of $[K_4(OSiPh_3)_4(DME)]_2(DME)$,[13] $HC(CPh_2)_2Na(OEt_2)$,[14] and $Na_2(Ph_2CCPh_2){\cdot}2OEt_2$,[15] the last showing another rare example of an alkali-metal bis(η^6-arene) bridge between adjacent molecules of a linear chain. However, to the best of our knowledge, $KBPh_4$ is the only other example of the formation of an infinite chain structure through potassium–η^6-arene interactions. Work is currently in progress to characterize the potassium salts of other lanthanide aryloxide anions to provide more information on the generality of this phenomenon. To this end, we have found at least one other example in the solid-state structure of $K[Er(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$.[16]

Acknowledgment. We thank Dr. A. P. Sattelberger and Dr. J. L. Atwood for helpful discussions, the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-36.

Supplementary Material Available: Tables of data collection parameters, fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters (8 pages); a table of observed and calculated structure factors for $K[Nd(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4]$ (10 pages). Ordering information is given on any current masthead page.

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Received January 24, 1992

Hexavanadium Polyoxo Alkoxide Anion Clusters: Structures of the Mixed-Valence Species $(Me_3NH)[V^{IV}_5V^VO_7(OH)_3\{CH_3C(CH_2O)_3\}_3]$ and of the Reduced Complex $Na_2[V^{IV}_6O_7\{CH_3CH_2C(CH_2O)_3\}_4]$

While the coordination chemistry of polyoxomolybdates has received considerable attention,[1] the chemistry of covalent polyoxovanadium derivatives remains largely unexplored. By employment of the tetraalkylammonium salts of polyvanadates,[2] a number of polyvanadate coordination complexes have been prepared in aprotic, polar solvents.[3-5] Among these is an example of the hexavanadate core, stabilized by organic ligand subunits, $[V_6O_{13}\{RC(CH_2O)_3\}_2]^{2-}$,[4] whose structural core is similar to that of $[(C_5Me_5)Rh]_4(V_6O_{19})$.[6] The latter species provides an example of the emerging class of oxoalkoxometalate aggregates.[4,7] Furthermore, the $[V_6O_{13}\{RC(CH_2O)_3\}_2]^{2-}$ clusters were found to undergo well-behaved reduction processes to give a series of mixed-valence and fully reduced clusters, $[V^V_{6-n}V^{IV}_nO_{13-n}(OH)_n\{RC(CH_2O)_3\}_2]^{2-}$ (n = 2, 4, 6),[8] novel examples of the growing class of V(IV)-containing polyoxoanions.[9-16] In an effort to extend the chemistry of oxoalkoxovanadium clusters, we have exploited hydrothermal synthesis[17] in the preparation of a series of hexavanadium clusters with variable alkoxide stoichiometries and numbers of reduced metal sites, as represented by $(Me_3NH)[V^{IV}_5VO_7(OH)_3\{CH_3C(CH_2O)_3\}_3]$ (**1**) and $Na_2[V^{IV}_6O_7\{CH_3CH_2C(CH_2O)_3\}_4]$. The results demonstrate that the hydrothermal technique, which has been shown to give numerous unusual polyoxomolybdates and polyoxovanadates of phosphorus,[18,19] may also be applied to the synthesis of complexes of polyoxometalates with common organic ligands.

