500–900 °C, $La_{2/3}TiO_3$ has a *c* of ~12 Å, which is probably due to its presence as a three-layered perovskite with one layer of vacant B sites for each two layers of occupied B sites. The dehydrated products for Ln = Sm, Gd, and Dy also retain the layer-like features. On heating at 950 °C, however, they transformed to $Ln_2Ti_2O_7$ pyrochlores rather than to the perovskites.

In summary, we have synthesized a new series of layered perovskites of the formula $A_2Ln_2Ti_3O_{10}$ for various rare earths and lanthanum and shown that the interlayer alkali-metal ions can be exchanged with protons as well as other alkali-metal ions under mild conditions. We are investigating Brønsted acidity and intercalation chemistry of $H_2Ln_2Ti_3O_{10}$.

At the end of this work we became aware of a recent paper on crystal chemistry and ion-exchange reactions of $Na_2Gd_2Ti_3O_{10}$.[13]

Acknowledgment. We thank Professor C. N. R. Rao, FRS, for valuable advice and encouragement. Our thanks are also due to Dr. A. J. Jacobson of Exxon Research and Engineering Co. for helpful suggestions. The Department of Sciences and Technology, Government of India, and the University Grants Commission, New Delhi, are thanked for support of this research.

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(13) Gondrand, M.; Joubert, J. C. *Rev. Chim. Miner.* **1987**, *24*, 33.

[†] Contribution No. 465 from the Solid State and Structural Chemistry Unit.

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Monomeric versus Dimeric Vanadium(III) Aryloxide Formation. Syntheses and Crystal Structures of $[(O\text{-}2,6\text{-}ArMe_2)_2(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)V^{III}]_2\cdot thf$ and $[(O\text{-}2,6\text{-}ArMe_2)_3V^{III}(py)_2]_2$ ($O\text{-}2,6\text{-}ArMe_2$ = 2,6-Dimethylphenoxide)

Sir:

Interest in the chemistry of low- and medium-valent transition-metal alkoxides has been steadily increasing in recent years.[1,2] Curiously, the group VB (group 5[17]) di- and trivalent metal alkoxides are almost unknown although an attractive reactivity has been shown in a few reported cases.[3-5]

These considerations prompted us to attempt the synthesis of low-valent vanadium aryloxides. In spite of the well-known ability of V(II) to disproportionate,[5] we have used the V(II) compounds $[[V(dmb)_2]_2\cdot(thf)]$[2] (dmb = dimethoxyphenyl)[6] (**1**) and $VCl_2(py)_4$ (**2**)[7] as starting reagents to gain some insights on the stability of complexes in this elusive oxidation state.

The room temperature reaction of **1** with 2,6-dimethylphenol in toluene, affords the unprecedented dinuclear V(III) tris(aryloxide) $[[(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)(O\text{-}2,6\text{-}ArMe_2)_2V]_2(thf)]\cdot C_7H_8$ (**3**)[8] (Scheme I). A single-crystal X-ray analysis[9] of **3** showed the molecule as a dimer containing the vanadium atoms in two different coordination environments (Figure 1). In fact, surprisingly, only one of the two interstitial thf molecules of the starting material remains coordinated to one of the two metallic centers. The geometry around V2 can be described as a slightly distorted trigonal bipyramid [O4–V2–O7 = 167.0 (1)°] in which the axial positions are occupied by the thf molecule and one bridging aryloxide group with the V2 atom lying in the O1–O2–O3 plane [distance from the plane 0.066 (1) Å]. The V1–O4–V2–O1 backbone is planar [dihedral angle 0.1 (3)°]. The coordination

