

Stereochemical Control of Cluster Size in Vanadium Phosphates

Ladd M. Mokry, Jeffrey Thompson, Marcus R. Bond, Tom Otieno, Madan Mohan, and Carl J. Carrano*

Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666

Received January 28, 1994

Vanadium phosphate systems have attracted much attention because of their unusual properties in the extended solid. Layered vanadium organophosphonates in particular have found applications as size selective inorganic hosts, catalyst supports, and ion exchangers.^{1–4} Zubieta and others have successfully exploited hydrothermal synthetic techniques to obtain a wealth of anionic cluster and layered oxovanadium organophosphonates that arise from a complex and incompletely understood chemistry.^{5–7} The biological effects of vanadium phosphates are also of current interest. Vanadocene dichloride, for example, has long been known as a potent anticancer agent⁸ and its *cis*-dichloro structure suggests a similarity to the widely studied *cis*-dichlorodiammineplatinum(II). However, Marks *et al.*⁸ have shown that unlike the latter complex the vanadocene reacts with the phosphate backbone of DNA rather than at the organic bases, indicating an entirely different mechanism of action.

Considering the fundamental interest in vanadium phosphate chemistry in terms of its solid-state and biological properties, it is surprising that little effort has been focused on its systematic development. Previous syntheses have relied primarily on extreme reaction conditions in which synthetic control is coarse and relatively unpredictable. It is only recently that more rational synthetic methods have begun to be explored.⁹ In this contribution we report on a series of vanadium phosphate clusters of varying nuclearities that, while differing widely in their structures, allow insight into a means for the rational design of such compounds. Specifically, by controlling the availability of open coordination sites on the metal (through variations in oxidation state and/or the ancillary organic ligation) and the denticity of the bridging phosphates, we have been able to achieve some influence over the nuclearity and structure of the resulting vanadium phosphate clusters.

All of the compounds reported in this study are readily obtained using standard synthetic techniques in organic or aqueous organic solvents. The divanadium(IV) complex $L_2(VO)_2[(\mu-C_6H_5O)_2-PO_2]_2$, **1** (where L is the tridentate hydridotris(pyrazolyl)borate ligand, $HB(pz)_3^-$), can be prepared by a number of routes. These include the aerobic oxidation of $L_2V_2(\mu-O)[(\mu-C_6H_5O)_2PO_2]_2$ ¹⁰ or the direct reaction of diphenyl phosphate with $LVO(acac)$ ¹¹ or $LVO(DMF)Cl$ ¹¹ in dichloromethane. In an attempt to prepare

the vanadium(III) analogue of **1** from the corresponding diacetate¹² using an excess of diphenyl phosphate the trimetallic complex $\{LV[(C_6H_5O)_2PO_2]_3\}_2Mg$, **2**, was isolated. The magnesium(II) ion comes from magnesium sulfate used as drying agent. The reaction of the vanadium(III) precursor, $LVCl_2 \cdot DMF$,¹¹ with the disodium salt of monophenyl phosphate in aqueous acetonitrile yields bright green crystals of the neutral tetravanadium(III) complex, $L_4V_4[(C_6H_5O)PO_3]_4$, **3**. The reaction of $[(t-Bupz)_4VO(H_2O)_2]Cl_2$ ¹³ (where *t*-Bupz is 3(5)-*tert*-butylpyrazole) and the sodium salt of monophenyl phosphate in water followed by recrystallization of the product from ethanol yielded blue crystals of the hexavanadium(IV) species, $(t-Bupz)_6-(C_6H_5OPO_3)_6(VO)_6(H_2O)_3 \cdot 2EtOH$, **4**.

The series of compounds containing vanadium capped by the facially coordinating tridentate hydridotris(pyrazolyl)borate ligand, **1–3**, shows the highest degree of synthetic control since only three *cis* coordination sites are open and available for ligation. The structure of the linear, centrosymmetric trimetallic cluster, **2**,¹⁴ illustrates this idea. Here the Mg(II) ion occupies the central position and is octahedrally coordinated to six bridging diphenyl phosphates. It is flanked on either side by V(III) ions which are also octahedrally coordinated with three facial sites occupied by oxygens from the bridging phosphates with the remaining three sites occupied by the tris(pyrazolyl)borate nitrogens. The rationale behind this structure is quite straightforward. Only three bridging ligands, at most, can coordinate to the $LV(III)^{2+}$ precursor because of the presence of the capping ligand. The resulting $LV[(C_6H_5O)_2PO_2]_3^-$ anion acts as a tridentate chelate, much like the Kläui ligand,¹⁵ two of which are perfectly suited for encapsulating a divalent metal atom.