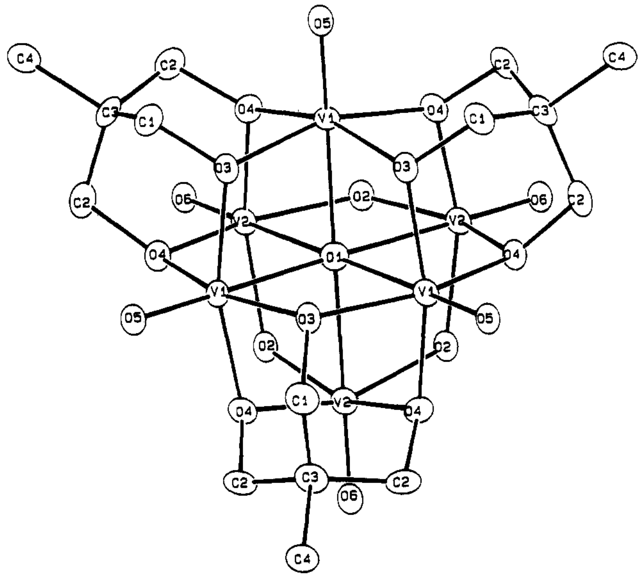

Figure 1. ORTEP view of the structure of $[V_6O_7(OH)_3\{CH_3C(CH_2O)_3\}_3]^-$ (**1a**). Selected bond lengths (Å): V1–O1, 2.236 (7); V1–O3, 2.001 (4); V1–O4, 2.010 (4); V1–O5, 1.608 (7); V2–O1, 2.382 (8); V2–O2, 1.974 (4); V2–O4, 1.976 (4); V2–O6, 1.600 (7).

The reaction of NH_4VO_3, V_2O_3, $CH_3C(CH_2OH)_3$, $(Me_3NH)Cl$, and water in the mole ratio 3:6:10:5:200 at 200 °C for 3 days gave sky blue crystals of $(Me_3NH)[V_6O_7(OH)_3$-

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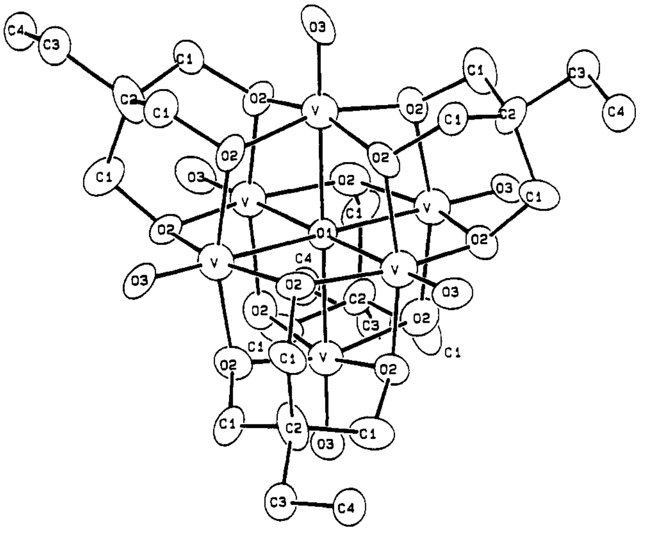
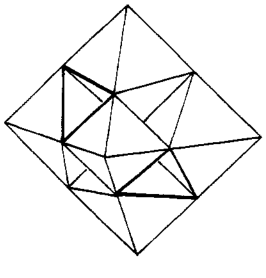


Figure 2. ORTEP view of $[\mathrm{V_6O_7\{CH_3CH_2C(CH_2O)_3\}_4}]^{2-}$ (**2a**). Selected bond lengths (Å): V–O1, 2.315 (2); V–O2, 2.003 (5); V–O3, 1.593 (7).

$\{\mathrm{CH_3C(CH_2O)_3}\}_3]$ (**1**).[20] The infrared spectrum of **1** exhibited characteristic features at 1044 cm^{-1} and 978 and 950 cm^{-1} associated with ν(C–O) of the ligand and $\nu(\mathrm{V{-}O_t})$, respectively. A band at 726 cm^{-1} was attributed to ν(V–O–V) of the bridging hydroxo groups. The complex $\mathrm{Na_2[V_6O_7\{CH_3CH_2C(CH_2O)_3\}_4]}$ (**2**) was synthesized in a similar fashion, using $\mathrm{NaVO_3}$ as the vanadate source and $\mathrm{CH_3CH_2C(CH_2OH)_3}$ as ligand and using the same mole ratio as for **1**.[21] The infrared spectrum of **2** exhibits a strong band at 950 cm^{-1} assigned to $\nu(\mathrm{V{-}O_t})$ and features at 1116 and 1047 cm^{-1} associated with ν(C–O) and group vibrations of the ligand. The absence of strong bands in the 750–900-cm^{-1} range indicates the absence of doubly-bridging oxo groups.

