Inorg. Chem. **1995**, *34*, 2629−2638 **2629**

Phosphatovanadium Chemistry: New Compounds, Including an Example of "Tenne's Prospect", and Oxidation of Cyclohexadiene

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Received October 7, 1994⊗

Reactions of various vanadyl (V^V) compounds with silyl phosphato, phosphonato, or alkyl phosphato compounds have provided the cluster compounds $(VO)_6(O_3POSiMe_3)_8Cl$ (**1**), $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ (**2**), and the methylphosphonato and butyl phosphato analogues of compound **2**. Both compounds **1** and **2** oxidize 1,4-cyclohexadiene to benzene, and the reduction product of the methylphosphonato analogue of compound **2** has been characterized as $[Et_4P]^+_{1.5}$ [(4-*tert*-butylpyridine)$_2$H]$^+_{0.5}$ $[(V_2O_3)_2(MePO_3)_4F]^{2-}$ (**3**). In the mixed-valence compounds **1** and **3** the odd electron is determined by EPR spectroscopy to be localized on a single VO unit in compound **1** and delocalized in compound **3**. Compound **1** crystallizes in the tetragonal space group *I*4/*m* with cell constants (at −100 °C) $a = b = 13.788(2)$ Å, $c = 19.126(3)$ Å, $V = 3636(1)$ Å^3, $Z = 2$; compound **2** crystallizes in the triclinic space group $P\bar{1}$ with cell constants (at −70 °C) $a = 12.541(5)$ Å, $b = 13.177(4)$ Å, $c = 14.761(5)$ Å, $\alpha = 83.26(4)°$, $\beta = 68.91(4)°$, $\gamma = 72.23(3)°$, $V = 2167(1)$ Å^3, $Z = 2$; compound **3** crystallizes in the orthorhombic space group *Iba*2 with cell constants (at −100 °C) $a = 17.462(3)$ Å, $b = 33.787(6)$ Å, $c = 14.623(2)$ Å, $V = 8627(2)$ Å^3, $Z = 8$. Features common to all compounds are the encapsulated halide ion and the role played by the phosph(on)ato moieties: by allowing only three oxygen atoms per phosphorus to participate in cluster bonding, the phosphorus centers become sites of positive Gaussian curvature and support closure into polyhedral structures. Compound **1** realizes "Tenne's prospect" of expressing a layered structure, in this case α-$VOPO_4$, in closed polyhedral form.

Introduction

Vanadium oxides have been used in organic oxidation reactions for many years. Recently phosphatovanadium oxides have become especially important in the commercial oxidation of butane to maleic anhydride.[1] Thus there are a great many studies of the heterogeneous catalytic oxidation chemistry, focused on the vanadyl pyrophosphate material $(VO)_2P_2O_7$ ("VPO") .[2] Even so, at the atomic/molecular level the actual mechanism(s) and intermediate species involved are incompletely understood. We have been studying the coordination chemistry of phosphatovanadium compounds in an effort to help decipher both (a) the structural and mechanistic patterns that are important in assembling phosphatovanadium structures[3] and (b) the structural aspects that may be important in the subsequent ability of phosphatovanadium compounds to selectively oxidize organic substrates.[4]

Phosphoric acid itself reacts with many vanadium compounds to make extended solid-state structures that are essentially insoluble (except for partial hydrolysis). Thus to make stable molecular/cluster "phosphatovanadium" compounds that survive intact upon dissolution in organic solvents, we, like other researchers,[3] have used organophosphorus compounds (organophosphates, organophosphonates) in our studies. Of course, the use of such organo-derivatized phosphorus(V) species introduces connectivity and topological features that differ intrinsically from those of the "purely inorganic" phosphato group; this enables the expression of layered motifs in closed polyhedral forms, a possibility recently raised by Tenne et al.[5] and a point to which we return in the Discussion. But first we describe reactions of tris(trimethylsilyl) phosphate ($(Me_3SiO)_3P{=}O$), methyl- and phenylphosphonic acid ($\{Me,Ph\}$-$P({=}O)(OH)_2$), and *n*-butyl phosphate (*n*-$BuOP{=}O(OH)_2$) which respectively have three, two and two *potentially* reactive PO−X groups (X = H, $SiMe_3$),[6] with commercially-available vanadium(V) compounds. We have used vanadium(V) starting materials since we are concerned here with obtaining phos-

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† Contribution No. 6990.

⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1995.

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(2) See, for example: Pepera, M. A.; Callahan, J. L.; Desmond, M. J.; Milberger, E. C.; Blum, P. R.; Bremer, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 4883−4892. Busca, G.; Centi, G. *J. Am. Chem. Soc.* **1989**, *111*, 46−54. Schiott, B.; Jorgensen, K. A.; Hoffmann, R. *J. Phys. Chem.* **1991**, *95*, 2297−2307.

(3) Some delightful phosphato- or arsenatovanadium cluster compounds and extended inorganic solids are already available in the literature. In addition to the articles specifically cited in later footnotes, see: Huan, G.; Jacobson, A. J.; Day, V. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 422-423. Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 261−263. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, *J. Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610−611. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596−1599. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J.; Lee, Y.-S. *Chem. Mater.* **1995**, *3*, 1690−1691. Mokry, L. M.; Thompson, J.; Bond, M. R.; Otiento, T.; Mohan, M.; Carrano, C. J. *Inorg. Chem.* **1994**, *33*, 2705−2706. Salta, J.; Chang, Y.-D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1039−1040. An overview of "inorganic" phosphatovanadium compounds is provided by: Beltran-Porter, D.; Beltran-Porter, A.; Amoros, P.; Ibanyez, R.; Martinez, E.; Le Bail, A.; Ferey, G.; Villeneuve, G. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 131−161.

(4) Isopolyvanadates, heteropolyvanadates, and heteropolymetallates in general are known as useful oxidants (see e.g.: Pope, M. T.; Müller, A. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34−48). How closely these oxidation reactions may be related to "butox" remains to be determined.

(5) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444−446; Tenne, R.; Margulis, L.; Hodes, G. *Adv. Mater.* **1993**, *5*, 386−388.

(6) We will describe elsewhere compounds and reactions of phosphorus compounds having one reactive PO−X group: Harlow, R. L.; Herron, N.; Thorn, D. L. To be submitted for publication.

0020-1669/95/1334-2629$09.00/0

Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
chem formula	$[(Me_3SiOPO_3)_8(VO)_6Cl]$	$[Et_4P][(V_2O_3)_2(O_3PPh)_4F]$	$[Et_4P]_{1.5}[(C_9H_{13}N)_2H]_{0.5}[(V_2O_3)_2(O_3PMe)_4F]$
fw	1782.41	1090.28	1051.32
space group	*I*4/*m*	$P\bar{1}$	*Iba*2
a, Å	13.788(2)	12.541(5)	17.462(3)
b, Å		13.177(4)	33.787(6)
c, Å	19.126(3)	14.761(5)	14.623(2)
α, deg		83.26(4)	
β, deg		68.91(4)	
γ, deg		72.23(3)	
V, Å^3	3636(1)	2167(1)	8627(2)
μ(Mo Kα), cm^{-1}	11.35	10.64	10.84
T, °C	−100	−70	−100
Z	2	2	8
R[a]	0.042	0.047	0.042
R_w[a]	0.044	0.044	0.037

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

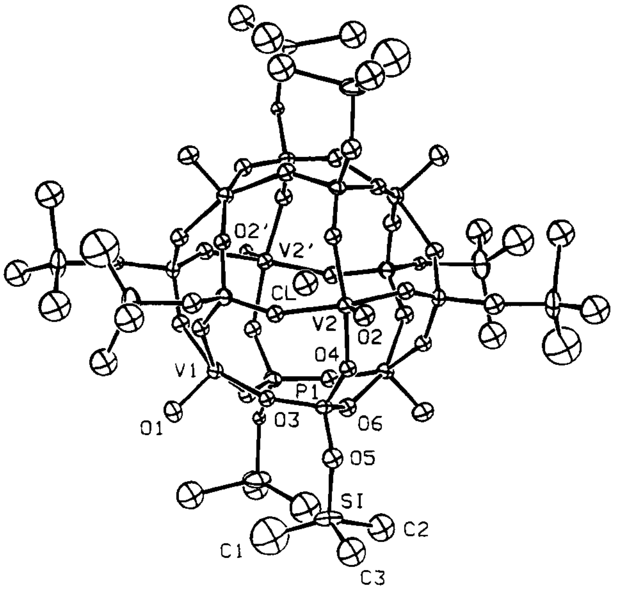

Figure 1. One component of disordered $(VO)_6(O_3POSiMe_3)_8Cl$, compound **1**. The crystallographic 4-fold axis passes through V2, V2′, Cl, O2, and O2′.

Table 2. Selected Interatomic Distances (A) for Compound **1**, $(VO)_6(O_3POSiMe_3)_8Cl$, with Estimated Standard Deviations in Parentheses

V(1)−O(1)	1.569(3)	P(1)−O(4)	1.477(4)
V(1)−O(3)	1.833(4)	P(1)−O(4′)	1.568(4)
V(1)−O(3′)	1.941(5)	P(1)−O(5)	1.545(2)
V(1)−O(6)[a]	1.850(4)	P(1)−O(6)	1.577(4)
V(1)−O(6′)[a]	1.947(4)	P(1)−O(6′)	1.494(4)
V(2)−O(2)	1.568(5)	Si(1)−O(5)	1.666(2)
V(2)−O(4)	1.889(4)		
V(2)−O(4′)	1.859(4)	O(3)−O(3′)	0.558(5)
P(1)−O(3)	1.547(4)	O(4)−O(4′)	0.663(5)
P(1)−O(3′)	1.470(5)	O(6)−O(6′)	0.770(5)

[a] 1 − y, x, z.

Table 3. Selected Intramolecular Angles (deg) for Compound **1**, $(VO)_6(O_3POSiMe_3)_8Cl$, with Estimated Standard Deviations in Parentheses

O(1)−V1)−O(3)	101.3(1)	O(3)−P(1)−O(3′)	21.1(2)
O(1)−V(1)−O(3′)	100.6(2)	O(3)−P(1)−O(4)	112.5(3)
O(1)−V(1)−O(6)[a]	101.5(2)	O(3)−P(1)−O(5)	109.1(2)
O(1)−V(1)−O(6′)[a]	100.7(1)	O(3)−P(1)−O(6)	106.3(3)
O(3)−V(1)−O(3)[b]	103.8(3)	O(3′)−P(1)−O(4′)	112.7(3)
O(3)−V(1)−O(3′)[b]	87.7(3)	O(3′)−P(1)−O(5)	107.2(2)
O(3)−V(1)−O(3′)	16.7(2)	O(3′)−P(1)−O(6′)	115.7(3)
O(3′)−V(1)−O(6′)[a]	85.6(2)	O(4)−P(1)−O(4′)	24.9(2)
O(6)a−V(1)−O(6′)[c]	86.6(2)	O(4)−P(1)−O(5)	107.9(2)
O(6)a−V(1)−O(6′)[a]	23.2(2)	O(4)−P(1)−O(6)	111.0(2)
O(2)−V(2)−O(4)	103.4(1)	O(4′)−P(1)−O(5)	103.2(2)
O(2)−V(2)−O(4′)	98.6(1)	O(4′)−P(1)−O(6′)	110.7(2)
O(4)−V(2)−O(4)[a]	86.9(1)	O(5)−P(1)−O(6)	110.1(2)
O(4)−V(2)−O(4′)	20.4(2)	O(5)−P(1)−O(6′)	106.4(2)
O(4′)−V(2)−O(4′)[a]	88.7(1)	O(6)−P(1)−O(6′)	28.9(2)
V(1)−O(3)−P(1)	149.5(3)	P(1)−O(5)−Si(1)	139.4(2)
V(1)−O(3′)−P(1)	145.6(3)		
V(2)−O(4)−P(1)	149.9(3)		
V(2)−O(4′)−P(1)	143.1(3)		
V(1)c−O(6)−P(1)	144.4(3)		
V(1)c−O(6′)−P(1)	142.8(3)		

[a] 1 − y, x, z. [b] x,y,1-z. [c] 1-y,x,1-z.

phatovanadium(V) compounds that may exhibit oxidation chemistry; with this in mind we also describe oxidation of 1,4-cyclohexadiene by the product compounds.

