Synthesis and Structural Characterization of Binuclear Vanadium–Oxo–Organophosphonato Complexes: Building Blocks for Oxovanadium Organophosphonate Solids

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The metal–organophosphonate system spans a rich variety of coordination chemistry including monomolecular coordination compounds,[1,2] linear one-dimensional complexes,[3] and layered solid compounds.[4–6] The layered metal organophosphonates exhibit unusual sorptive and catalytic properties and serve as catalyst supports and ion exchangers.[7–11] Most specifically, the oxovanadium organophosphonate solids possess structurally well-defined internal void spaces and coordination sites which intercalate alcohols by coordination of the substrate molecule to the vanadium centers of the inorganic V/P/O layer. The shape selectivity of these phases in absorbing alcohols is related to the steric constraints imposed by the organic residues of the phosphonates surrounding the metal sites and to the interplay of hydrophobic and hydrophilic domains in the structure.[12] Reproducible syntheses of crystalline oxovanadium organophosphonates have been achieved by exploiting the techniques of hydrothermal synthesis. Minor modification of this preparative method has also yielded a number of polyoxovanadium organophosphonate anion clusters,[13–16] which are formed by condensation reactions about a guest molecule which serves as a template.[17]

In contrast to these developments in the self-assembly of oxovanadium organophosphonate solids and polyanions, the chemistry of small molecular systems in organic solvents under conventional synthetic conditions remains relatively unexplored.[18] In an attempt to isolate low molecular weight oxovanadium organophosphonates to serve as precursors for predictable fragment condensation into higher oligomers, we have isolated examples of binuclear oxovanadium(IV) and oxovanadium(V) organophosphonate complexes, $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]\cdot 2(C_6H_5)_4PCl$, **1**$\cdot 2(C_6H_4)_4PCl$, and $[(n\text{-}C_4H_9)_4N]_2[V_2O_4(C_6H_4CH_2PO_3)_2]$, **2**, respectively.

The reaction of $(C_6H_4)_4P[VO_2Cl_2]$ with $C_6H_4PO_3H_2$ in alcohol treated with a small amount of aqueous acid (eq 1) yields shiny blue paramagnetic crystals of $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]\cdot 2(C_6H_5)_4PCl$ **1**$\cdot 2(C_6H_5)_4PCl$, in 90% yield.[19] While the identity of the reducing agent has not been confirmed, alcoholic solvents are required for product formation, suggesting that the alcohol serves in this capacity. It is also noteworthy that **1** may be isolated only from the $(C_6H_5)_4P^+$ salt of $[VO_2Cl_2]^-$, an observation which implicates the large cation of the cocrystallized organic salt in preventing the close approach of binuclear units of **1** and condensation into large oligomers or into layered solids. Thus, attempts to prepare **1** from smaller quaternary ammonium salts $(R_4N)[VO_2Cl_2]$ (R = –Me, –Et, n-C_4H_9) invariably resulted in insoluble materials, analyzing as $[VO(C_6H_5PO_3)]\cdot H_2O$.[5] The infrared spectrum of **1**$\cdot 2(C_6H_5)_4PCl$ exhibited a band at 929 cm^{-1} attributed to $\nu(V{=}O)$ and features in the 1000–1200-cm^{-1} range associated with the phosphonate ligand.

$$2(C_6H_5)_4P[VO_2Cl_2] + 2C_6H_5PO_3H_2 + RCH_2OH \xrightarrow{H^+} [V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2] + 2RCHO + 2(C_6H_5)_4PCl \quad (1)$$

The structure of **1**$\cdot 2(C_6H_5)_4PCl$[20] consists of discrete binuclear units of $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]$ (**1**), shown in Figure 1, cocrystallizing with $(C_6H_5)_4P^+$ cations and Cl^- anions. The neutral binuclear complex **1** sits at a crystallographic inversion center located at the midpoint of the V1–V1a vector. The overall structure may be described in terms of two vanadium(IV) square pyramids and two phosphonate tetrahedra in a corner-sharing arrangement. Each vanadium site is coordinated to a terminal oxo group, two phosphonate oxygen donors, and exocyclic chloride and H_2O ligands. The crystallographically imposed symmetry dictates that the vanadium oxo groups adopt an *anti* orientation. Each organophosphonate ligand bridges vanadium centers through two oxygen donors, while the third oxygen is protonated and pendant. The resultant eight-membered ring $[V{-}O{-}P{-}O{-}]_2$ is a structural motif common to vanadium organophosphonate solids[5] and to layered vanadium oxide phosphate solids.[21–23]

In contrast to the chemistry of $(C_6H_5)_4P[VO_2Cl_2]$ with organophosphonates in alcoholic solutions, $[(n\text{-}C_5H_9)_4N]_3V_5O_{14}$