The X-ray structure of **1**[22] revealed the presence of $\mathrm{Me_3NH^+}$ cations and discrete molecular anions $[\mathrm{V_6O_7(OH)_3\{CH_3C(CH_2O)_3\}_3}]^-$ (**1a**), shown in Figure 1. The structure may be viewed as a partially reduced hexavanadate core $\{\mathrm{V_6O_{19}}\}$ supporting three $[\mathrm{CH_3C(CH_2)_3}]^{3+}$ subunits. The structure of **1a** is related to that of the conventional hexametalate core $\{\mathrm{M_6O_{19}}\}$ by replacement of nine doubly-bridging oxo groups by nine ligand alkoxy donors. The substitution pattern adopted by the ligands reflects the steric requirements of the trisalkoxy groups which preferentially bridge three metals in a triangular arrangement. The ligands cap the triangular faces of the tetrahedral cavities of the hexametalate framework shown schematically as follows:



Although four of eight cavities may be occupied by the bridging tridentate ligands, only three sites are occupied in **1a**. It is clear that an additional trisalkoxy ligand may be incorporated into the core.

The oxidation-state assignment of cluster **1a** is consistent with potentiometric titrations which show five V(IV) sites and with valence sum calculations.[23] This assignment requires that the bridging oxygen atoms be in the protonated or hydroxy form. The V–O3 distances of 1.98 (1) Å are consistent with this assignment, since doubly-bridging oxo groups in reduced vanadium clusters exhibit distances of 1.87 (1) Å,[17] while doubly-bridging hydroxy groups fall in the 1.97–2.00-Å range.[8]

The structure of the molecular anion $[\mathrm{V_6O_7\{CH_3CH_2C(CH_2O)_3\}_4}]^{2-}$ (**2a**),[24] shown in Figure 2, confirms that four ligand sites may be occupied about the $\{\mathrm{V_6O_{19}}\}$ core, with substitution of all twelve doubly-bridging oxo groups by doubly-bridging alkoxy donors. The geometric consequences of substitution and reduction of the $\{\mathrm{V_6O_{19}}\}$ core are most clearly manifest in core expansion. As illustrated in Figure 3, the effect is clearly demonstrated by comparing the spacings *c* between the outermost approximately planar layers of negatively charged oxygen atoms for $[\mathrm{V_6O_{19}\{Rh(C_5Me_5)\}_4}]$, $[\mathrm{V^V{}_6O_{13}\{CH_3C(CH_2O)_3\}_2}]^{2-}$, $[\mathrm{V^VV^{IV}{}_5O_7(OH)_3\{CH_3C(CH_2O)_3\}_3}]^-$ (**1a**), and $[\mathrm{V^{IV}{}_6O_7\{CH_3CH_2C(CH_2O)_3\}_4}]^{2-}$ (**2a**) of 4.40, 4.36, 4.53, and 4.54 Å, respectively.