Results

Tris(trimethylsilyl) Phosphate. The reaction between tris(trimethylsilyl) phosphate ($(Me_3SiO)_3P{=}O$) and $VOCl_3$ in acetonitrile at room temperature is complex; the solution darkens rapidly upon combining the reagents, presumably with partial elimination of $ClSiMe_3$, but the extent of the initial reaction has not been determined. Warming the solution to 70−80 °C results in precipitation of dark green octahedral crystals, in yields up to ca. 60% after several hours. The dark green crystalline product may be sublimed in vacuo, without decomposition, at 300 °C. The nature of this product, compound **1**, was established by a single-crystal X-ray structure determination, which demonstrated that compound **1** has the composition $(VO)_6(O_3POSiMe_3)_8Cl$ and the molecular structure illustrated in Figure 1. Crystallographic data for compound **1** are included in Table 1, and selected interatomic distances and angles are provided in Tables 2 and 3. Given the composition of compound **1**, five of the vanadium centers are in the +5 oxidation state and one is in the +4 oxidation state. In the crystal, molecules of compound **1** sit on sites of 4/*m* symmetry thus having no unique vanadium sites to which to assign the odd electron, but the EPR spectrum of compound **1** in pyridine solution is fully consistent with the odd electron being confined to a single vanadyl center on the timescale of the ESR experiment, at temperatures up to ca. 100 °C (8-line spectrum at g ∼ 2.00 and with J_V = ∼102 G). We have not identified what species is oxidized concomitant with formation of the vanadium(IV) center but we suspect the formation of chloro-derivatives of acetonitrile or silyl groups.

The structure of compound **1** can be described as a cube, with a vanadyl group centered on each cube face, a Me_3SiOPO_3 group on each corner, and a chloride at the cube center.[7] Ideally the compound has rigorous O_h symmetry (Figure 2a). In the crystal lattice each molecule sits on a site of 4/*m* (C_{4h}) symmetry,

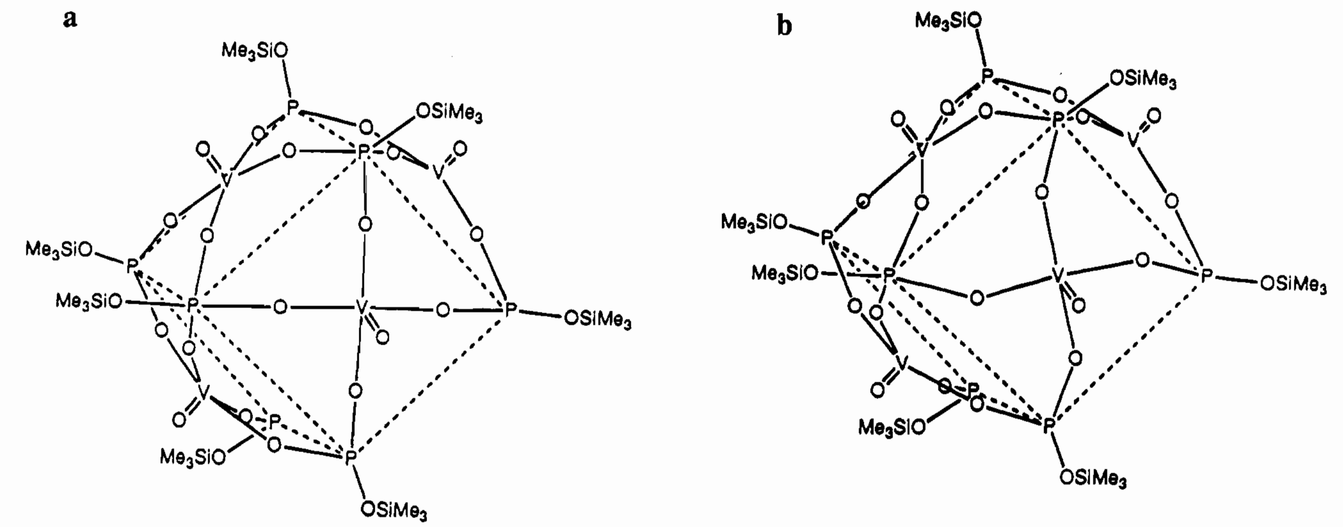

Figure 2. (a) Idealized representation of compound **1**. O_h symmetry has been imposed. Dashed lines outline the underlying cubic "framework" of the cluster. The central chloride has been omitted for clarity. (b) More realistic representation of compound **1**. Imposed symmetry is relaxed to O to illustrate the correlated "geared" rotation of the phosphato groups. The central chloride ion has been omitted for clarity.

but the true molecular symmetry is lower as the X-ray diffraction data reveals disordering of the cluster phosphato oxygen atoms and of the trimethylsilyl methyl groups. Our model for the disorder of the cluster phosphato oxygen atoms puts two oxygen atoms, each half-occupancy, at each of the three crystallographically-independent bridging sites, separated respectively by 0.56, 0.66, and 0.77 Å (Table 2). Physically this disordering corresponds to a correlated ("geared") rotation of each phosphato group of approximately 12−13° about the C_3 cube axes accompanied by rotation of each vanadyl square pyramid by approximately 10 degrees about the C_4 cube axes. The resulting structure (Figure 2b) ideally has O symmetry. Depending on the sense of this correlated rotation, either of two enantiomers results, and the observed structure is a superposition of the two enantiomers although in Figures 1 and 2b we artificially portray only one. A consequence of this disorder is that refined V−O(phosphato) and O(cluster)−P bond lengths are subject to large errors, possibly even greater than indicated by the estimated standard deviations included in Table 2. However, the shorter V−O_P bond lengths are consistent with values reported for other vanadyl V(+5)−O_P compounds (1.858(7) Å in α-$VOPO_4$;[8] 1.849(4), 1.866(4) Å in $[V_2O_4(CH_3C_6H_4CH_2PO_3)_2]^{2-}$;[9] 1.848(9)−1.863(8) Å in $(VO)_6(O_3P^tBu)_8Cl$[7]). Terminal V=O bond lengths are normal.[10] The role of the central chloride ion, in particular whether it serves as a crucial template for the assembly of the cluster compound **1** or as a convenient filler for an otherwise empty hole, is not determined, although we note precedents for such centrally-located anions in other vanadate structures.[7,11,12] The V- - -Cl separations in compound **1** (3.388(1), 3.369(1) Å) greatly exceed normal V−Cl bond lengths (e.g. 2.288(4) Å[9]).

Methyl- and Phenylphosphonic Acids. We note that in the formation of compound **1**, each reacting tris(trimethylsilyl) phosphate molecule loses only two $SiMe_3$ groups and only three phosphato-oxygen atoms participate in cluster bonding. A similar structural role can be played by alkyl- or arylphosphonato species and indeed there are ample precedents in the literature. In addition to the *tert*-butylphosphonato compound $(VO)_6(O_3P^tBu)_8Cl$,[7] another compound, $[(V_2O_2(OH)_2)_6(O_3PPh)_8]^{4-}$, bears a resemblance to compound **1** in that it is quasi-cubic, in this case having vanadyl dimers (hydroxyl-bridged) on each "cube" face and water in the interior.[13] We have not obtained tractible products from reactions of $VOCl_3$ with methyl- or phenylphosphonic acid, but we have obtained pure compounds from reactions of $VO(OiPr)_3$ with methyl- and phenylphosphonic acids in methanol containing added water and $cat^+AlF_4^-$ salts, a convenient source of cat^+F^-.[14] These compounds have the formula $cat^+ (V_2O_3)_2(O_3PR)_4F^-$ where R is methyl or phenyl and "cat^+" is, e.g., tetraalkylammonium or tetraalkylphosphonium. A very recent report[12] describes the preparation of an analogous tetrabutylammonium compound using HBF_4 as the fluoride source.

The structure of the phenylphosphonato compound $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ (**2**) has been determined by single-crystal X-ray diffraction. The molecular structure is illustrated in Figure 3; crystallographic data are included in Table 1, and selected interatomic distances and angles are listed in Tables 4 and 5. A detailed discussion of cluster bond distances is deferred to a later section. Compound **2** exhibits no definite disorder but the carbon atoms of the Et_4P cation suffer from

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(7) The analogous *tert*-butylphosphonato compound has been characterized by Salta, J.; Chen, Q.; Chang, Y.-D.; Zubieta, J. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 757−760.

(8) (a) Gopal, R.; Calvo, C. *J. Sol. State Chem.* **1972**, *5*, 432−435. Jordan, B. D.; Calvo, C. *Acta Crystallogr.* **1976**, *B32*, 2899−2900; *Can. J. Chem.* **1973**, *51*, 2621−2625. (b) Tietze, H. R. *Aust. J. Chem.* **1981**, *34*, 2035−2038. (c) There appear to be two different forms of "alpha"-$VOPO_4$ itself, the high-temperature form characterized by Calvo and co-workers[8a] sometimes referred to as "alpha$_{II}$-$VOPO_4$", and a form obtained by low-temperature dehydration of $VOPO_4{\cdot}2H_2O$, sometimes referred to as "alpha$_I$-$VOPO_4$" and believed to be isostructural with $VOSO_4$. In their current assignments, the structures of alpha$_I$ and alpha$_{II}$ forms are related by inversion at vanadyl sites and are otherwise topologically comparable. See: Benabdelouahab, F.; Volta, J. C.; Olier, R. *J. Catal.* **1994**, *148*, 334−340 and references therein.

(9) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485−4486.

(10) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds;* Wiley-Interscience: New York, 1988; Table 5.2.

(11) Müller, A.; Krickemeyer, E.; Penk, M.; Rohlfing, R.; Armatage, A.; Bögge, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1674−1677; Müller, A.; Penk, M.; Rohlfing, R.; Krickemeyer, E.; Döring, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 926−927; Müller, A.; Rohlfing, R.; Barra, A.-L.; Gatteschi, D. *Adv. Mater.* **1993**, *5*, 915−917; Chang, Y.-D.; Salta, J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 325−327; Kahn, M. I., Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 760−762. In addition, "bowl-shaped" polyvanadates can bind halide or solvent; see: Heinrich, D. D.; Folting, K.; Streib, W. E.; Huffman, J. C.; Christou, G. *J. Chem. Soc. Chem. Commun.* **1989**, 1411−1413. Day, V. W.; Klemper, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959−5961.