The interplay between open metal coordination sites and bridging ligand denticity is underscored by the structure of the tetrametallic species **3**,¹⁶ obtained when the potentially tridentate monophenyl phosphate is used as a bridging ligand. Once again only three open coordination sites are available on the $LV(III)^{2+}$ precursor but now each coordinating phosphate is capable of bridging to two other $LV(III)^{2+}$ moieties. The result is a cubane-type structure (Figure 1) in which each phosphate coordinates three different V(III) centers and each V(III) center is, in turn, coordinated by three different phosphates. The cubane aspect of the structure is easily visualized in the polyhedral representation by placing four V(III) octahedra and four phosphate tetrahedra

- Müller, A.; Hovemeier, K.; Rohlfing, R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1192.
- Reuter, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1185.
- Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55.
- Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.
- Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 3700. Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J.; O'Connor, C. J. *Inorg. Chem.* **1993**, *32*, 3966. Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *212*, 199. Khan, M. I.; Chang, Y.; Chen, Q.; Hope, H.; Parking, S.; Goshorn, D. P.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1197.
- Kang, H. Y.; Lee, W. C.; Wang, S. L.; Lii, K. H. *Inorg. Chem.* **1992**, *31*, 4743. Lii, K. H.; Wu, L. S.; Gau, H. M. *Inorg. Chem.* **1993**, *32*, 4153.
- Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, Jr., E. W. *Chem. Mater.* **1990**, *2*, 91. Huan, G.; Jacobson, A. J.; Day, V. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 422. Huan, G.; Day, V. W.; Jacobson, A. J.; Goshorn, D. P. *J. Am. Chem. Soc.* **1991**, *113*, 3188.
- Toney, J. H.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7263.
- Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485.
- Carrano, C. J. Manuscript in preparation.
- Mohan, M.; Holmes, S. M.; Butcher, R. J.; Jasinski, J. P.; Carrano, C. J. *Inorg. Chem.* **1992**, *31*, 2029.

- Carrano, C. J.; Verastgue, R.; Bond, M. R. *Inorg. Chem.* **1993**, *32*, 3589.
- Mohan, M.; Otieno, T.; Bond, M. R.; Carrano, C. J. Submitted for publication.
- Crystal data for $\{[HB(pz)_3]V[(C_6H_5O)_2PO_2]_3\}_2Mg$, **2**: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 13.410(3)$ Å, $b = 14.179(3)$ Å, $c = 15.694(3)$ Å, $\alpha = 112.22(3)^\circ$, $\beta = 101.31(3)^\circ$, $\gamma = 106.15(3)^\circ$, $V = 2496.5(9)$ Å³, $\rho_{calc} = 1.412$ g cm⁻³, $Mo K\alpha \lambda = 0.71073$ Å, $\mu = 0.369$ mm⁻¹, 5811 unique data collected (θ - 2θ technique, $3.5 \leq 2\theta \leq 45.0^\circ$) of which 4299 have $I > 2\sigma(I)$ and were used for structure solution and refinement, $R = 0.0589$, $R_w = 0.0820$. Details of this and the other structures reported herein will be reported elsewhere.
- Kläui, W.; Müller, A.; Eberspach, W.; Boese, R.; Goldberg, I. *J. Am. Chem. Soc.* **1987**, *109*, 164. Shinar, H.; Navon, G.; Kläui, W. *J. Am. Chem. Soc.* **1986**, *108*, 5005.
- Crystal data for $[HB(pz)_3]_4V_4[(C_6H_5O)PO_3]_4$, **3**: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 15.495(3)$ Å, $b = 17.000(3)$ Å, $c = 17.949(4)$ Å, $\alpha = 89.17(3)^\circ$, $\beta = 86.00(3)^\circ$, $\gamma = 78.60(3)^\circ$, $V = 4623.5(16)$ Å³, $\rho_{calc} = 1.382$ g cm⁻³, $Mo K\alpha \lambda = 0.71073$ Å, $\mu = 0.536$ mm⁻¹, 12039 unique data collected (θ - 2θ technique, $3.5 \leq 2\theta \leq 45.0^\circ$) of which 9083 have $I > 2\sigma(I)$ and were used for structure solution and refinement, $R = 0.0504$, $R_w = 0.0692$.