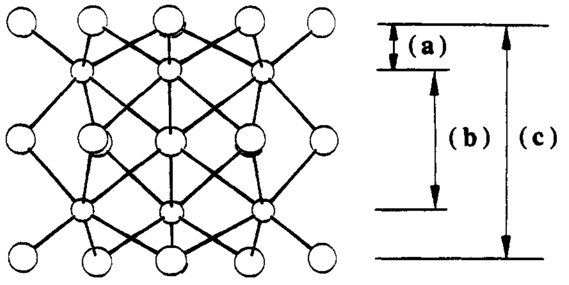


Figure 3. Schematic representation of the $\{\mathrm{V_6O_{19}}\}$ core viewed as planar layers of negatively changed closed-packed oxygen atoms separated by layers of vanadium cations: for $[\mathrm{V_6O_{19}\{Rh(C_5Me_5)\}_4}]$, *a* = 0.89 Å, *b* = 2.59 Å, and *c* = 4.40 Å; for $[\mathrm{V_6O_{13}\{CH_3C(CH_2O)_3\}_2}]^{2-}$, *a* = 1.01 Å, *b* = 2.36 Å, and *c* = 4.36 Å; for $[\mathrm{V_6O_7(OH)_3\{CH_3C(CH_2O)_3\}_3}]^-$, *a* = 0.93 Å, *b* = 2.69 Å, and *c* = 4.53 Å; for $[\mathrm{V_6O_7\{CH_3CH_2C(CH_2O)_3\}_4}]^{2-}$, *a* = 0.94 Å, *b* = 2.67 Å, and *c* = 4.54 Å.

The magnetic properties of **1** and **2** are quite distinct. Compound **1** exhibits a room-temperature effective moment (μ_{eff}) per molecule of 3.40 μ_B, compared to a theoretical spin-only moment of 3.87 μ_B for a system of five V(IV) d^1 sites. The data approach Curie–Weiss behavior with a Curie temperature $\Theta = -40$ K. The magnetic moment decreases from a value of 1.52 μ_B/V(IV) site at 300 K to 1.27 μ_B at 40 K, indicating net antiferromagnetic exchange coupling. The effective magnetic moment of **2** is 3.52 μ_B/molecule at 300 K, compared to a spin-only value of 4.24 μ_B/molecule for six V(IV) d^1 centers. The magnetic susceptibility behavior with temperature exhibits an antiferromagnetic transition at a Néel temperature of 38 K. The effective magnetic moment at 5 K is 0.49 μ_B/molecule, indicative of long-range antiferromagnetic ordering.

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(20) Anal. Calcd for $\mathrm{C_{18}H_{40}NO_{19}V_6}$: C, 24.5; H, 4.55; N, 1.59; V, 34.8. Found: C, 24.3; H, 4.72; N, 1.38; V, 34.7. IR (KBr pellet, cm^{-1}): 2890 (m), 2847 (m), 1460 (w), 1397 (w), 1136 (m), 1044 (s), 978 (s), 949 (s), 726 (m), 615 (m), 574 (s), 487 (m). Potentiometric titration was consistent with an average vanadium oxidation state of 4.2.

(21) Anal. Calcd for $\mathrm{C_{24}H_{44}O_{19}Na_2V_6}$: C, 29.1; H, 4.45; V, 31.0. Found: C, 28.8; H, 4.30; V, 29.8. IR (KBr pellet, cm^{-1}): 2966 (sh), 2912 (m), 2858 (m), 1632 (m), 1467 (m), 1445 (m), 1402 (m), 1303 (w), 1202 (m), 1116 (s), 1047 (s), 983 (sh), 950 (s), 771 (w), 603 (s), 570 (s), 488 (s).

(22) Crystal data for $\mathrm{C_{18}H_{40}NO_{19}V_6}$ (**1**): hexagonal space group $P6_3mc$, $a = 12.792$ (2) Å, $c = 10.692$ (2) Å, $V = 1515.2$ (12) Å^3, $Z = 2$, $D_{\mathrm{calc}} = 2.17$ g cm^{-3}. Structure solution and refinement based on 651 reflections with $I_0 \geq 3\sigma(I_0)$ converged at $R = 0.046$. Attempts to refine the structure in the alternative space groups $P\bar{6}2c$ and $P6_3/mmc$ proved unsuccessful.

(23) Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1976**, *B32*, 1957. On the basis of the averaged summation $\sum_i (d(\mathrm{V}-\mathrm{O}_i)/1.78)^{-5.15}$, the average valence sum for the V centers of **1** is 4.25, consistent with five V(IV) sites and one V(V) site. The valence sum for the V centers of **2** is 4.1, confirming the assignment of the cluster as fully reduced.