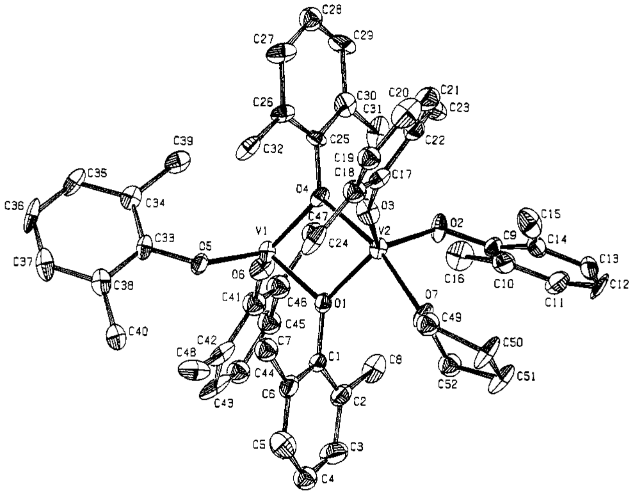

Figure 1. ORTEP drawing of **3**. Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): V1–V2 = 3.113 (1), V1–O1 = 1.999 (4), V2–O1 = 1.972 (3), V2–O4 = 2.084 (4), V1–O4 = 1.926 (3), V2–O7 = 2.119 (4), V2–O2 = 1.836 (4), V2–O3 = 1.842 (4), V1–O6 = 1.818 (4), V1–O5 = 1.831 (3), V1–C39 = 3.043 (6), O5–C33 = 1.363 (6), O2–C9 = 1.378 (6), O3–C17 = 1.346 (7), O6–C41 = 1.365 (7); V1–O4–V2 = 101.8 (2), V1–O1–V2 = 103.2 (2), O1v1–O4 = 79.0 (1), O1–V2–O4 = 76.0 (1), O2–V2–O4 = 95.0 (2), O2–V2–O7 = 94.2 (2), O1–V2–O_2 = 117.0 (2), O1–V2–O7 = 91.7 (1), O1–V2–O3 = 123.1 (2), O2–V2–O3 = 119.5 (2), O3–V2–O4 = 93.1 (2), O2–V2–O4 = 95.0 (2), O4–V2–O7 = 167.0 (1), O3–V2–O7 = 90.3 (2), O4–V1–O5 = 117.5 (2), O5–V1–O6 = 113.5 (2), O1–V1–O5 = 103.5 (2), O1–V1–O6 = 112.1 (2), O4–V1–O6 = 123.0 (2), V2–O2–C9 = 139.6 (4), V2–O3–C17 = 158.3 (3), V1–O6–C41 = 154.1 (4), V1–O5–C33 = 134.6 (4), C33–C38–C40 = 121.0 (5), C33–C34–C39 = 121.1 (5), V1–O5–C33–C34 = 25.7 (1), V2–O2–C9–C14 = 66.4 (1).

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(1) Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 2514 and references cited therein.

(2) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 3509.

(3) La Pointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 2659.

(4) Coffindaffer, T. W.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1519.

(5) (a) Schrauzer, G. N.; Palmer, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 2659. (b) Isaeva, S. A.; Nikolova, N. A.; Shilov, A. E. *Nouv. J. Chem.* **1981**, *5*, 21.

(6) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 560.

(7) Brauer, D. J.; Kruger, C. *Cryst. Struct. Commun.* **1973**, *2*, 421.

(8) In a standard experiment, a solution of $[V(dmb)_2thf]_2$ (2.00 g, 2.5 mmol) in toluene (100 mL), was reacted with neat 2,6-dimethylphenol (1.8 g, 15.0 mmol). The color changed almost instantaneously to a deep emerald green. After evaporation to dryness, the residual oil was dissolved in 50 mL of *n*-hexane. After the mixture was filtered and allowed to stand for 2 days at room temperature, deep green crystals of $[[(\mu\text{-}O\text{-}2,6\text{-}ArMe_2)(O\text{-}2,6\text{-}ArMe_2)_2V]_2(thf)]\cdot C_7H_8$ separated (0.4 g, 0.4 mmol). Another crop of crystals can be obtained by on cooling the mother liquor. Anal. Calcd (found after toluene removal in vacuo) for $C_{52}H_{62}O_7V_2$: C, 69.33 (69.25); H, 6.88 (6.92); V, 11.38 (11.40). EI-MS: no parent peak observed for $[^{12}C_{52}{}^{1}H_{62}{}^{16}O_7{}^{51}V_2]$; *m/e* 535 $[V(OR)_4]$, 414 $[V(OR)_3]$, 293 $[V(OR)_2]$. IR [KBr, Nujol mull, ν in cm^{-1}, under N_2]: 2730 (vw), 1591 (7), 1470 (s), 1420 (s), 1270 (s), 1218 (vs), 1091 (s), 880 (s), 852 (s), 790 (m), 767 (s), 760 (s), 742 (m), 723 (s), 695 (m), 589 (m), 540 (m), 510 (m).