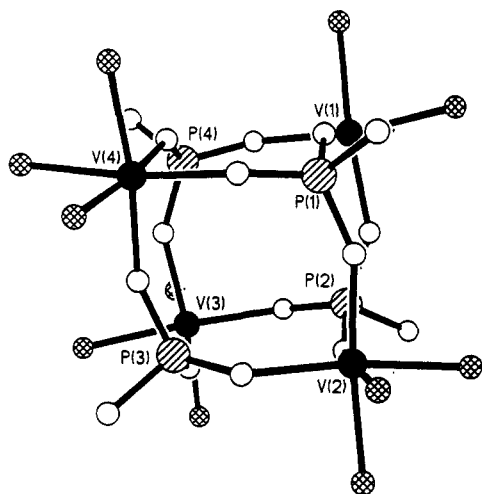


Figure 1. Ball and stick diagram of the core structure of **3** (V, solid; O, open; P, shaded; N, hatched; H, small open).

at alternate corners of a cube in a corner sharing arrangement. Vanadium(III) phosphates are in general uncommon,⁵ and discrete molecular complexes like **3** are to our knowledge unprecedented.

Limiting the availability of coordination sites on the metal by oxidation of V(III) to vanadyl appears to produce a concomitant reduction in cluster nuclearity. In this case three coordination sites are now occupied by the capping ligand and one by the vanadyl oxygen. Reaction with diphenyl phosphate therefore produces a simple bis(μ -phosphato) dimer, **1**,¹⁷ very much like one recently reported by Zubieta *et al.*,⁹ where the restrictions on both the vanadium coordination sphere and the denticity of the bridging ligand combine to suppress the condensation into a larger polynuclear cluster.

Conversely, cluster size can be increased when the V(IV) coordination sphere is opened up and a potentially tridentate bridge is employed. Thus the reaction between aquotetrakis-(3(5)-*tert*-butylpyrazole)vanadyl chloride and monophenyl phosphate yields a unique hexanuclear cluster, **4** (Figure 2).¹⁸ Although the starting compound would appear to have all of its coordination sites filled, the individual pyrazole ligands are easily displaced, and consequently, the cluster contains three distinctly different V(IV) coordination spheres. The structure of **4** is by far the most complicated of the discrete vanadium organophosphate compounds reported here. Nevertheless, the cluster exhibits a high degree of organization in which several diverse structural elements are pieced together with great efficiency. The cluster is on a site of 2-fold symmetry; thus, only half the cluster is unique. The three vanadyl coordination octahedra within the unique portion can be characterized as follows: (i) V(1), a tris(μ -phosphato)(μ -aqua)vanadyl hydrate with no coordinated pyrazoles, (ii) V(3), a tris(μ -phosphato)(pyrazolyl)vanadyl in

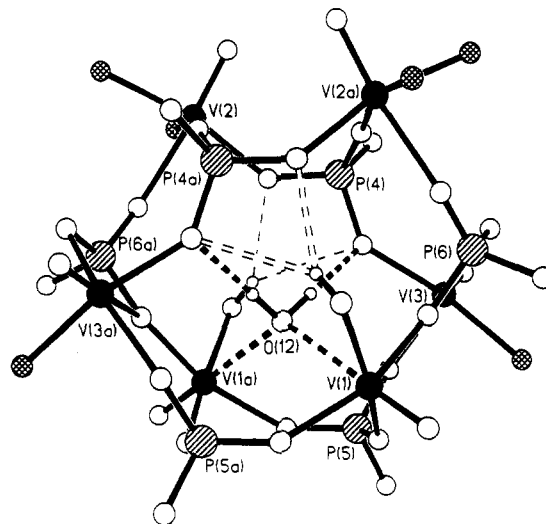


Figure 2. Ball and stick diagram of the core structure of **4**. Heavy dashed lines denote interactions with the included water; single and double dashed lines denote hydrogen bonding interactions with coordinated water at equatorial position V(1).