(12) Chen, Q.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2663−2664.

(13) Huan, G.; Day, V. W.; Jacobson, A. J.; Goshorn, D. P. *J. Am. Chem. Soc.* **1991**, *113*, 3188−3189. Herron, N.; Harlow, R. L.; Thorn, D. L. To be submitted for publication.

(14) Herron, N.; Thorn, D. L.; Harlow, R. L.; Davidson, F. *J. Am. Chem. Soc.* **1993**, *115*, 3028−3029. Herron, N.; Harlow, R. L.; Thorn, D. L. *Inorg. Chem.* **1993**, *32*, 2985−2986.

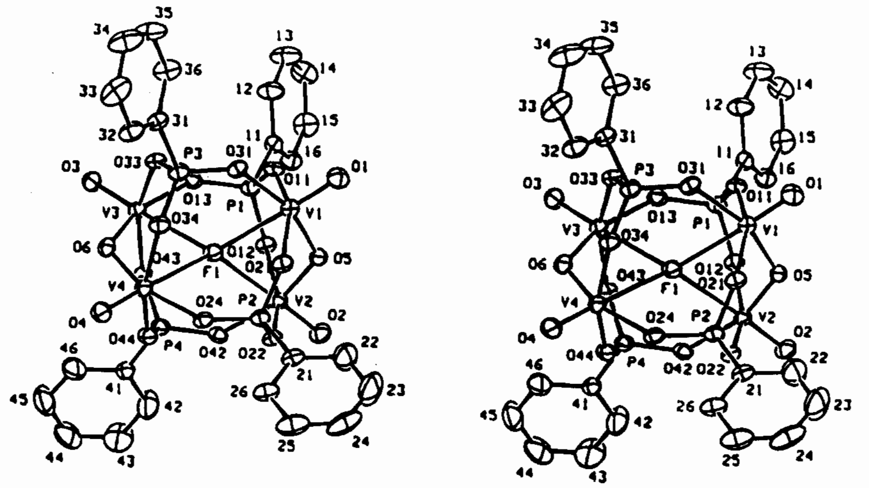

Figure 3. Stereoview of the cluster anion of compound **2**, $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$.

Table 4. Interatomic Distances (Å) for Compound **2**, $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ with Estimated Standard Deviations in Parentheses

V(1)−F(1)	2.443(3)	V(4)−O(34)	1.944(4)
V(2)−F(1)	2.412(3)	V(4)−O(44)	1.919(4)
V(3)−F(1)	2.454(4)	P(1)−O(11)	1.531(4)
V(4)−F(1)	2.445(3)	P(1)−O(12)	1.543(4)
V(1)−O(1)	1.564(4)	P(1)−O(13)	1.527(4)
V(1)−O(5)	1.815(4)	P(2)−O(21)	1.541(4)
V(1)−O(11)	1.906(4)	P(2)−O(22)	1.542(4)
V(1)−O(21)	1.919(4)	P(2)−O(24)	1.526(4)
V(1)−O(31)	1.935(4)	P(3)−O(31)	1.522(4)
V(2)−O(2)	1.581(4)	P(3)−O(33)	1.534(4)
V(2)−O(5)	1.773(4)	P(3)−O(34)	1.531(4)
V(2)−O(12)	1.949(4)	P(4)−O(42)	1.523(4)
V(2)−O(22)	1.924(4)	P(4)−O(43)	1.537(4)
V(2)−O(42)	1.946(4)	P(4)−O(44)	1.541(4)
V(3)−O(3)	1.573(4)	P(1)−C(11)	1.780(6)
V(3)−O(6)	1.802(4)	P(2)−C(21)	1.786(6)
V(3)−O(13)	1.921(4)	P(3)−C(31)	1.788(6)
V(3)−O(33)	1.930(4)	P(4)−C(41)	1.769(6)
V(3)−O(43)	1.915(4)		
V(4)−O(4)	1.567(4)		
V(4)−O(6)	1.793(4)		
V(4)−O(24)	1.943(4)		

Table 5. Intramolecular Angles (deg) for Compound **2**, $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ with Estimated Standard Deviations in Parentheses

F(1)−V(1)−O(1)	178.2(4)	O(1)−V(1)−O(5)	102.4(2)
F(1)−V(1)−O(5)	79.4(1)	O(1)−V(1)−O(11)	102.4(2)
F(1)−V(1)−O(11)	77.7(1)	O(1)−V(1)−O(21)	101.7(2)
F(1)−V(1)−O(21)	78.2(1)	O(1)−V(1)−O(31)	98.8(2)
F(1)−V(1)−O(31)	79.5(1)	O(5)−V(1)−O(11)	86.6(2)
F(1)−V(2)−O(2)	178.2(2)	O(5)−V(1)−O(21)	87.0(2)
F(1)−V(2)−O(5)	81.0(2)	O(5)−V(1)−O(31)	158.9(2)
F(1)−V(2)−O(12)	79.2(1)	O(11)−V(1)−O(21)	155.9(2)
F(1)−V(2)−O(22)	77.8(1)	O(11)−V(1)−O(31)	89.0(2)
F(1)−V(2)−O(42)	80.1(1)	O(21)−V(1)−O(31)	88.7(2)
F(1)−V(3)−O(3)	177.5(2)	O(2)−V(2)−O(5)	100.8(2)
F(1)−V(3)−O(6)	80.5(2)	O(2)−V(2)−O(12)	101.2(2)
F(1)−V(3)−O(13)	78.9(1)	O(2)−V(2)−O(22)	101.9(2)
F(1)−V(3)−O(33)	77.8(1)	O(2)−V(2)−O(42)	98.1(2)
F(1)−V(3)−O(43)	77.9(1)	O(5)−V(2)−O(12)	87.0(2)
F(1)−V(4)−O(4)	177.6(2)	O(5)−V(2)−O(22)	87.6(2)
F(1)−V(4)−O(6)	81.0(2)	O(5)−V(2)−O(42)	161.1(2)
F(1)−V(4)−O(24)	79.4(1)	O(12)−V(2)−O(22)	156.9(2)
F(1)−V(4)−O(34)	78.9(1)	O(12)−V(2)−O(42)	88.7(2)
F(1)−V(4)−O(44)	77.6(1)	O(22)−V(2)−O(42)	89.3(2)
O(3)−V(3)−O(6)	102.0(2)	O(11)−P(1)−O(12)	112.7(2)
O(3)−V(3)−O(13)	98.6(2)	O(11)−P(1)−O(13)	111.1(2)
O(3)−V(3)−O(33)	102.5(2)	O(12)−P(1)−O(13)	111.6(2)
O(3)−V(3)−O(43)	101.9(2)	O(21)−P(2)−O(22)	111.6(2)
O(6)−V(3)−O(13)	159.4(2)	O(21)−P(2)−O(24)	112.1(2)
O(6)−V(3)−O(33)	86.5(2)	O(22)−P(2)−O(24)	111.5(2)
O(6)−V(3)−O(43)	87.7(2)	O(31)−P(3)−O(33)	111.2(2)
O(13)−V(3)−O(33)	88.2(2)	O(31)−P(3)−O(34)	112.3(2)
O(13)−V(3)−O(43)	89.1(2)	O(33)−P(3)−O(34)	112.6(2)
O(33)−V(3)−O(43)	155.6(2)	O(42)−P(4)−O(43)	111.6(2)
O(4)−V(4)−O(6)	101.3(2)	O(42)−P(4)−O(44)	111.6(2)
O(4)−V(4)−O(24)	98.3(2)	O(43)−P(4)−O(44)	111.3(2)
O(4)−V(4)−O(34)	101.7(2)	O(11)−P(1)−C(11)	105.6(2)
O(4)−V(4)−O(44)	101.9(2)	O(12)−P(1)−C(11)	109.6(2)
O(6)−V(4)−O(24)	160.3(2)	O(13)−P(1)−C(11)	105.9(2)
O(6)−V(4)−O(34)	86.6(2)	O(21)−P(2)−C(21)	106.0(3)
O(6)−V(4)−O(44)	87.4(2)	O(22)−P(2)−C(21)	107.8(2)
O(24)−V(4)−O(34)	88.1(2)	O(24)−P(2)−C(21)	107.5(3)
O(24)−V(4)−O(44)	90.0(2)	O(31)−P(3)−C(31)	105.6(3)
O(34)−V(4)−O(44)	156.4(2)	O(33)−P(3)−C(31)	106.8(2)
O(34)−P(3)−C(31)	107.8(3)	V(2)−F(1)−V(3)	126.5(1)
O(42)−P(4)−C(41)	108.7(3)	V(2)−F(1)−V(4)	126.8(1)
O(43)−P(4)−C(41)	105.8(2)	V(3)−F(1)−V(4)	78.8(1)
O(44)−P(4)−C(41)	107.7(2)	V(1)−O(5)−V(2)	120.0(2)
V(1)−F(1)−V(2)	79.6(1)	V(3)−O(6)−V(4)	119.7(2)
V(1)−F(1)−V(3)	126.0(1)		
V(1)−F(1)−V(4)	126.4(1)		

unusually large "thermal motion." Compound **2** and the methylphosphonate and *n*-butyl phosphate analogues contain vanadium only in the +5 oxidation state and exhibit normal diamagnetic NMR spectra. It is interesting to note that the ^{19}F NMR spectrum reveals coupling of the F at the cluster center to four equivalent ^{31}P nuclei of the phosphonate ligands, with $^3J = 15$ Hz despite the very long V- -F bond distances (~2.4 Å). The structure of compound **2** can be described as distorted tetrahedral, with vanadyl groups on each tetrahedral face and phosphonato groups on each corner, bridging oxygens sitting on a pair of opposite edges, and fluoride in the center of each cluster. Ideally the compound has D_{2d} symmetry as sketched in Figure 4. The bridging oxygen atoms are almost certainly derived from the water present in the synthesis mixture as isolated yields of compound **2** and the methylphosphonato analogue diminish to nearly zero when water is excluded. And, here it appears that fluoride ion plays a critical role in "templating" the cluster formation, as only intractible mixtures of ill-defined compounds are obtained when fluoride sources are excluded.

