.

(12) (a) Leonowicz, M. E.; Johnson, J. W.; Shannon, H. F., Jr.; Brody, J. F.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370. (b) Torardi, C. C.; Calabrese, J. C. *Inorg. Chem.* **1984**, *23*, 1308.

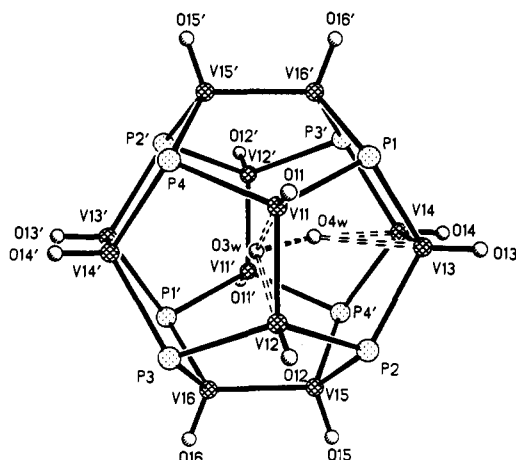
(13) Johnston, D. C.; Johnson, J. W.; Goshorn, D. P.; Jacobson, A. J. *J. Phys. Rev. B* **1987**, *35*, 219.

(14) Huan, G.; Johnson, J. W.; Jacobson, A. J.; Goshorn, D. P.; Merola, J. S. *Chem. Mater.*, in press.

(15) (a) Trombe, J.-C.; Gleizes, A.; Galy, J. C. *R. Seances Acad. Sci. Ser. II* **1983**, *297*, 667. (b) Trombe, J.-C.; Gleizes, A.; Galy, J.; Renard, J.-P.; Journaux, Y.; Verdager, M. *Nouv. J. Chim.* **1987**, *11*, 321.



**Figure 1.** Perspective plot of one of the two crystallographically independent  $[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8]^{4-}$  anions in **1** with the phenyl groups omitted for clarity. Hydrogen bonds are represented by dashed lines. Atoms labeled with a prime are related to nonprimed atoms by the crystallographic inversion center. Bond distances ( $\text{\AA}$ ) and angles (deg) of interest: V-V, 3.082 (2)-3.106 (1); V-O<sub>term</sub>, 1.568 (6)-1.590 (7); V-( $\mu_2$ -O(H)), 1.936 (6)-1.980 (6); V-( $\mu_2$ -O), 1.942 (5)-1.986 (4); O<sub>term</sub>-V-( $\mu_2$ -O(H)), 105.7 (2)-110.7 (2); O<sub>term</sub>-V-( $\mu_2$ -O), 103.6 (2)-108.9 (3); ( $\mu_2$ -O)-V-( $\mu_2$ -O), 74.4 (2)-76.1 (2); ( $\mu_2$ -O)-V-( $\mu_2$ -O(H)), 89.5 (2)-92.4 (2) and 140.7 (2)-150.5 (2); ( $\mu_2$ -O)-V-( $\mu_2$ -O(H)), 82.9 (2)-84.3 (2).



**Figure 2.** A drawing of the dodecahedral arrangement of the 12 vanadium and eight phosphorus atoms in the  $[\text{H}_{12}(\text{VO}_2)_{12}(\text{C}_6\text{H}_5\text{PO}_3)_8]^{4-}$  anion of Figure 1. The terminally bonded oxygen on each vanadium is also shown as is one pair of included and weakly complexed water molecules ( $\text{O}_{3w}$  and  $\text{O}_{4w}$ ).

water molecules during synthesis. However, the presence of additional atoms in the  $\{\text{V}_{12}\text{P}_8\text{O}_{48}\}$  sphere results in a larger central diameter and consequently a greater free volume. The average distance from the center of the sphere to an oxygen atom is 4.4  $\text{\AA}$  compared to the value of 3.675  $\text{\AA}$  observed in  $[\text{H}_4\text{V}_{18}\text{O}_{42}(\text{X})^9]^{9-}$  ( $\text{X} = \text{Br}, \text{I}$ ), suggesting that the inclusion of still larger molecules or ions by the vanadium organophosphonate structure may be possible.

**Supplementary Material Available:** Crystal structure analysis report including Tables I-VIII containing atomic coordinates for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for anion hydrogen atoms, bond lengths and angles for the anion and cation non-hydrogen atoms, and close contacts involving hydrogen atoms for compound **1** (38 pages); table of observed and calculated structure factors for compound **1** (43 pages). Ordering information is given on any current masthead page.

