A Cyclic Octanuclear Polyoxoalkoxyvanadate(IV) with an Oxalate-Binding Cavity, $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$. Structural Comparison with the Analogous Polymolybdate(V) Complex $[(n\text{-}C_4H_9)_4N]_2[Mo_8O_{16}(OC_2H_5)_8(C_2O_4)]$

Although the coordination chemistry of polyoxomolybdates has received considerable attention,[1] the synthesis of analogous covalent polyoxovanadate derivatives remains relatively undeveloped.[2] The recent isolation and characterization of several polyvanadate tetra-*n*-butylammonium salts soluble in aprotic, polar solvents, such as $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$,[3] $[(n\text{-}C_4H_9)_4N]_4[V_{12}O_{32}]\cdot CH_3CN$,[4] and $[(n\text{-}C_4H_9)_4N]_3[V_5O_{14}]$,[5] provide a starting point for such syntheses. We report here a structurally characterized example of a polyoxovanadate coordination complex, $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$.

When rhodizonic acid dihydrate, $C_6H_2O_6\cdot 2H_2O$ (0.305 g, 1.48 mmol), is added to a solution of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.00 g, 0.592 mmol) in 50 mL of methanol under an atmosphere of dry N_2 and stirred for 6 h at room temperature, a deep green solution is obtained. After concentration of this solution to 20 mL, followed by addition of 20 mL of diethyl ether and allowing this mixture to stand for 48 h at −40 °C, light green, needlelike, crystals of $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$ were obtained in 73% yield.[6] The diamagnetic compound is slightly air- and moisture-sensitive, requiring some care in handling. The infrared spectrum exhibits a band at 2820 cm^{-1} associated with the C–H stretching modes of the methoxy groups, a strong band at 1618 cm^{-1} assigned to the carbonyl stretching vibrations of oxalate CO residues, and a strong band at 980 cm^{-1} associated with $\nu(V{=}O_t)$ stretching vibrations (O_t = terminal oxo group). The absence of bands in the 800–900-cm^{-1} range establishes the absence of bridging oxo groups.

X-ray structural analysis of $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$[7] revealed the presence of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$ anions that contain an octagonal array of $[VO]^{2+}$ centers, doubly bridged by methoxy groups to produce a cyclic tiara framework $[V_8O_8(OCH_3)_{16}]^0$. The V–V distances are nearly identical, with an average value of 2.997 (2) Å. The methyl substituents of the bridging methoxy groups are oriented such that the O–C bond vectors are directed away from the cycle of point inward for alternate bridging pairs. The V_2O_2 rhombi of the former groupings are planar, in contrast to those for the latter, which are folded about the O···O vectors. The bridging methoxy groups are further distinguished by the V–O–V valance angles, which average 92.3 (3) and 99.6 (3)° for the units with exocyclic and endocyclic directed O–C vectors, respectively.

The cavity produced by the cyclic $[V_8O_8(OCH_3)_{16}]^0$ units is occupied by an oxalate moiety, $[C_2O_4]^{2-}$. Each oxygen of the oxalate group bridges two V centers spanned by the alkoxy bridge pairs with O–C vectors oriented in the exocyclic fashion. The oxalate unit, the eight V centers, and the eight terminal oxo groups form a planar $[V_8O_8(C_2O_4)]^{14+}$ unit, with a maximum deviation of 0.01 Å from the best plane through all atoms.