Considerable stability of this cluster's structure is evident when one notes the preparation of the *n*-butyl phosphate analogue of the phosphonate materials. As in the phosphonates, *n*-butyl phosphate has only three oxygen atoms available for coordination to V and one might dare anticipate the formation of similar structure types. Indeed, a cluster analogous to **2** containing mono-*n*-butyl phosphate does result even when using commercially available 1:1 mixtures of mono- and di-*n*-butyl phosphate; the cluster of structure-type **2** crystallizes directly from the synthesis mixture in close to quantitative yield, utilizing

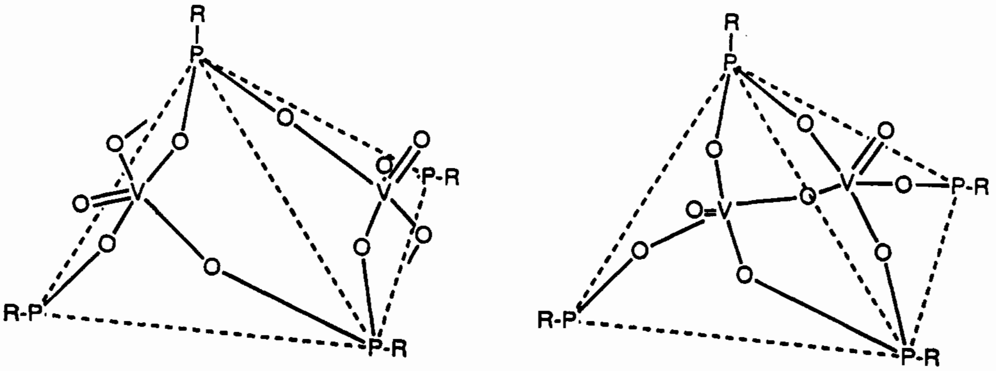

Figure 4. (Left) Idealized representation of compound **2**, in a perspective similar to that of Figure 3. (Right) Representation rotated to show one V−O−V bridge across the front "tetrahedral" edge. In both drawings the central fluoride is omitted and the dashed lines outline the underlying "tetrahedral" framework of the cluster.

all of the available monobutyl phosphate while leaving the equivalent amount of the di-*n*-butyl phosphate untouched in solution.

Oxidation of Cyclohexadiene. Our interest in phosphatovanadium chemistry is ultimately derived from the importance of phosphatovanadium oxides in oxidation and oxygenation chemistry. To begin exploring this aspect, we needed an organic substrate that could indeed be oxidized by at least one of our compounds at temperatures where gross decomposition was not prevalent. At the same time we wanted a purely hydrocarbon organic substrate, i.e. one having no oxygen or other heteroatoms that could attach themselves to the metal compounds and direct the subsequent oxidation chemistry. (In other articles we will describe complementary studies where organic substrates do bear heteroatoms which are attached to vanadium compounds and direct the oxidation chemistry.) We chose 1,4-cyclohexadiene owing to the ease of detection of its oxidation product, benzene. We note that oxidizing 1,4-cyclohexadiene is not especially challenging; the compound is susceptible to autoxidation to benzene, and commercial samples contain an inhibitor. Taking this into account, we have demonstrated that compounds **1** and **2** stoichiometrically oxidize this hydrocarbon compound at modest temperatures (90 °C) in pyridine solution under nitrogen at rates that noticeably exceed spontaneous conversion to benzene.

In reactions of 1,4-cyclohexadiene with compounds **1** and **2** benzene was the sole organic product detected, and unreacted 1,4-cyclohexadiene was not isomerized. In the case of compound **1** the reaction mixture became heterogeneous as the oxidation reaction progressed and a massive green precipitate was formed. This precipitate remains uncharacterized as it would not redissolve in nonhydroxylic solvents and reacted with alcohols or water. In the case of the methylphosphonato analogue of compound **2** a very clean redox reaction was observed, summarized in eq 1. The product methylphosphonatovanadium cluster **3** was obtained in single crystalline form by evaporating the pyridine solvent and recrystallizing the oily residue from acetonitrile/4-*tert*-butylpyridine. Reduction of the tetrabutylammonium analogue of compound **2** using diphenylhydrazine or electrolysis has been described.[12]

$$[Et_4P]^+[(V_2O_3)_2(MePO_3)_4F]^- + 0.5C_6H_8 + \text{pyridine} =$$
$$[Et_4P]^+[\text{pyridineH}]^+[(V_2O_3)_2(MePO_3)_4F]^{2-} + 0.5\ C_6H_6 \quad (1)$$

The mechanism(s) of oxidation of 1,4-cyclohexadiene by compound **1** and the methylphosphonato analogue of compound **2** has not been established, but assuming the overall rate law for the formation of benzene given in eq 2 our data roughly fits $k_{\text{bimol}} \approx 0.15\ M^{-1}\ h^{-1}$ for compound **1** and $0.05\ M^{-1}\ h^{-1}$ for the methylphosphonato analogue of compound **2**, in pyridine-d_5 solution at 90 °C under nitrogen in NMR tubes. The presumably unimolecular rate constant for adventitious conversion of 1,4-cyclohexadiene to benzene is $k_{\text{unimol}} \approx 0.0002\ h^{-1}$ under these conditions. Note that both per cluster and per vanadium(V), compound **1** oxidizes 1,4-cyclohexadiene somewhat more rapidly than does the methylphosphonato analogue of compound **2**. This argues against the possibility that O=V−O−V=O entities (found in compound **2** and its analogues) might be profoundly more active oxidants than isolated vanadyl sites.

Table 6. Selected Interatomic Distances (A) for Compound **3**, $[Et_4P]_{1.5}[(4\text{-}tert\text{-butylpyridine})_2H]_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$, with Estimated Standard Deviations in Parentheses

V(1)−F(1)	2.486(4)	V(4)−O(23)	1.916(4)
V(2)−F(1)	2.528(4)	V(4)−O(33)	1.925(5)
V(3)−F(1)	2.403(3)	V(4)−O(43)	1.929(5)
V(4)−F(1)	2.392(4)	P(1)−O(11)	1.526(5)
V(1)−O(1)	1.584(5)	P(1)−O(12)	1.532(4)
V(1)−O(5)	1.841(4)	P(1)−O(13)	1.539(5)
V(1)−O(11)	1.987(4)	P(2)−O(21)	1.538(5)
V(1)−O(21)	1.971(4)	P(2)−O(22)	1.526(5)
V(1)−O(31)	1.989(4)	P(2)−O(23)	1.541(5)
V(2)−O(2)	1.588(5)	P(3)−O(31)	1.510(5)
V(2)−O(5)	1.789(4)	P(3)−O(32)	1.539(5)
V(2)−O(12)	1.970(4)	P(3)−O(33)	1.535(5)
V(2)−O(22)	1.969(4)	P(4)−O(41)	1.506(5)
V(2)−O(41)	1.988(5)	P(4)−O(42)	1.538(4)
V(3)−O(3)	1.586(4)	P(4)−O(43)	1.540(5)
V(3)−O(6)	1.789(4)	P(1)−C(1)	1.803(7)
V(3)−O(13)	1.924(4)	P(2)−C(2)	1.785(7)
V(3)−O(32)	1.945(5)	P(3)−C(3)	1.785(8)
V(3)−O(42)	1.945(4)	P(4)−C(4)	1.791(7)
V(4)−O(4)	1.589(5)		
V(4)−O(6)	1.813(4)		

$$d[C_6H_6]/dt = k_{\text{bimol}}\ [\text{cluster}][C_6H_8] + k_{\text{unimol}}[C_6H_8] \quad (2)$$

From the reaction of the methylphosphonato analogue of compound **2**, the reduced vanadium product has been recrystallized from 4-*tert*-butylpyridine/CH$_3$CN and the resulting crystals shown by single crystal X-ray diffraction to have the composition $[Et_4P]^+_{1.5}\ [(4\text{-}tert\text{-butylpyridine})_2H]^+_{0.5}\ [(V_2O_3)_2(MePO_3)_4F]^{2-}$ (compound **3**); crystallographic data are included in Table 1, and selected bond distances and angles are listed in Tables 6 and 7. The half-molecule of $[Et_4P]^+$ is disordered about a 2-fold axis. The hydrogen of the half-molecule of $[(4\text{-}tert\text{-butylpyridine})_2H]^+$ also is disordered about a 2-fold axis, in a highly unsymmetrical N- -H- -N unit with refined N- -H bond distances of 0.89(7) and 1.74(7) Å, and an apparent $H_{0.5}$- - -$H_{0.5}$ separation of 0.85(15) Å. But, note that the position of a half-"proton" is not well determined by X-ray data. The structure of the phosphonatovanadium anion of compound **3**, shown in Figure 5, is superficially the same as in compound **2**, apart from the

Table 7. Selected Intramolecular Angles (deg) for Compound **3**, $[Et_4P]_{1.5}[(4\text{-}tert\text{-butylpyridine})_2H]_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$, with Estimated Standard Deviations in Parentheses

F(1)−V(1)−O(1)	177.2(2)	O(1)−V(1)−O(5)	102.6(2)
F(1)−V(1)−O(5)	80.2(2)	O(1)−V(1)−O(11)	103.3(2)
F(1)−V(1)−O(11)	77.0(2)	O(1)−V(1)−O(21)	101.8(2)
F(1)−V(1)−O(21)	78.0(2)	O(1)−V(1)−O(31)	98.8(2)
F(1)−V(1)−O(31)	78.4(2)	O(5)−V(1)−O(11)	86.5(2)
F(1)−V(2)−O(2)	177.0(2)	O(5)−V(1)−O(21)	87.1(2)
F(1)−V(2)−O(5)	79.9(2)	O(5)−V(1)−O(31)	158.5(2)
F(1)−V(2)−O(12)	77.3(1)	O(11)−V(1)−O(21)	154.9(2)
F(1)−V(2)−O(22)	76.2(1)	O(11)−V(1)−O(31)	87.7(2)
F(1)−V(2)−O(41)	78.8(2)	O(21)−V(1)−O(31)	89.5(2)
F(1)−V(3)−O(3)	178.7(3)	O(2)−V(2)−O(5)	102.9(2)
F(1)−V(3)−O(6)	79.3(2)	O(2)−V(2)−O(12)	103.7(2)
F(1)−V(3)−O(13)	80.9(1)	O(2)−V(2)−O(22)	102.8(2)
F(1)−V(3)−O(32)	78.0(2)	O(2)−V(2)−O(41)	98.4(2)
F(1)−V(3)−O(42)	79.5(2)	O(5)−V(2)−O(12)	87.3(2)
F(1)−V(4)−O(4)	179.4(4)	O(5)−V(2)−O(22)	87.6(2)
F(1)−V(4)−O(6)	79.1(2)	O(5)−V(2)−O(41)	158.7(2)
F(1)−V(4)−O(23)	82.2(2)	O(12)−V(2)−O(22)	153.5(2)
F(1)−V(4)−O(33)	78.5(2)	O(12)−V(2)−O(41)	88.9(2)
F(1)−V(4)−O(43)	78.6(2)	O(22)−V(2)−O(41)	86.6(2)
O(3)−V(3)−O(6)	101.9(2)	O(11)−P(1)−O(12)	114.4(2)
O(3)−V(3)−O(13)	97.9(2)	O(11)−P(1)−O(13)	110.8(3)
O(3)−V(3)−O(32)	101.6(2)	O(12)−P(1)−O(13)	110.9(3)
O(3)−V(3)−O(42)	101.0(2)	O(21)−P(2)−O(22)	114.6(2)
O(6)−V(3)−O(13)	160.1(2)	O(21)−P(2)−O(23)	110.7(2)
O(6)−V(3)−O(32)	86.6(2)	O(22)−P(2)−O(23)	111.0(3)
O(6)−V(3)−O(42)	86.8(2)	O(31)−P(3)−O(32)	112.6(3)
O(13)−V(3)−O(32)	88.7(2)	O(31)−P(3)−O(33)	111.4(2)
O(13)−V(3)−O(42)	90.2(2)	O(32)−P(3)−O(33)	111.9(3)
O(32)−V(3)−O(42)	157.4(2)	O(41)−P(4)−O(42)	112.4(3)
O(4)−V(4)−O(6)	101.1(2)	O(41)−P(4)−O(43)	113.0(3)
O(4)−V(4)−O(23)	97.6(2)	O(42)−P(4)−O(43)	111.5(3)
O(4)−V(4)−O(33)	102.0(2)	O(11)−P(1)−C(1)	105.8(4)
O(4)−V(4)−O(43)	100.9(2)	O(12)−P(1)−C(1)	108.2(3)
O(6)−V(4)−O(23)	161.3(2)	O(13)−P(1)−C(1)	106.2(3)
O(6)−V(4)−O(33)	86.4(2)	O(21)−P(2)−C(2)	108.4(4)
O(6)−V(4)−O(43)	85.4(2)	O(22)−P(2)−C(2)	106.1(4)
O(23)−V(4)−O(33)	91.3(2)	O(23)−P(2)−C(2)	105.4(3)
O(23)−V(4)−O(43)	89.5(2)	O(31)−P(3)−C(3)	107.1(4)
O(33)−V(4)−O(43)	156.8(2)	O(32)−P(3)−C(3)	106.9(3)
		O(33)−P(3)−C(3)	106.6(4)
O(41)−P(4)−C(4)	107.3(4)	V(1)−O(5)−V(2)	121.6(2)
O(42)−P(4)−C(4)	107.5(4)	V(3)−O(6)−V(4)	120.3(2)
O(43)−P(4)−C(4)	104.7(4)		
V(1)−F(1)−V(2)	78.4(1)		
V(1)−F(1)−V(3)	127.4(1)		
V(1)−F(1)−V(4)	125.6(2)		
V(2)−F(1)−V(3)	125.1(2)		
V(2)−F(1)−V(4)	126.0(1)		
V(3)−F(1)−V(4)	81.3(1)		