(9) X-ray diffraction data for **3**: crystal size, 0.40 × 0.30 × 0.30 mm; deep green prisms; space group $P\bar{1}$ with $a = 10.797$ (4) Å, $b = 12.032$ (3) Å, $c = 19.697$ (6) Å, $\alpha = 72.29$ (2)°, $\beta = 81.98$ (0)°, $\gamma = 86.35$ (2)°, $V = 2413.1$ (4) Å^3, $Z = 2$, and $d_{calcd} = 1.369$ g/cm^3, $\mu(Mo) = 4.28$ cm^{-1}; $F(000) = 1056$; data were collected on an Enraf-Nonius CAD-4F diffractometer; Mo radiation $\lambda = 0.71073$ Å, scan mode = $\theta/2\theta$, scan width = 0.90°; $T = -130$, °C; measured reflection range $hkl = +h,\pm k,\pm l$; $(\sin\theta)/\lambda$ limit (Å^{-1}) = 0.57 ($2\theta_{max} = 48°$); number of unique reflections, 6805; number of reflections used in analysis, 5177 $[I > 3\sigma(I)]$; structure solved by direct methods; all non-hydrogen atom positions were located and refined anisotropically including an extremely disordered molecule of toluene (isotropically refined); all hydrogen atom positions were located from difference Fourier maps, but isotropic refinement was not possible for the methyl hydrogen atoms except those bonded to C31, C47, and C48; number of variables, 787; $R = 0.056$; $R_w = 0.067$, $w = 1/\sigma^2(F_o)$; GOF = 1.78; largest remaining peak, 1.23 e/Å^3; largest shift/esd, final cycle, 0.03.

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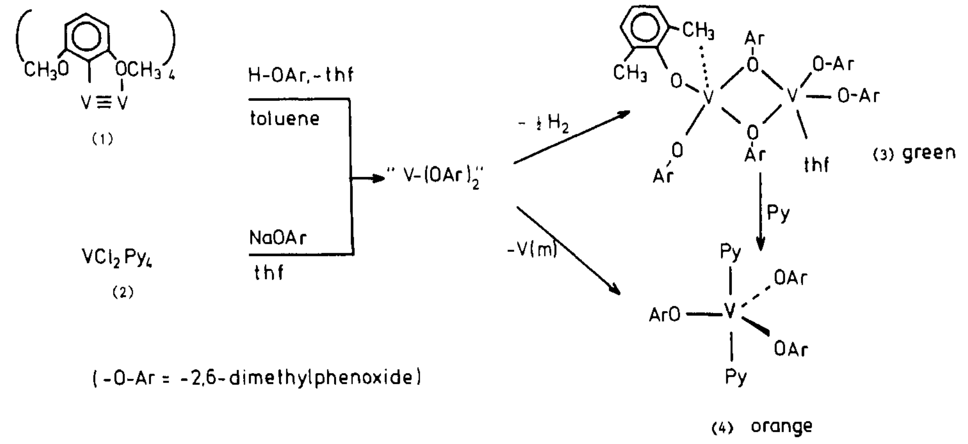
Scheme I



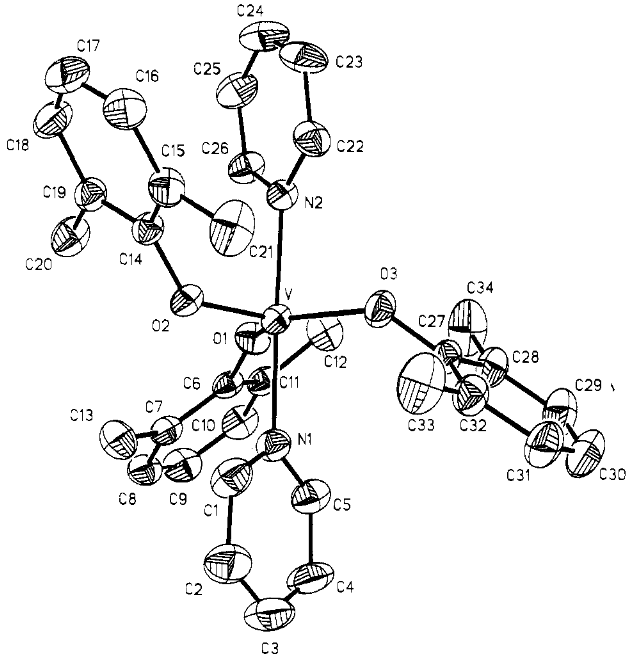


Figure 2. ORTEP drawing of **4**. Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): V–O1 = 1.861 (3), V–O2 = 1.869 (3), V–O3 = 1.870 (3), V–N1 = 2.149 (5), V–N2 = 2.167 (4); N1–V–N2 = 177.4(2), O1–V–O2 = 116.1 (1), O2–V–O3 = 118.0 (1), O1–V–O3 = 125.8 (1), V–O3–C27 = 137.3 (3), V–O2–C14 = 131.2 (3), V–O1–C6 = 150.0 (3).