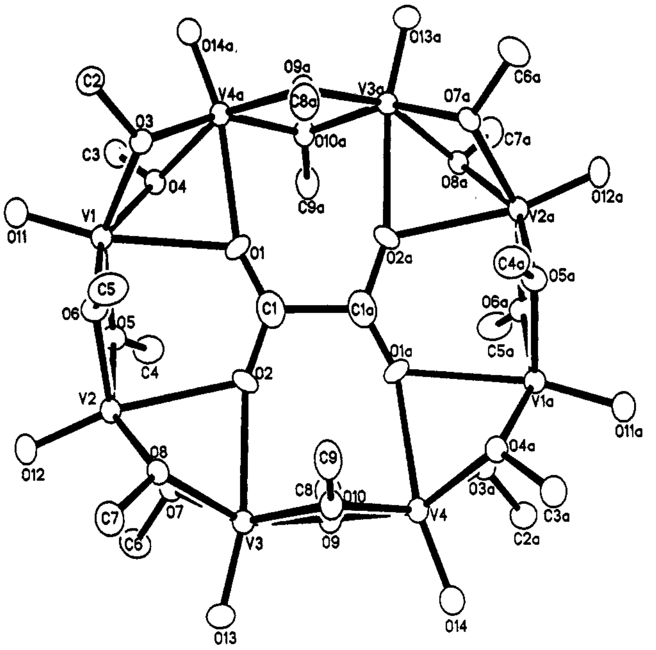

Figure 1. ORTEP plot of the $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$ anion, showing the atom-labeling scheme and 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): V(1)–O(3), 2.008 (3); V(1)–O(4), 2.008 (3); V(1)–O(5), 1.977 (3); V(1)–O(6), 1.968 (2); V(2)–O(5), 1.975 (3); V(2)–O(6), 1.974 (3); V2–O(7), 2.006 (3); V(2)–O(8), 2.001 (3); V(3)–O(7), 2.005 (4); V(3)–O(8), 2.005 (2); V(3)–O(9), 1.962 (3); V(3)–O(10), 1.972 (3); V(4)–O(9), 1.963 (3); V(4)–O(10), 1.962 (4); V(4)–O(1A), 2.398 (3); V(4)–O(3A), 2.002 (3); V(4)–O(4A), 2.005 (3); C(1)–C(1), 1.281 (7); C(1)–O(2), 1.275 (1); C(1)–C(1A), 1.561 (12); V–O_t (av), 1.596 (8); V–O(oxalate) (av), 2.394 (8); V···V, 2.997 (2); V–O(methoxy)–V (av) 92.3 (3) and 99.6 (3)°; V–O(oxalate)–V (av), 77.2 (2)°.

The structure of $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$ is similar to that previously reported for $[(n\text{-}C_4H_9)_4N]_2[Mo_8O_{16}(OCH_3)_8(C_2O_4)]$,[8] with the exceptions that the vanadium analogue exhibits methoxy bridging exclusively, rather than alternating methoxy and oxo bridging pairs associated with the molybdenum cluster, that the V···V distances are nearly identical rather than in the alternating short–long configuration, and that the C–O distances of the oxalate group are identical in the title complex (Figure 2). The synthesis of the Mo(V)–oxalate cluster from polyoxomolybdate(VI) and rhodizonic acid precursors was rationalized by invoking the well-documented carbonyl insertion reaction[9-11] coupled with ligand dissociation via a succession of two-electron transfers and cationic intermediates. The same mechanism is presumably operative in the vanadate chemistry, although the mechanistic details have not been established in either case.

Although the species $[(n\text{-}C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$ is a unique example of a cyclic polyoxovanadate coordination complex, a structural analogue exists in the recently reported V(V) species $[(n\text{-}C_4H_9)_4N]_4[V_{12}O_{32}]\cdot CH_3CN$, which also displays an octanuclear core, $[V_8O_8(\mu\text{-}O)_{16}]^{8-}$. In general, the polyoxovanadates appear to possess a rich structural chemistry and coordination chemistry, similar to that of the polyoxomolybdates. We are currently investigating the chemistry of polyoxovanadates with other "oxocarbons",[12] such as squaric acid, $H_2C_4O_4$, and

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(1) For recent representative studies, see: (a) Day, V. W.; Klemperer, W. G. *Science (Washington, D.C.)* **1985**, *228*, 533. (b) Chilou, V.; Gouzerh, P.; Jeannin, Y.; Robert, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1469. (c) Ma, L.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 175.