different organic groups on the phosphonates and changes in bond lengths resulting from the extra electron in compound **3**, which we describe in the next section. The peculiar cation composition of compound **3** is a consequence of the recrystallization process and does not reflect the overall solution stoichiometry of the redox reaction, which we summarize in eq 1.

The EPR spectrum of compound **3** is solvent-dependent. In acetonitrile, a 29-line pattern at $g = 2.00$ is evident above 273 K ($J_V = 29.1$ G) due to coupling of the unpaired electron to the four spin $^{7}/_{2}$ vanadium nuclei with equivalent probability. The EPR spectrum of a pyridine solution, under otherwise similar conditions, reveals a much more complex coupling pattern (not yet fully analyzed) of the unpaired electron indicative of the electron becoming localized on one pair of V atoms. As the temperature is raised to 373 K, however, the spectrum collapses to the same 29-line symmetric pattern observed in acetonitrile.

Discussion

Structure of Compound 1. The structure of compound **1** exhibits several aspects we find intriguing; among these are its encapsulated chloride, its juxtaposition of crystallographic symmetry with electronic asymmetry (as revealed by its EPR spectrum where the unpaired electron is localized on a single V center even up to 100 °C), and its "geared" internal rotational disorder. But perhaps the most significant feature of compound **1** is that it exemplifies how a layered structural motif, in the present case that of α-VOPO$_4$,[8,15] can be expressed in a closed polyhedral cluster once the requisite number of sites of positive Gaussian curvature[16] have been introduced. In this sense, compound **1** is related to α-VOPO$_4$ as fullerenes are to graphite, a prospect alluded to by Tenne et al.[5]

Exploring for a moment this layer−polyhedron relationship, we sketch the structure of α-VOPO$_4$ [8] in Figure 6a. Each vanadyl group is coordinated by four phosphato groups and each phosphato group by four vanadyl groups, defining a network of 8-member -VOPOVOPO- rings. Each phosphato group sits on a site of $\bar{4}$ symmetry (S_4 or essentially D_{2d}) and, in the language of topology, is a site of negative Gaussian curvature ("saddle").[16,17] To form a topologically-level infinite surface recognizable as an infinite 2-dimensional layer, the negative curvature of the phosphato groups must be compensated by positive Gaussian curvature at other groups. In the actual structure (Figure 6a) positive Gaussian curvature is associated with the vanadyl sites.[17] For purposes of discussion we assume a structurally-absurd but topologically-acceptable model wherein there is no mean curvature at bridging oxygen sites, i.e. V−O−P angles are adjusted to 180° (a two-coordinate oxygen atom, regardless of angle, is a site of zero Gaussian curvature), all phosphato groups are ideally tetrahedral (O−P−O angles 109.5°), and all remaining mean and Gaussian curvature is "displaced to" or "absorbed by" the vanadyl sites. In this model, then, the α-VOPO$_4$ layer is comprised of sites (vanadyls) of positive Gaussian curvature, half being oriented upward and half being oriented downward, connected by sites (phosphates) of negative Gaussian curvature.[18] The α-VOPO$_4$ [8] layer (Figure 6a) is topologically equivalent to the (2,2) mode of a quantum particle in a square box, or of a vibrating rectangular membrane (Figure 6b);[18] the phosphato groups map onto nodal points and the vanadyls onto antinodes.

In their recent article, Tenne et al. [5] anticipated the "promising prospect" that many layered inorganic structures could be synthesized in closed fullerene-like nanocrystallites, using structural defects or deviations from usual microstructure both to provide the necessary Gaussian curvature and to eliminate any dangling bonds. In the context of compound **1**, by retaining one SiMe$_3$ group each derivatized phosphato center has only three oxygens available to coordinate to vanadyl groups; thus these phosphato groups automatically become sites of positive Gaussian curvature,[19,20] and support formation of closed polyhedral structures. The use of organophosphates and organophosphonates to modify "phosphato" structures is well established in the literature,[21] although often without forming cluster

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(15) Intercalation reactions of α-VOPO$_4$ are described by: Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. M. *Inorg. Chem.* **1982**, *21*, 3820−3825. Hydration/dehydration is described by Benabdelouahab et al. in ref 8c.

(16) A concise and readable introduction to "curvature" as relevant to chemical structures is provided by: Terrones, H.; Mackay, A. L. *Carbon* **1992**, *30*, 1251−1260.

(17) In this discussion we assign the curvature as "belonging" to specific atomic sites. In a broader sense it can be useful to assign curvature to groups of atoms, e.g. 5- or 7-member rings as in ref 16.

(18) Morse, P. M. *Vibration and Sound*; McGraw-Hill: New York, 1936; p 142. Other physics textbooks provide similar drawings.

(19) Another method of obtaining closed polyhedral structures from related compounds is to omit phosphato groups altogether and rely upon positive Gaussian curvature provided by vanadyl groups. See: Klemperer, W. G.; Marquet, T. A.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 49−51 and references therein, especially the articles by Müller et al.[11]

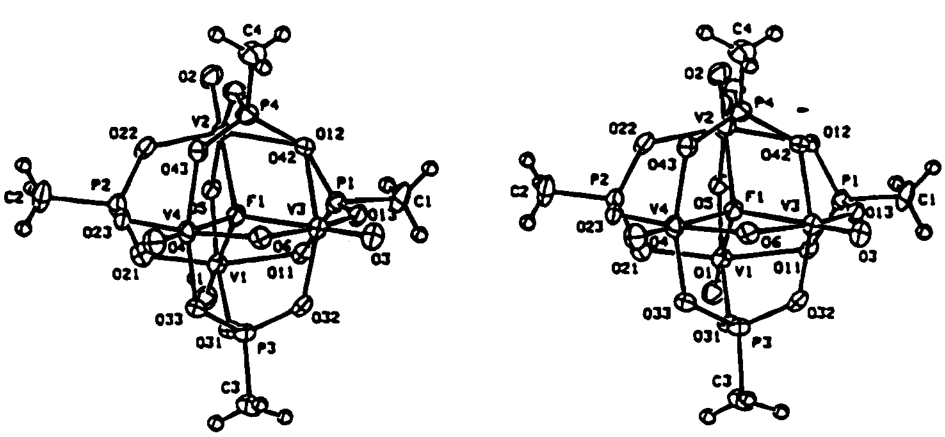

Figure 5. Stereoview of the cluster anion of compound **3**, $[Et_4P]^+_{1.5}[(4\text{-t-butylpyridine})_2H]^+_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$.

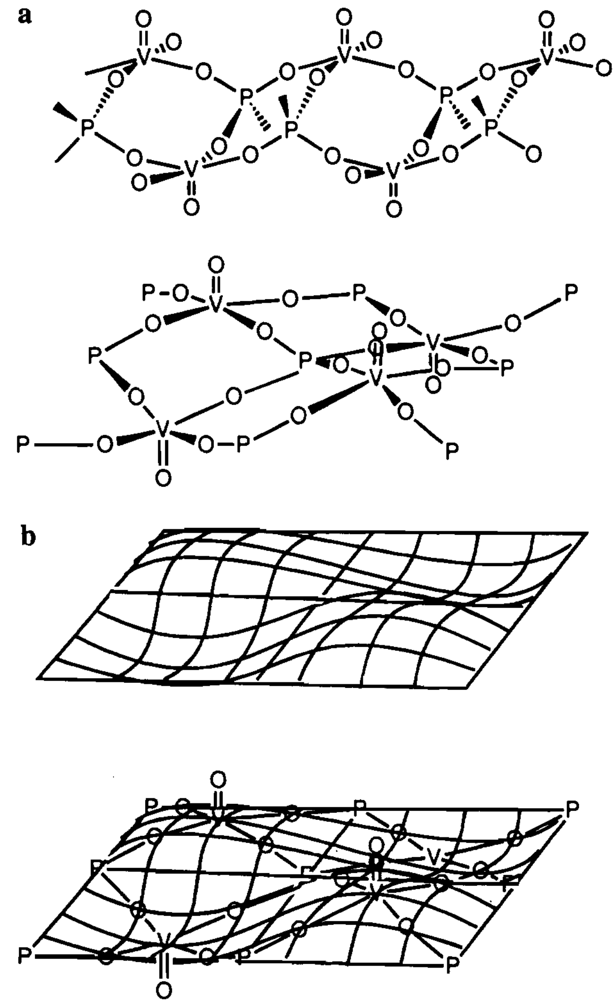

Figure 6. (a) Views of the layered structure of "alpha$_{II}$-VOPO$_4$" (single layer).[8] The bottom view is rotated ca. 45° relative to the top. The proposed structure of "alpha$_I$-VOPO$_4$" inverts each vanadyl center. (b) Views of the (2,2) mode of a quantum particle in a square box. In the bottom view the "alpha$_{II}$-VOPO$_4$"[8] layer is superimposed.

compounds[22] and with somewhat different rationalizations than what we present here.[23]

The correlated "geared" rotational disorder exhibited by compound **1** likewise parallels the correlated rotation of vanadyl square-pyramids in α-VOPO$_4$ itself,[8a] where each vanadyl square-pyramid is also rotated by about 10° from ideal *p*4*m* symmetry. This compound is subject to disorder in which case the bridging phosphato oxygen atoms of the superimposed components are separated by 0.64 Å (much like the observed values in compound **1**). Jordan and Calvo[8a] make the important point that whether the disorder is observed can depend on the particular details of the refinement procedure, thus whether the disorder is "characteristic of the structure rather than the compound" is not easily established. By way of contrast, in one of the hydrated forms of VOPO$_4$ [8b] each vanadyl square-pyramid apparently exhibits no rotation and does sit on a site of ideal *p*4*m* symmetry. Likewise, the *tert*-butylphosphonato compound $(VO)_6(O_3P^tBu)_8Cl$ [7] has a core "isostructural" with that of compound **1** but exhibits essentially ideal symmetry apparently without the correlated internal rotation.