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(19) Synthesis of **1**$\cdot 2(C_6H_5)_4PCl$: Phenylphosphonic acid (1.3 g, 8 mmol) was dissolved in degassed $ClCH_2CH_2OH$ (30 mL) under a dinitrogen atmosphere. Addition of $(C_6H_5)_4P[VO_2Cl_2]$ (2.0 g, 4 mmol) resulted in an intense red solution. After addition of a small amount of aqueous acid (0.5 mL, 5% HCl), the reaction mixture was stirred for 48 h at room temperature. The resultant red solution was evaporated under vacuum to 20 mL and carefully layered with diethyl ether (60 mL) to give shiny blue plates of **1**$\cdot 2(C_6H_5)_4PCl$. Yield: 1.70 g (90%). Anal. Calcd for $C_{60}H_{56}O_{10}P_4Cl_4V_2$: C, 55.2; H, 4.30. Found: C, 55.0; H, 4.42. IR (KBr pellet, cm^{-1}): 1586 (m), 1484 (m), 1436 (s), 1202 (m), 1136 (m), 1106 (m), 1068 (s), 1015 (2), 929 (s), 758 (m), 722 (s), 687 (m), 584 (w), 528 (s).

(20) Crystal data for $C_{60}H_{56}Cl_4O_{10}P_4V_2$ (**1**$\cdot 2(C_6H_5)_4PCl$): triclinic space group $P\bar{1}$, a = 11.489(2) Å, b = 13.523(3) Å, c = 10.956(2) Å, α = 103.60(2)°, β = 106.58(2)°, γ = 102.50(2)°, V = 1510,4(8) Å^3, Z = 1, D_{calc} = 1.430 g cm^{-3}. Structure solution and refinement based on 3346 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, λ = 0.710 73 Å) converged at R = 0.0814.

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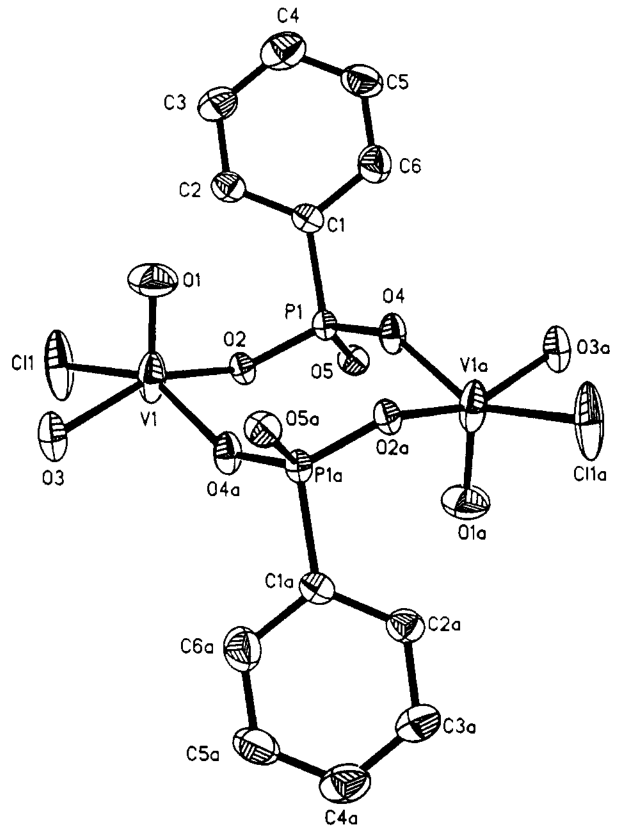

Figure 1. View of the structure of $[V_2O_2Cl_2(C_6H_5PO_3H)_2]$ (**1**). Selected bond lengths (Å): V1–Cl1, 2.288(4); V1–O1, 1.627(6); V1–O2, 1.971(6); V1–O3, 2.003(6); V1–O4, 1.932(7); P1–O2, 1.505(5); P1–O4, 1.504(7); P1–O5, 1.567(7).

reacts with $2\text{-}CH_3C_6H_4CH_2PO_3H_2$ in methanol to give bright red diamagnetic crystals of the binuclear V(V) species $[(n\text{-}C_4H_9)_4N]_2[V_2O_4(CH_3C_6H_4CH_2PO_3)_2]$ **2**.[25] The infrared spectrum of **2** exhibits bands at 969 and 942 cm^{-1} atributed to ν_s and ν_{as} for the *cis*-dioxovanadate group and features in the 1000–1220-cm^{-1} range associated with the organophosphonate ligand. The ^{51}V NMR spectrum of **2** shows a single band at −564 ppm.

The structure of the anion of **2**,[26] shown in Figure 2, sits at a crystallographic inversion center and may be described as two vanadium tetrahedra bridged by two phosphorus tetrahedra through corner-sharing interactions. Each vanadium(V) site bonds to two terminal oxo groups in a *cis* geometry and to two oxygens from the μ_2-bridging $(CH_3C_6H_4CH_2PO_3)^{2-}$ ligands. Curiously, the pendant oxygen of the (2-methylbenzyl)phosphonato(2−) ligand is *not* protonated, as indicated by the short P–O bond distance of 1.459(4) Å and by the charge requirements of the anion of **2**. While complex **2** contains V(V) rather than V(IV), the cyclic eight-membered structural unit $[V–O–P–O]_2$ displayed by **1** is retained.