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(6) Anal. Calcd for $[(C_4H_9)_4N]_2[V_8O_8(OCH_3)_{16}(C_2O_4)]$, $C_{50}H_{120}N_2O_{28}V_8$: C, 37.4; H, 7.48; N, 1.75. Found: C, 37.1; H, 7.23; N, 1.63. IR (KBr pellet, cm^{-1}): 2965 (m), 2920 (s), 2882 (m), 2820 (s), 1618 (vs), 1470 (m), 1390 (w), 1327 (m), 1080 (vs), 980 (vs), 791 (m), 579 (m), 532 (vs).

(7) Crystal data: monoclinic space group $P2_1/n$, a = 9.619 (1) Å, b = 23.154 (4) Å, c = 19.469 (3) Å, β = 90.49 (1)°, V = 4336.0 (9) $Å^3$, Z = 2, and D_{calc} = 1.24 g cm^{-3}. Structure solution and refinement based on 5562 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, λ = 0.71073 Å) converged at R = 0.0594.

(8) Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1724.

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(12) West, R., Ed., *Oxocarbons*; Academic Press: New York, 1980.

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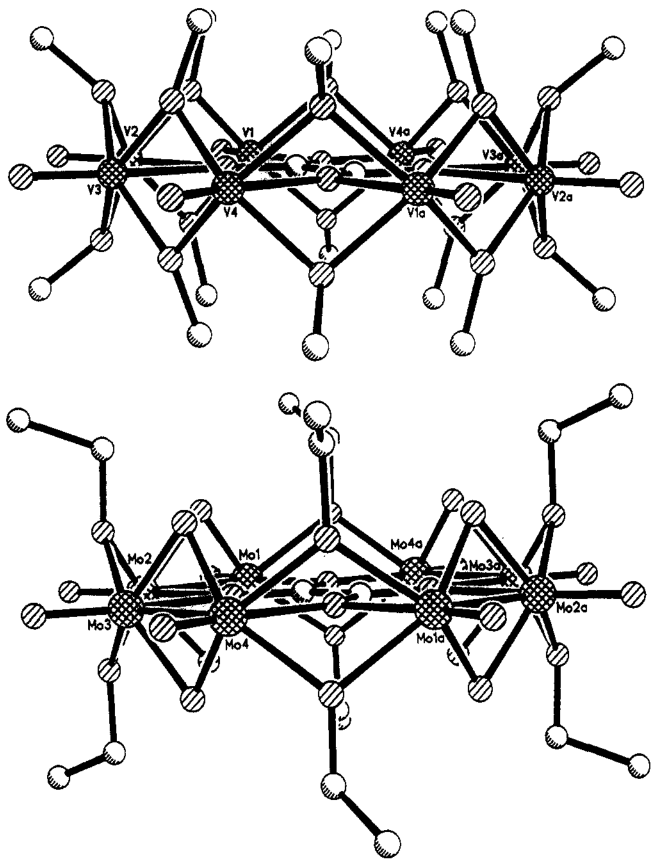

Figure 2. Schematic representations of the structures of $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$ (top) and $[Mo_8O_{16}(OC_2H_5)_8(C_2O_4)]^{2-}$ (bottom)[14] illustrating exclusively alkoxy bridging in the former and the alternating bis(alkoxy)/dioxo bridging of the latter.

croconic acid, $H_2C_5O_5$, and with various organohydrazines.[13]

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Supplementary Material Available: Tables of experimental details for the X-ray diffraction studies, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (17 pages); tables of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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(13) Polyoxomolybdate complexes of squaric acid have been described recently: Chen, Q.; Ma, L.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 5944; Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem.*, in press.