Structures of Compounds 2 and 3. We see a similar topological theme in compounds **2** and **3**, that is, derivatized phosphorus(V) centers that contribute three oxygen centers to cluster bonding serve as sites of positive Gaussian curvature and support a closed polyhedral structure. But unlike compound **1**, here we do not recognize a related "parent" layered structure. We focus on a comparison of bond distances between the fully oxidized (compound **2**) and one-electron-reduced (compound **3**) clusters, bearing in mind the two compounds have different organic groups on the phosphonato ligands, different counterions, and necessarily different crystalline environments.

Bond distances in compounds **2** and **3** are presented in Tables 4 and 6. From a close inspection of the bond distances, we believe the "extra" electron in the one-electron-reduced cluster (**3**) is confined to only one of the two O=VOV=O units, and is essentially delocalized over that unit. This follows from the average V—OP bond distance of 1.93(2) Å in the fully oxidized cluster (**2**); in the one-electron-reduced cluster (**3**) the V—OP

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(20) By derivatizing two phosphate oxygens (or blocking two tetrahedral directions) and allowing the phosphorus center to contribute only two oxygen atoms to cluster bonding, the phosphorus center becomes a site having no Gaussian curvature, thus unable (by itself) to contribute to polyhedral closure. We describe our work with such systems elsewhere.[6]

(21) Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990**, *2*, 91–93. Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842–3844. Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431–436. Kahn, M. I.; Lee, Y.-S.; O'Connor, C. J.; Haushalter, R. C.; Zubieta, J. *J. Am. Chem. Soc.* **1994**, *116*, 4525–4526. Kahn, M. I.; Lee, Y.-S.; O'Connor, C. J.; Haushalter, R. C.; Zubieta, J. *J. Chem. Mater.* **1994**, *6*, 721–723. Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420–427 and references therein.

(22) Many metal–organophosphonato compounds have layered structures (see ref 21) even though the phosphonato sites exhibit positive Gaussian curvature. Such structures are, conceptually, the "inverse" of alpha-VOPO$_4$ in that the topological roles of metal and phosphorus sites are transposed; in such structures the metal sites are able to contribute negative Gaussian curvature by virtue of having coordination different from C_{4v} square-pyramidal.

(23) Directing structural types by manipulating substituents around tetrahedral atomic centers is a familiar aspect of organic chemistry: Tetrahedral CH_2 units (or trigonal CH units) form linear or monocyclic structures, tetrahedral CH units (or trigonal C) form polycyclic or polyhedral structures, and tetrahedral C forms spiro compounds or, ultimately, diamond.

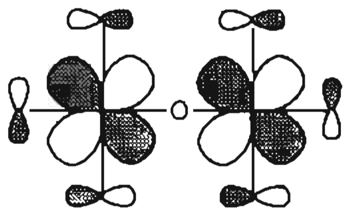

Figure 7. LUMO/SOMO of the O=VOV=O unit.

bond distances also average 1.93(2) Å about the unreduced O=VOV=O unit (V(3)−O(6)−V(4)), whereas they average 1.98(2) Å about the reduced O=VOV=O unit (V(1)−O(5)−V(2)). It is also apparent in the V- - -F separations, which average 2.43(2) Å for the fully oxidized compound **2** and 2.40(1) Å for the unreduced O=VOV=O unit in compound **3**, whereas they average 2.51(3) Å for the reduced O=VOV=O unit in compound **3**.

The V−O−V distances in the fully oxidized cluster (**2**) are 1.793(4), 1.802(4) Å in one O=VOV=O unit (V(3)−O(6)−V(4)) and 1.773(4), 1.815(4) Å in the other (V(1)−O(5)−V(2)). In the one-electron-reduced cluster (**3**) the V−O−V distances are 1.789(4), 1.813(4) Å in the unreduced O=VOV=O unit (V(3)−O(6)−V(4)) and 1.789(4), 1.841(4) Å in the reduced O=VOV=O unit (V(1)−O(5)−V(2)). There has been some discussion in the literature about localized vs delocalized electrons in one-electron-reduced O=VOV=O compounds,[24] and crystallographic examples of each have been reported. We promote the interpretation, based on V−OP bond lengths, that in compound **3** there is nearly complete delocalization of the odd electron over one O=VOV=O unit; the unsymmetrical position of the bridging oxygen atom as determined by X-ray diffraction (V−O−V distances differ by 0.05 Å for V(1)−O(5)−V(2) in compound **3**), for whatever reason, is not a compelling indication of valence trapping since one of the fully oxidized O=VOV=O units also exhibits a comparably unsymmetrical oxygen bridge (V−O−V distances differ by 0.04 Å for V(1)−O(5)−V(2) in compound **2**).

The average V−OP bond distances increase more in going from V^{5+} to $V^{4.5+}$ (average 1.93 Å increasing to 1.98 Å) than do the average V−O−V bond distances (average 1.79 Å increasing to 1.82 Å). This may reflect constraints imposed by the interconnections inherent in a cluster, or statistical aberrations, but is at least consistent with a simple MO picture (Figure 7). The LUMO of a symmetrical $O{=}V^{v}OV^{v}{=}O$ unit has local a_2 symmetry[24a] and is composed mostly of vanadium d orbitals having a node at the bridging oxygen atom, but having π-antibonding with the phosphonato oxygen atoms. Partial occupancy of this MO would, in the simplest analysis, weaken (thus lengthen) the V−OP bonds more than the V−OV bonds.

It is important to recall that the counterions and organic substituents differ in compounds **2** and **3**, making direct structural comparisons somewhat problematic. Despite this we claim that V−OP bond distances around phosphato/phosphonatovanadyl(IV) centers are larger by at least 0.05 Å than around vanadyl(V) centers in comparable coordination environments. Restated, in a constrained phosphato/phosphonato system, i.e. an infinite lattice or perhaps a cluster, an isolated vanadyl(V) center in an otherwise all vanadyl(IV) compound is likely to be a site of strain, having V(V)-OP bond distances greater than optimal. Conversely, in a constrained system, an isolated vanadyl(IV) center in an otherwise all vanadyl(V) compound is likewise a high-energy site, having V(IV)-OP bond distances less than optimal. Thus an isolated vanadyl(V) center in an otherwise all vanadyl(IV) lattice could be more easily reduced, i.e. a better oxidant, than a vanadyl(V) center in an all vanadyl(V) lattice. This suggests the possibility that vanadyl(V) "holes" in an otherwise vanadyl(IV) lattice could be better one-electron oxidants than vanadyl(V) sites in an all vanadyl(V) lattice.

Summary and Conclusions

We have described the syntheses and structures of three phosphato/phosphonatovanadyl cluster compounds, a "cubic" cluster (compound **1**) and two "tetrahedral" clusters (compounds **2** and **3**). These clusters are related in several senses: they bear derivatized phosphorus ligands which provide only three oxygen atoms for cluster bonding and hence serve as sites of positive Gaussian curvature and contributors to closure; each contains an encapsulated halide ion, the presence and size of which may play a crucial role in assembling ("templating") the respective clusters; compounds **1** and **2** contain pentavalent vanadium centers and are capable of oxidizing at least one hydrocarbon, albeit one not difficult to oxidize and by a mechanism(s) not yet established.

Concerning the abilities of these clusters to oxidize organics, i.e. to be reduced: At least for the "tetrahedral" cluster **2** we know the cluster framework is not permanently altered upon one-electron reduction.[12] In the reduced cluster **3** both structural and EPR data in pyridine solution demonstrate slow hopping of the electron across OPO bridges, but rapid electron hopping/delocalization across a single oxygen atom bridge. In compound **1**, crystallographic symmetry precludes a structural location of the odd electron, but (as in compound **3**) EPR data demonstrates, at most, slow hopping of the electron from vanadyl to vanadyl across OPO bridges.

Finally, we redescribe the role of phosphorus centers in oxymetalphosphate structures using the concepts of mean and Gaussian curvature. We see that unadorned phosphato groups using all four oxygen atoms in the bonding network tend to serve as sites of negative Gaussian curvature and oppose formation of closed polyhedral structures (although they could support the formation of loops/cylinders). By excluding one phosphato oxygen, or one tetrahedral direction of the phosphorus site, from the bonding network, we see the phosphorus sites acquiring positive Gaussian curvature and supporting (but not necessarily guaranteeing[22]) closure into polyhedral structures. "Excluding one oxygen" can be done by chemically derivatizing the phosphorus center. But it could also be done as an accident in the growth of extended-structure particles resulting in the "excluded" oxygen being unadorned. It is tempting to speculate that such accidents cause irregularities/defects in the surface structures of (pyro)phosphatovanadyl compounds leading to particularly reactive sites which may be important in the performance of (pyro)phosphatovanadyl compounds as selective oxidants.

Experimental Section

All reactions were carried out using dried solvents (unless otherwise noted) and standard inert-atmosphere techniques. NMR data were obtained using GE QE300 instruments; chemical shifts are reported in ppm downfield from external standards ($Si(CH_3)_4$ for ^1H, 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F) with coupling constants in Hz. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Vanadium compounds $VO(OiPr)_3$ and $VOCl_3$ as well as phosphorus-containing reagents were obtained commercially. The acetonitrile adduct $VOCl_3{\cdot}CH_3CN$ was prepared by following ref 25. AlF_4^- salts were prepared as described in ref 14. EPR spectra were collected on

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(24) See, for example: (a) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168−1174. (b) Launay, J.-P.; Jeannin, Y.; Daoudi, M. *Inorg. Chem.* **1985**, *24*, 1052−1059. (c) Pessoa, J. C.; Silva, J. A. L.; Vieira, A. L.; Vilas-Boas, L.; O'Brien, P.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1745−1749. (d) Chakravarty, J.; Dutta, S.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2857−2858.