## Preparation of Molecular Sieves from Dense, Layered Metal Oxides

M. E. Landis,\* B. A. Aufdembrink, P. Chu, I. D. Johnson, G. W. Kirker, and M. K. Rubin

Mobil Research and Development Corporation  
Paulsboro Research Laboratory, P.O. Box 480  
Paulsboro, New Jersey 08066-0480

Received November 19, 1990

We now report a novel pillaring procedure to convert dense, layered metal oxides and silicates into high surface area molecular sieves with large interlayer separations. The procedure is applicable to a wide variety of layered phases and allows for the engineering of microporous materials with diverse compositions and physical properties.

Over the past three decades, zeolite catalysis has had a dramatic impact upon petroleum refining and petrochemical processing.<sup>1</sup> Catalytic differences among zeolites are typically manifested by differences in product distributions as a consequence of unique zeolite channel or pore size and their framework aluminum content. To exploit the selectivity differences possible with different pore geometries and catalyst compositions, other classes of molecular sieves have been prepared which include aluminum phosphates ( $\text{AlPO}_4$ )<sup>2,3</sup> and silica- and metal-modified  $\text{AlPO}_4$ s such as SAPOs<sup>4</sup> and MeAPOs.<sup>5</sup> Pillared or intercalated clays,<sup>6</sup> layered phosphates,<sup>7</sup> and a layered tetratitanate<sup>8</sup> are other classes of molecular sieves. Historically, these have been synthesized by incorporating cationic precursors to stable metal oxide pillars.<sup>6</sup> The pore sizes of these pillared materials are determined by the size of the exchanging cation and are typically in the 8-9- $\text{\AA}$  range.<sup>6,7</sup>

The pillaring procedures developed for smectite clays are not generally applicable to the wide variety of laminar metal oxides that do not spontaneously delaminate in water. To tailor-make materials with varied but controllable pore sizes from metal oxides with unique chemistries, a new synthetic approach was created.

We found that pillaring could be facilitated by utilizing a preswelling step in which the interlayer is exposed to organoammonium ions. According to procedures developed earlier, layered metal oxides<sup>9</sup> and silicates<sup>10</sup> were first intercalated with an aqueous solution of long-chain organoammonium salt or amine. An organic pillar precursor, such as tetraethyl orthosilicate (TEOS), was then absorbed into the organophilic interlayer region, where it was converted to a metal oxide pillar. Typically, the organoammonium ion exchanged product was stirred with excess TEOS for 1-3 days at 25-80  $^\circ\text{C}$ , filtered, and dried. The final microporous material was produced by calcination for several hours in air at 538  $^\circ\text{C}$ , which removes the water, preswelling organoammonium ion, and organic byproducts from TEOS hydrolysis, affording a silica-pillared product. Using this procedure, we have prepared porous products from a wide variety of layered oxides, including alkali titanates,<sup>11</sup> alkali metal-substituted titanates

(1) (a) Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *Chem. Technol.* **1976**, *86*, 6. (b) Chen, N. Y.; Goring, R. L.; Ireland, H. R.; Stein, T. R. *Oil Gas J.* **1977**, *75*, 165.

(2) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *105*, 1146.

(3) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Nature* **1988**, *331*, 698.

(4) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6092.

(5) Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. *Stud. Surf. Sci. Catal.* **1986**, *28*, 103.

(6) (a) Pinnavaia, T. J. *Science* **1983**, *220*, 365. (b) Vaughan, D. E. W.; Lussier, R. J. In *Proceedings of the 5th International Conference on Zeolites*; Rees, L. V. C., Ed.; Hyden: London, 1980; p 94. (c) Vaughan, D. E. W. *ACS Symp. Ser.* **1988**, *368*, 308.

(7) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237.

(8) Cheng, S.; Wang, T.-C. *Inorg. Chem.* **1989**, *28*, 1283.

(9) Weiss, A. *Angew. Chem.* **1960**, 413.

(10) (a) Lagaly, G.; Beneke, K.; Weiss, A. *Am. Mineral.* **1975**, *60*, 650. (b) Beneke, K.; Lagaly, G. *Am. Mineral.* **1983**, *68*, 818.