(24) Crystal data for $\mathrm{C_{24}H_{44}O_{19}Na_2V_6}$ (**2**): cubic space group $Fd3$, $a = 19202$ (2) Å, $V = 7076.7$ (21) Å^3, $Z = 8$, $D_{\mathrm{calc}} = 1.854$ g cm^{-3}. Structure solution and refinement based on 316 unique reflections with $I \geq 3\sigma(I)$ converged at $R = 0.056$. The methyl carbon C4 is disordered about the 3-fold axis, occupying a general position at $^1/_3$ occupancy. Attempts to refine the structure in the alternative space group $Fd3m$ resulted in a significantly higher residual and several unreasonably large temperature factors.

Acknowledgment. This work was supported by NSF Grant CHE 9119910.

Supplementary Material Available: For the X-ray studies of 1 and 2, tables of crystal data and experimental conditions, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors (11 pages); tables of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Articles

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$Zn_4O(acetate)_6$, a Well-Tailored Molecular Model of ZnO. An Experimental and Theoretical Investigation of the Electronic Structure of $Zn_4O(acetate)_6$ and ZnO by Means of UV and X-ray Photoelectron Spectroscopies and First Principle Local Density Molecular Cluster Calculations

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Received November 21, 1991

A thorough investigation of the electronic structure of $Zn_4O(acetate)_6$ and ZnO has been used to test the hypothesis that the former compound is a well-tailored molecular model of the latter solid. First principle local density molecular cluster calculations relative to $Zn_4O(acetate)_6$ and ZnO indicate that the tetrahedral arrangement of four Zn atoms around the central oxygen present in the title compound is a very good model of the oxygen chemical environment in ZnO. Furthermore, the obtained theoretical results allowed us to describe the rather complex nature of the lowest energy electronic absorption transition of $Zn_4O(acetate)_6$, pointing out once more the leading role played by the tetrahedral arrangement of the central oxygen to explain the observed optical properties. Moreover, the computed different electronic charges found in the nearest volume surrounding unlike oxygen atoms in $Zn_4O(acetate)_6$ and transition state ionization energies were found to agree very well with X-ray and UV photoelectron measurements, respectively. Quite surprisingly, a satisfactory description of the electronic structure of the solid ZnO by means of the $OZn_4O_{12}{}^{18-}$ cluster, embedded in the ZnO crystalline potential, was obtained only by using an extended basis set for the oxygen atoms, including their 3s and 3p virtual levels. In such a case, the agreement between the computed Zn and O partial density of states, the HOMO–LUMO ΔE, and literature experimental data was excellent and allowed to gain new insights into the Zn–O covalent interaction.

Introduction

In the last decade several theoretical molecular cluster investigations have been devoted to the study of the electronic structure of metal oxides and of defect centers in these materials.[2] Actually, a common feature of these oxides is their nonstoichiometry as a consequence of a significant percentage of oxygen vacancies which combine to determine the electronic properties of these materials.[3] In such cases, the molecular cluster approach is not only computationally attractive with respect to the ordinary band structure approximation but also physically reasonable, obviously by providing suitable boundary conditions, because it allows one to obtain a detailed estimate of the local values of the potential very close to the crystal structure defect.

In a recent contribution Kunkely and Vogler[4] reported the electronic absorption and emission spectra in the visible and UV regions of an EtOH solution of $Zn_4O(acetate)_6$ [(μ_4-oxo)hexakis(μ-acetato)tetrazinc], which was assumed to be a well-suited molecular model of ZnO. An interesting feature of the experimental data they measured was the relative highly efficient luminescence (quantum yield $\phi = 0.15$ in solution at room temperature) for a compound containing the formally closed shell d^{10} Zn^{2+} ion. Moreover, it is worth of note that Blasse et al.[5,6] reported and discussed in the near past the emission and excitation spectra in the visible and UV regions of crystalline $Zn_4O(BO_2)_6$, which also shows a relatively high luminescence efficiency at room temperature.

Both $Zn_4O(acetate)_6$ and $Zn_4O(BO_2)_6$ are characterized by the presence of an oxygen ion at the center of a tetrahedron of zinc ions tetrahedrally coordinated by oxygen (see Figure 1a),[7,8] so

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