Table 8. Fractional Coordinates and Isotropic (Refined or Equivalent) Thermal Parameters (Å^2) for Compound **1**, $(VO)_6(O_3POSiMe_3)_8Cl$

atom	x	y	z	$B_{iso/eq}$
V(1)	0.73570(5)	0.43060(5)	0.5000	1.68(2)^a
V(2)	0.5000	0.5000	0.32387(6)	1.62(2)^a
Cl(1)	0.5000	0.5000	0.5000	3.34(5)^a
P(1)	0.60451(5)	0.30864(5)	0.38865(4)	1.64(2)^a
Si(1)	0.7045(1)	0.1248(1)	0.3434(1)	3.34(3)^a
O(1)	0.8449(2)	0.3985(2)	0.5000	2.4(1)^a
O(2)	0.5000	0.5000	0.2419(3)	2.5(1)^a
O(3)	0.6888(3)	0.3633(3)	0.4246(2)	1.5(1)
O(3')	0.6795(3)	0.3310(4)	0.4409(3)	1.7(1)
O(4)	0.5424(3)	0.3737(3)	0.3467(2)	1.6(1)
O(4′)	0.5834(3)	0.3960(3)	0.3385(2)	1.6(1)
O(5)	0.6469(2)	0.2309(2)	0.3392(1)	2.33(4)
O(6)	0.5445(3)	0.2588(3)	0.4490(2)	1.8(1)
O(6′)	0.5121(3)	0.2678(3)	0.4169(2)	1.7(1)
C(1)	0.8104(12)	0.1298(12)	0.3911(8)	8.3(4)
C(1′)	0.8401(7)	0.1657(7)	0.3518(5)	4.2(2)
C(2)	0.6040(7)	0.0388(7)	0.3859(5)	4.1(2)
C(2′)	0.6640(8)	0.0603(8)	0.4172(6)	5.4(2)
C(3)	0.7169(9)	0.0816(9)	0.2571(7)	4.8(3)
C(3′)	0.6848(8)	0.0723(8)	0.2525(6)	3.8(2)

^{a} Refined with anisotropic thermal parameters: $B_{eq} = {}^4/_3\Sigma\Sigma b_{ij}a_ia_j$, where a_i and a_j refer to the real lattice constants.

Table 9. Fractional Coordinates and Isotropic (Refined or Equivalent) Thermal Parameters (Å^2) for Compound **2**, $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$

atom	x	y	z	$B_{iso/eq}$
V(1)	0.18352(9)	0.36757(8)	0.38317(7)	1.64(3)^a
V(2)	0.03470(9)	0.23660(8)	0.34674(7)	1.63(3)^a
V(3)	0.41334(9)	0.08911(8)	0.20511(7)	1.59(3)^a
V(4)	0.31580(9)	0.27482(8)	0.07948(7)	1.73(3)^a
P(1)	0.2421(1)	0.1234(1)	0.4249(1)	1.6(1)^a
P(2)	0.0799(1)	0.4338(1)	0.2148(1)	1.8(1)^a
P(3)	0.4373(1)	0.3161(1)	0.2167(1)	1.8(1)^a
P(4)	0.1877(1)	0.0961(1)	0.1581(1)	1.7(1)^a
P(5)	0.3093(2)	0.7106(2)	0.3250(2)	4.5(1)^a
F(1)	0.2352(3)	0.2424(3)	0.2541(2)	1.8(1)^a
O(1)	0.1542(4)	0.4484(3)	0.4643(3)	2.4(2)^a
O(2)	−0.0967(3)	0.2308(3)	0.4047(3)	2.3(1)^a
O(3)	0.5259(3)	−0.0111(3)	0.1784(3)	2.1(1)^a
O(4)	0.3624(4)	0.2991(3)	−0.0321(3)	2.4(2)^a
O(5)	0.0469(3)	0.3289(3)	0.4181(3)	1.7(1)^a
O(6)	0.4267(3)	0.1543(3)	0.0888(3)	1.8(1)^a
O(11)	0.2481(3)	0.2349(3)	0.4376(3)	1.7(1)^a
O(12)	0.1251(3)	0.1249(3)	0.4116(3)	1.6(1)^a
O(13)	0.3512(3)	0.0643(3)	0.3425(3)	1.7(1)^a
O(21)	0.1297(3)	0.4596(3)	0.2880(3)	1.8(1)^a
O(22)	0.0091(3)	0.3515(3)	0.2566(3)	1.7(1)^a
O(24)	0.1770(3)	0.3983(3)	0.1171(3)	1.7(1)^a
O(31)	0.3441(3)	0.3725(3)	0.3083(3)	1.8(1)^a
O(33)	0.4749(3)	0.1951(3)	0.2325(3)	1.6(1)^a
O(34)	0.3979(3)	0.3474(3)	0.1279(3)	1.8(1)^a
O(42)	0.0751(3)	0.1355(3)	0.2453(3)	1.7(1)^a
O(43)	0.2949(3)	0.0360(3)	0.1896(3)	1.6(1)^a
O(44)	0.2149(3)	0.1879(3)	0.0870(3)	1.7(1)^a
C(11)	0.2520(5)	0.0520(5)	0.5331(4)	1.7(2)^a
C(12)	0.3410(6)	0.0574(5)	0.5650(5)	2.7(2)^a
C(13)	0.3568(6)	0.0016(6)	0.6455(5)	3.5(3)^a
C(14)	0.2836(7)	−0.0617(6)	0.6948(5)	3.1(3)^a
C(15)	0.1975(6)	−0.0710(5)	0.6618(5)	2.6(2)^a
C(16)	0.1810(5)	−0.0142(5)	0.5814(5)	2.2(2)^a
C(21)	−0.0214(5)	0.5555(5)	0.1949(5)	2.1(2)^a
C(22)	−0.1081(7)	0.6138(6)	0.2738(6)	4.4(3)^a
C(23)	−0.1902(7)	0.7044(7)	0.2595(7)	5.4(3)^a
C(24)	−0.1869(7)	0.7371(6)	0.1670(8)	4.7(4)^a
C(25)	−0.1028(7)	0.6814(6)	0.0890(6)	3.6(3)^a
C(26)	−0.0195(6)	0.5892(5)	0.1024(5)	2.6(2)^a
C(31)	0.5655(5)	0.3607(5)	0.1955(5)	2.0(2)^a
C(32)	0.6094(6)	0.4188(5)	0.1128(5)	2.6(2)^a
C(33)	0.7081(6)	0.4529(6)	0.0984(6)	3.8(3)^a
C(34)	0.7642(7)	0.4274(7)	0.1666(7)	4.5(3)^a
C(35)	0.7220(6)	0.3696(6)	0.2480(6)	3.8(3)^a
C(36)	0.6225(6)	0.3367(5)	0.2633(5)	2.8(2)^a
C(41)	0.1659(5)	0.0025(5)	0.0949(4)	1.8(2)^a
C(42)	0.0626(6)	−0.0268(6)	0.1244(6)	4.3(3)^a
C(43)	0.0531(7)	−0.1030(7)	0.0740(7)	5.3(4)^a
C(44)	0.1446(8)	−0.1536(6)	−0.0028(6)	4.0(3)^a
C(45)	0.2474(7)	−0.1264(6)	−0.0324(5)	4.1(3)^a
C(46)	0.2582(6)	−0.0494(6)	0.0166(5)	3.6(3)^a
C(51)	0.1601(11)	0.7042(10)	0.3580(7)	8.0(5)^a
C(52)	0.0805(10)	0.7989(10)	0.3415(8)	11.4(6)^a
C(53)	0.3687(9)	0.7308(10)	0.1960(7)	8.3(5)^a
C(54)	0.3494(10)	0.6647(10)	0.1353(7)	9.4(6)^a
C(55)	0.3903(11)	0.5827(7)	0.3607(10)	8.8(6)^a
C(56)	0.3586(12)	0.5627(9)	0.4655(10)	9.1(7)^a
C(57)	0.3243(8)	0.8121(6)	0.3837(7)	5.3(4)^a
C(58)	0.4525(9)	0.8037(8)	0.3692(8)	7.4(5)^a

^{a} Refined with anisotropic thermal parameters: $B_{eq} = {}^4/_3\Sigma\Sigma b_{ij}a_ia_j$, where a_i and a_j refer to the real lattice constants.

a Bruker ESP300 spectrometer using solutions of the clusters in a capillary tube to allow use of lossy solvents such as pyridine and acetonitrile.

Preparation of $(VO)_6(O_3POSiMe_3)_8Cl$ (1). A solution of 0.49 g of $VOCl_3{\cdot}CH_3CN$ in ca. 8 mL of CH_3CN was treated with 0.72 g of $(SiMe_3)_3PO_4$; the solution quickly became dark brown. After it was warmed to 40−50 °C for ca. 4 h the solution deposited 0.32 g of dark green octahedral crystals. After being allowed to stand for 2 days at room temperature, the filtered solution deposited an additional 0.08 g of dark green crystals, total yield 0.40 g (59%). Anal. Calcd $C_{24}H_{72}Cl_1O_{38}P_8Si_8V_6$: C, 16.17; H, 4.07; Cl, 1.99. Found: C, 16.39; 16.35; H, 4.11; 3.96; Cl, 2.06. EPR spectra were collected in pyridine as solvent (eight-line spectrum, $g = 2.00$, J_v=102 G).

Preparation of $[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ (2). Phenylphosphonic acid (0.63 g) was dissolved in 25 mL of methanol and 0.976 g of $VO(OiPr)_3$ was added dropwise with stirring. The dark brown mixture was stirred continuously as first 0.3 g of $[Et_4P][AlF_4]$ and then ~0.1 mL of water was added to it. As the water was added, the solution turned bright orange and an orange precipitate began to form. After stirring the resultant slurry for 10 min, the solid orange product was filtered and washed with a little methanol. The solid was then dissolved in 10 mL of acetonitrile, filtered, and allowed to crystallize by slow evaporation yielding bright orange crystals; yield 0.84 g (76%) Anal. Calcd $C_{32}H_{40}O_{18}F_1P_5V_4$: C, 35.25; H, 3.70; F, 1.74; P, 14.2; V, 18.69. Found: C, 35.30; H, 3.80; F, 1.68; P, 12.71; V, 18.91. ^{19}F NMR (CD_3CN): −176.0 (quintet, J_{F-P} 15.2 Hz). $\{^1H\}^{31}P$ NMR (CD_3CN): 20.5 br ($PhPO_3$); 41.2 s (Et_4P).

Preparation of $[Et_4P]^+[(V_2O_3)_2(O_3PO\text{-}n\text{-}Bu)_4F]^-$. Mixed mono-*n*-butyl and di-*n*-butyl phosphate (measured by ^{31}P NMR to be a 1:1 molar mixture; 0.364 g) was dissolved in 10 mL of methanol and 0.244 g of $VO(OiPr)_3$ was added dropwise with stirring, giving a brown solution. Addition of first 0.07 g of $[Et_4P][AlF_4]$ and then ~0.1 mL of water gave a bright orange solution. The remainder of the synthesis follows that described for **2** above except that evaporation of the orange acetonitrile solution gave only powdery material in 0.26 g yield (95%). ^{19}F NMR (CD_3CN): −174.3 (quintet, 15 Hz). $\{^1H\}^{31}P$ NMR (CD_3CN): 3.9 br ($BuOPO_3$), 41.8 s (Et_4P). ^1H NMR (CD_3CN): 4.07 (q), 2.09 (dq), 1.69 (tt), 1.44 (tq), 1.16 (dt), 0.94 (t).