which one phosphate ligand is coordinated in a rare bidentate chelate bridging mode,¹⁹ and (iii) V(2), a tris(μ -phosphato)bis-(pyrazolyl)vanadyl species. Symmetry generation of the other half of the cluster produces a vase-like structure in which the symmetry related pair of V(1) octahedra from the base, the V(3) octahedra define the walls, and the V(2) octahedra define the mouth. The water molecule that bridges between the V(1) octahedra is actually found within the cavity of the vase with each oxygen lone pair coordinated to a different V(IV) ion (and *trans* to the vanadyl oxygens) and each hydrogen atom linked to a bridging phosphate (P(4)) oxygen. In addition the terminal water molecule of the V(1) octahedra also forms a bidentate hydrogen bond to oxygens on the same bridging phosphate to finish tying the cluster together.

Despite the serendipitous formation of this last cluster it in fact supports the basic ideas of vanadium phosphate cluster formation that we have formulated, i.e. use of a precursor V(IV) complex with a more open coordination sphere and of a tridentate bridging ligand leads to the largest cluster of this series. The manner in which the various pieces are fit together suggests a selectivity that could be controlled through a judicious choice of starting reagents or reaction conditions. For example most reactions reported here were carried out in organic media, resulting in a strong preference for neutral species over the anionic clusters typically found in oxovanadium organophosphate systems. The predictive utility of these synthetic ideas is still at an early stage; nonetheless, we have been able to use them to prepare a series of metal complexes with metal nuclearities ranging from 2 to 6 and to account for their structures in a rational way. The synthetic possibilities of this approach are now being examined by us.

Acknowledgment. This work was supported by grants from the Robert A. Welch Foundation (AI-1157), the NIH (GM47676-01), and the Texas Advanced Research Program (3615-002). Partial support for the X-ray diffraction facilities at SWT were provided by NSF-ILI Grant USE-9151286.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic thermal parameters for compounds **1–4** and selected bond lengths and angles for compounds **3** and **4** (10 pages). Ordering information is available on any current masthead page.

(17) Crystal data for $[\text{HB}(\text{pz})_3]_2(\text{VO})_2[(\mu\text{-C}_6\text{H}_5\text{O})_2\text{PO}_2]_2$, **1**: monoclinic, space group $P2_1/n$, $Z = 2$, $a = 9.4180(10)$ Å, $b = 19.5260(10)$ Å, $c = 13.1860(10)$ Å, $\beta = 90.080(10)^\circ$, $V = 2424.8(3)$ Å³, $\rho_{\text{calc}} = 1.449$ g cm⁻³, $\text{Mo K}\alpha \lambda = 0.71073$ Å, $\mu = 0.520$ mm⁻¹, 3682 unique data collected (θ - 2θ technique, $3.5 \leq 2\theta \leq 47.5^\circ$) of which 2743 have $I > 2\sigma(I)$ and were used for structure solution and refinement, $R = 0.0380$, $R_w = 0.0496$.

(18) Crystal data for $(t\text{-Bupz})_6(\text{C}_6\text{H}_5\text{OPO}_3)_6(\text{VO})_6(\text{H}_2\text{O})_3 \cdot 2\text{EtOH}$, **4**: monoclinic, space group $C2/c$, $Z = 4$, $a = 25.750(4)$ Å, $b = 15.171(2)$ Å, $c = 27.537(5)$ Å, $\beta = 95.00(1)^\circ$, $V = 10716(2)$ Å³, $\rho_{\text{calc}} = 1.438$ g cm⁻³, $\text{Mo K}\alpha \lambda = 0.71073$ Å, $\mu = 0.674$ mm⁻¹, 6910 unique data collected (θ - 2θ technique, $3.5 \leq 2\theta \leq 45.0^\circ$) of which 3216 have $I > 2\sigma(I)$ and were used for structure solution and refinement, $R = 0.0689$, $R_w = 0.0699$.

(19) Shoemaker, G. L.; Kostiner, E.; Anderson, J. B. Z. *Kristallogr.* **1980**, *152*, 317.