(14) Crystal data for $[(n\text{-}C_4H_9)_4N]_2[Mo_8O_{16}(OC_2H_5)_8(C_2O_4)]$, $C_{50}H_{112}N_2O_{28}Mo_8$: monoclinic space group $P2_1/n$, $a = 12.054$ (1) Å, $b = 12.322$ (2) Å, $c = 26.075$ (4) Å, $\beta = 100.20$ (1)°, $V = 3811.7$ (12) Å^3, $Z = 2$, $D_{calc} = 1.70$ g cm^{-3}. Structure solution and refinement based on 3576 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, $\lambda = 0.71073$ Å) converged at a final discrepancy value of 0.0564.

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Skeletal Rearrangement of $[Rh_2Fe_4(CO)_{16}B]^-$. An Example of an Associative Cluster Isomerization

The mechanisms for the interchange of fragments in molecules of all types have fascinated chemists for a long time. Perhaps because of this, the challenge of understanding the complexities of cluster rearrangements has not lacked champions beginning with the work of Lipscomb in 1960.[1] Recently, on the basis of continuing developments in the understanding of the electronic structure of clusters, there has been an increase in the number of reports proposing a variety of mechanistic rules to rationalize and predict the ease of rearrangement for various cluster shapes both for main-group and transition-metal cluster systems.[2] In one study, particularly relevant here, it was suggested that, among other criteria, large barriers are to be associated with mechanisms involving intermediates having skeletal electron counts different from that of the rearranging cluster.[3] Nearly all these theoretical studies restrict discussion to unimolecular pathways. This, plus the fact that examples of kinetically characterized transition-metal cluster framework isomerizations are rare,[4-7] leads us to report the kinetics of the facile isomerization of the octahedral, closed boride $[Rh_2Fe_4(CO)_{16}B]^-$. For octahedral closed clusters, high barriers are suggested by the theoretical studies. Our results show that in transition-metal cluster systems the presence of adventitious Lewis bases, e.g., CO, can open efficient bimolecular rearrangement pathways presumably by the stabilization of intermediates of higher skeletal electron count.[8]

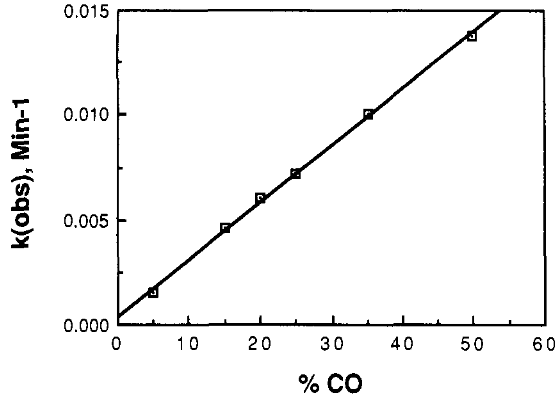

Figure 1. Plot of the pseudo-first-order rate constant for the isomerization of the sodium salt of $[1,2\text{-}\{Rh(CO)_2\}_2\text{-}3,4,5,6\text{-}\{Fe(CO)_3\}_4B]^-$ to $[1,6\text{-}\{Rh(CO)_2\}_2\text{-}2,3,4,5\text{-}\{Fe(CO)_3\}_4B]^-$ in THF at 22 °C vs the volume percent CO in N_2 with a total pressure of 1 atm. The line is a least-squares fit corresponding to the equation $k(\text{obs,m}^{-1}) = 4.03 \times 10^{-4} + 2.71 \times 10^{-4}[\%\ CO]$: $R = 1.00$.

As reported earlier[9] the preparation of the trans or $[1,6\text{-}\{Rh(CO)_2\}_2\text{-}2,3,4,5\text{-}\{Fe(CO)_3\}_4B]^-$ isomer of the boride proceeds through an intermediate proposed to be the cis or $[1,2\text{-}\{Rh(CO)_2\}_2\text{-}3,4,5,6\text{-}\{Fe(CO)_3\}_4B]^-$ isomer.[10] In contrast to the former, the latter has not been isolated or crystallographically characterized in the solid state but the spectroscopic parameters are structurally definitive.[11] Hence, we have now investigated the

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