Preparation of $[Et^4P]^+_{1.5}[(4\text{-}tert\text{-}butylpyridine)_2H]^+_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$ (3). A solution of 0.022 g $[Et_4P]^+[(V_2O_3)_2(O_3PMe)_4F]^-$ (prepared as for compound **2** above except using methylphosphonic acid) in pyridine-d_5 was treated with 0.0056 g of 1,4-cyclohexadiene and warmed to 90 °C. After 15 days the emerald-green solution was evaporated and the residue redissolved in CH_3CN (ca. 0.5 mL) with added 4-*tert*-butyl-pyridine (ca. 0.5 mL). Allowing the solvent to evaporate slowly under a N_2 atmosphere resulted in formation of a large, irregular-shaped green crystal of compound **3**; a portion of this crystal was used for the single crystal X-ray structure determination described below.

In a separate reaction, 0.045 g of $[Et_4P]^+[(V_2O_3)_2(O_3PMe)_4F]^-$ dissolved in a mixture of pyridine (1 mL), CH_3CN (ca. 0.5 mL), and 4-*tert*-butylpyridine (2 mL). The solution was boiled briefly to expel most of the CH_3CN and then treated with 0.13 g 1,4-cyclohexadiene

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(25) Daran, J.-C.; Jeannin, Y.; Constant, G.; Morancho, R. *Acta Cryst.* **1975**, *B31*, 1833−1837. Funk, H.; Weiss, W.; Zeising, M. *Z. Anorg. All. Chem.* **1958**, *296*, 36−45.

Table 10. Fractional Coordinates and Isotropic (Refined or Equivalent) Thermal Parameters (Å^2) for Compound **3**, $[Et_4P]_{1.5}[(4\text{-}\textit{tert}\text{-butylpyridine})_2H]_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$

atom	*x*	*y*	*z*	$B_{iso/eq}$
V(1)	0.12859(6)	0.35709(3)	0.45431	1.67(2)[a]
V(2)	0.27502(7)	0.33620(3)	0.57276(11)	1.77(2)[a]
V(3)	0.31404(6)	0.44205(3)	0.40685(11)	1.67(3)[a]
V(4)	0.33460(6)	0.36552(3)	0.28957(11)	1.75(2)[a]
P(1)	0.2075(1)	0.4227(1)	0.5767(1)	1.72(4)[a]
P(2)	0.2477(1)	0.2945(1)	0.3822(1)	1.85(4)[a]
P(3)	0.1789(1)	0.4110(1)	0.2847(1)	1.87(4)[a]
P(4)	0.4216(1)	0.3745(1)	0.4766(1)	1.90(4)[a]
P(5)	0.5210(2)	0.4961(1)	0.1998(2)	2.1(1)
P(6)	0.0069(1)	0.2643(1)	0.6834(2)	2.9(1)[a]
F(1)	0.2641(2)	0.3764(1)	0.4275(3)	1.8(1)[a]
O(1)	0.0412(3)	0.3458(1)	0.4667(4)	2.5(1)[a]
O(2)	0.2865(3)	0.3106(1)	0.6629(3)	2.5(1)[a]
O(3)	0.3456(3)	0.4858(1)	0.3947(3)	2.4(1)[a]
O(4)	0.3820(3)	0.3580(1)	0.1984(3)	2.4(1)[a]
O(5)	0.1740(2)	0.3331(1)	0.5534(3)	1.8(1)[a]
O(6)	0.3538(2)	0.4176(1)	0.3094(3)	1.8(1)[a]
O(11)	0.1383(2)	0.4074(1)	0.5236(3)	1.8(1)[a]
O(12)	0.2572(3)	0.3901(1)	0.6192(3)	1.7(1)[a]
O(13)	0.2562(3)	0.4505(1)	0.5171(3)	1.8(1)[a]
O(21)	0.1668(3)	0.3125(1)	0.3805(3)	2.1(1)[a]
O(22)	0.2879(3)	0.2968(1)	0.4748(3)	2.0(1)[a]
O(23)	0.2979(3)	0.3126(1)	0.3062(3)	2.0(1)[a]
O(31)	0.1198(3)	0.3895(1)	0.3412(3)	1.9(1)[a]
O(32)	0.2187(3)	0.4444(1)	0.3382(3)	2.0(1)[a]
O(33)	0.2369(3)	0.3822(1)	0.2424(3)	1.9(1)[a]
O(41)	0.3839(3)	0.3506(1)	0.5509(3)	2.2(1)[a]
O(42)	0.3962(2)	0.4181(1)	0.4776(3)	1.9(1)[a]
O(43)	0.4121(3)	0.3560(1)	0.3810(3)	2.0(1)[a]
N(1)	−0.0552(3)	0.4739(2)	0.4587(5)	2.3(1)[a]
C(1)	0.1693(6)	0.4527(2)	0.6679(5)	2.8(2)[a]
C(2)	0.2406(6)	0.2431(2)	0.3552(6)	3.0(2)[a]
C(3)	0.1294(5)	0.4338(2)	0.1917(6)	2.9(2)[a]
C(4)	0.5226(4)	0.3735(3)	0.4975(6)	2.9(2)[a]
C(51)	0.5183(4)	0.4584(2)	0.2728(6)	3.3(2)[a]
C(52)	0.5349(5)	0.4193(3)	0.2205(7)	4.8(3)[a]
C(53')	0.4594(9)	0.4879(4)	0.1001(11)	3.5(5)[a]
C(53")	0.3792(9)	0.4955(5)	0.1600(11)	2.8(4)[a]
C(54)	0.3697(7)	0.4705(4)	0.1071(10)	7.8(5)[a]
C(61)	−0.0425(6)	0.2689(2)	0.5795(7)	4.9(3)[a]
C(62)	−0.1245(7)	0.2816(3)	0.5848(11)	7.5(4)[a]
C(63)	−0.0082(5)	0.3080(2)	0.7497(6)	4.3(3)[a]
C(64)	0.0155(6)	0.3464(2)	0.7018(7)	4.6(3)[a]
C(65)	0.1077(5)	0.2582(2)	0.6688(6)	3.8(2)[a]
C(66)	0.1310(6)	0.2317(3)	0.5901(8)	5.4(3)[a]
C(67)	−0.0320(6)	0.2214(3)	0.7395(8)	6.0(4)[a]
C(68)	−0.0206(7)	0.2209(4)	0.8398(10)	8.4(5)[a]
C(71)	−0.1262(4)	0.4857(2)	0.4417(5)	2.1(2)[a]
C(72)	−0.1850(4)	0.4593(2)	0.4265(5)	2.3(2)[a]
C(73)	−0.1708(4)	0.4191(2)	0.4272(5)	1.9(2)[a]
C(74)	−0.0967(4)	0.4075(2)	0.4457(5)	2.5(2)[a]
C(75)	−0.0402(4)	0.4348(2)	0.4630(6)	2.9(2)[a]
C(76)	−0.2325(4)	0.3880(2)	0.4092(6)	2.6(2)[a]
C(77)	−0.3030(5)	0.4063(2)	0.3630(6)	3.3(2)[a]
C(78)	−0.2557(5)	0.3698(2)	0.5015(6)	3.7(2)[a]
C(79)	−0.2019(5)	0.3569(2)	0.3435(6)	3.9(2)[a]

[a] Refined with anisotropic thermal parameters: $B_{eq} = 4/3 \Sigma \Sigma b_{ij}a_ia_j$, where a_i and a_j refer to the real lattice constants.

and maintained at 70−90 °C for 2 days, depositing 0.030 g of green microcrystalline compound **3** (80% yield based on $[Et_4P]^+$). EPR (CH_3CN): 29-line pattern (g 2.00, J_v = 29.1 gauss).

X-ray Structural Analysis. Each of the three crystal structures was determined from intensity data collected on a diffractometer equipped with Mo Kα radiation and a low-temperature apparatus. The data sets were corrected for Lorentz and polarization effects but not for absorption (in all cases, ψ scans failed to show any significant variations). All the structures were solved by direct methods and refined by full-matrix, least-squares techniques. The refinement and analysis of the structures were carried out using a package of local programs.[26] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[27] In the least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weights, *w*, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. The crystallographic highlights are given in Table 1. Atomic coordinates, and selected distances and angles, are given in the tables described in the text. Atomic coordinates, anisotropic thermal parameters, and (for compounds **2** and **3** only) hydrogen atom positions, are available as supplementary material. Some important crystallographic details for each of the three structures are given below.

$(VO)_6(O_3POSiMe_3)_8Cl$ (1). The vanadyl phosphate chloride cluster was found to be disordered about a crystallographic 4/*m* site. While the heavy atoms (V, Cl, P, and Si) and the terminal vanadyl oxygen atoms were ordered, all of the phosphato oxygen atoms within the cluster surface as well as the methyl carbons were 2-fold disordered. A mirror plane is not possible for a static ordered structure but the attempted refinement of an ordered cluster in space group I4 was not successful. The V, P, Si, Cl, and vanadyl oxygen atoms were refined with anisotropic thermal parameters; the remaining oxygen atoms were refined with isotropic thermal parameters. Atomic coordinates are listed in Table 8. The hydrogen atoms were not included in the refinement. As a result of the disorder, the bond distances and angles (Tables 2 and 3) must be viewed with caution.

$[Et_4P]^+[(V_2O_3)_2(O_3PPh)_4F]^-$ (2). Although this structure is "ordered", the thermal parameters of the atoms associated with the Et_4P cation are rather high (even at −70 ° C) and this seems to have affected the overall quality of the data and, hence, of the structure. A particular manifestation of this effect was the inability to refine all of the hydrogen atoms into acceptable positions with reasonable thermal parameters. As a result, the hydrogen atoms were placed in idealized positions. Atomic coordinates of the non-hydrogen atoms are listed in Table 9. All of the non-hydrogen atoms were refined with anisotropic thermal parameters.

$[Et_4P]^+_{1.5}[(4\text{-}\textit{tert}\text{-butylpyridine})_2H]^+_{0.5}[(V_2O_3)_2(O_3PMe)_4F]^{2-}$ (3). One of the two crystallographically-independent Et_4P cations is disordered about a crystallographic 2-fold axis. Two of the ethyl groups are reasonably ordered but the phosphorous atom and the α-carbon atoms of the two other ethyl groups are disordered. In addition, the hydrogen atom which forms a hydrogen bond between the two *tert*-butylpyridine molecules is also disordered. All of the non-hydrogen atoms were refined with anisotropic thermal parameters, and their coordinates are listed in Table 10. The hydrogen atoms associated with the cluster were refined with isotropic thermal parameters as was the disordered hydrogen atom located between the two pyridine moieties. The hydrogen atoms of the *tert*-butylpyridine molecule and of the ordered Et_4P cation were placed in idealized positions. The hydrogen atoms of the disordered Et_4P cation were not included in the refinement. Attempts to determine the true polarity of the crystal were not successful.

Acknowledgment. We thank J. B. Jensen, S. Hill, P. Pulcher, and W. Marshall for technical assistance and J. Calabrese for a preliminary structure of compound **3**.

Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters for the nonhydrogen atoms, and hydrogen atom positions (for compounds **2** and **3** only) (20 pages). Ordering information is provided on any current masthead page.

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[26] Calabrese, J. C. Central Research and Development, E. I. Du Pont de Nemours and Co., PO Box 80228, Wilmington DE 19880−0228, 1991.

[27] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.