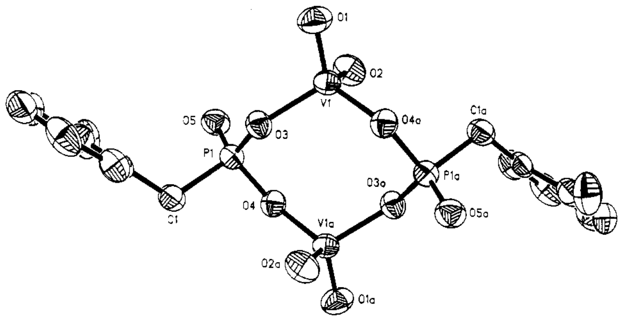

Figure 2. View of the structure of the molecular anion of **2**, $[V_2O_4(CH_3C_6H_5CH_2PO_3)_2]^{2-}$. Selected bond lengths (Å) and angles (deg): V1–O1, 1.607(4); V1–O2, 1.605(4); V1–O3, 1.866(4); V1–O4, 1.849(4); P1–O3, 1.554(4); P1–O4, 1.575(4); P1–O5, 1.458(4); O1–V1–O2, 108.0(2); O1–V1–O3, 109.8(2); O1–V1–O4, 108.4(2); O2–V1–O3, 109.4(2); O2–V1–O4, 110.1(2); O3–V1–O4, 111.1(2).

Although binuclear oxovanadium(V) complexes are common,[27] those with tetrahedrally coordinated vanadium are relatively unusual and were limited to complexes of siloxide, aryloxide, or alkoxide ligands.[27–29] Furthermore, **2** represents an unusual example of a tetrahedral V(V) complex with the *cis*-dioxovanadate core, $[VO_2]^+$.[30]

As anticipated, both **1** and **2** serve as precursors for condensation into larger oligomers and inorganic solids. The controlled hydrolysis of **1** in methanol yields microcrystalline green products, one of which has been identified as $[(C_6H_5)_4P]_2[V_6O_{10}(C_6H_5PO_3)_4(C_6H_5PO_3H)_2]$, which is most likely structurally analogous to $(TBA)_2\{V_6O_{10}(C_6H_5AsO_3)_4(C_6H_5AsO_3H)_2]$.[31] Under more rigorous conditions, **1** will react to give an insoluble material of composition $VO(C_6H_5PO_3)\cdot H_2O$. Comparison of the structures of **1** and $VO(C_6H_5PO_3)\cdot H_2O$[5] reveals that **1** is a building block for the layer structure. Thus, binuclear units of **1** may fuse by ligation of the pendant oxygens of the organophosphonate groups to adjacent $\{VO(C_6H_5PO_3)\}_2$ units with concomitant loss of HCl and displacement of the coordinated water into the interlamellar region. Similarly, the reaction of **2** in methanol with excess organophosphonate yields $(TBA)[V_5O_7(OCH_3)_2(CH_3C_6H_4CH_2PO_3)_5]$.[18] In contrast, under refluxing conditions, the alcohol serves as a reductant for the vanadium and a mixture of oligomers containing V(IV) is obtained. The identity of these products is currently under investigation.

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Supplementary Material Available: Tables of crystallographic parameters, atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom positions for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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[25] Synthesis of **2**: (2-Methylbenzyl)phosphonic acid (0.926 g, 5.00 mmol) was added to a suspension of $[(C_4H_9)_4N]_3V_5O_{14}$ (1.20 g, 1.00 mmol) in methanol (35 mL). After stirring at room temperature for 16 h, the brownish red solution which developed was evaporated to dryness. The resultant viscous material was dissolved in CH_2Cl_2 (20 mL), and the solution was carefully layered with hexane. After the solution was left standing at 0 °C for 8 days, light yellow crystals of **2** were collected and washed with acetone and diethyl ether. Recrystallization from hexane/dichloromethane afforded X-ray-quality crystals (yield: 40%). The crystals of **2** rapidly became opaque upon removal from solution, necessitating mounting of wet crystals and rapid transfer to the diffractometer cold stream (−60 °C) for the X-ray study. Anal. Calcd for $C_{48}H_{90}N_2O_{10}P_2V_2$: C, 56.5; H, 8.82. Found: C, 56.6; H, 8.75. IR (KBr pellet, cm^{-1}): 2956 (s), 2864 (m), 1481 (m), 1452 (w), 1378 (w), 1212 (s), 1005 (s), 969 (s), 942 (s), 782 (w), 730 (w), 639 (w). ^{51}V NMR (ppm): −564, $VOCl_3$ reference.

[26] Crystal data for $C_{48}H_{90}N_2O_{10}P_2V_2$ (**2**): monoclinic space group $P2_1/c$, $a = 9.689(2)$ Å, $b = 16.670(3)$ Å, $c = 17.081(3)$ Å, $\beta = 93.85(3)°$, $V = 2752(1)$ Å^3, $Z = 2$, $D_{calc} = 1.229$ g cm^{-3}. Structure solution and refinement based on 2478 reflections (Mo Kα, $\lambda = 0.710\ 73$ Å) converged at $R = 0.0603$.

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