around the V1 can be described as a highly distorted tetrahedron, with the V1 lying a little above the O5–O4–O6 plane [distance from the plane 0.263 (1) Å]. All the other angles and distances around V1 are as expected.[10]

The value of the intermetallic distance [V1···V2 = 3.113 (1) Å] shows either a weak or nonexistent V–V bond.[11] Magnetic susceptibilities measurements of **3** are in good agreement with the Curie–Weiss law (90–280 K) with μ_{eff} = 1.41 μ_B/vanadium (calculated spin only for d^2 = 2.83 μ_B). The absence of both *T*-independent values of magnetic susceptibility in the range 4.1–65 K and any significant structural distortion of the frame V1–O1–V2–O4 seems to indicate the absence of either M–M bond occurrence and direct antiferromagnetic exchange interaction.[12] We suggest that a ligand-mediated superexchange mechanism is responsible for the observed low value of μ_{eff}.

An interatomic contact has been observed between V1 and C39 [3.043 (6) Å]. The distance between V1 and the H atoms bonded to C39 appears to be 2.556 Å [C39–H39–V = 109.0°][13] and the value of the degree of C–H to metal interaction (d_{bp} = 2.63 Å) calculated according to Crabtree, falls in the range observed for the M–H agostic distances.[14]

Apart from the highly distorted coordination geometry around V1, and the absence of coordination of a second molecule of thf, no other structural features support the presence of the V–H interaction; only a very weak band in the IR spectrum at 2750 cm^{-1} might be due to ν(C–H–V). Therefore we cannot completely exclude that a particularly favorable geometry is responsible for the observed V–H short distance.

Addition of an excess of coordinating solvent like thf or pyridine to **3**, breaks up the dimeric structure, forming monomeric tris(aryloxo)–V(III) disolvated species. The pyridine-solvated complex (O-2,6-ArMe$_2$)$_3$V(py)$_2$ (**4**) can be prepared easily by direct reaction of sodium 2,5-dimethylphenoxide with VCl$_2$(py)$_4$. This reaction gives an initially purple solution (probably containing [(O-2,6-ArMe$_2$)$_2$V^{II}(py)$_4$]), which disproportionates completely within a few minutes, forming a tarry pyrophoric product (probably metallic V) and bright orange **4**.[15] The X-ray analysis reveals a mononuclear complex with trigonalbipyramidal coordination geometry around the vanadium center[16] (Figure 2). The

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(10) Shepherd, R. E.; Hatfield, W. E.; Ghosh, D.; Stout, D. C.; Kristine, F. T.; Ruble, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 5511.

(11) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

(12) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(13) On the basis of the difference electron density maps, H39″, which is potentially involved in the agostic interaction with vanadium, seems to show a V–H distance of 2.556 Å (C–H distance 0.950 Å). However, assuming a free rotation around the C34–C39 bond, a distance as short as 2.215 Å can be calculated.

(14) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

(15) A suspension of VCl$_2$(py)$_4$ (2.6 g, 5.9 mmol) in thf (100 mL) was reacted with neat sodium 2,5-dimethylphenoxide (4.6 g; 56.9% thf solvated, 18.2 mmol). The resulting deep red solution slowly turned brown, giving a black pyrophoric powder. After filtration, the resulting orange solution was evaporated to dryness and extracted with 70 mL of boiling hexane. After further filtration and cooling, the resulting light orange solution yielded 0.8 g (1.4 mmol) of bright orange crystals of [(O-2,6-ArMe$_2$)$_3$V(py)$_2$]. Anal. Calcd (found) for C$_{34}$H$_{37}$O$_3$N$_2$V: C, 71.32 (71.18); H, 6.46 (6.51); N, 4.89 (4.83); V, 8.91 (8.88). EI-MS shows the same fragmentation pathway as **3**: no parent peak was observed for [^{12}C$_{34}$^{1}H$_{37}$^{16}O$_3$^{14}N$_2$^{51}V]; *m/e* 535 [V(OR)$_4$], 414 [V(OR)$_3$], 292 [V(OR)$_2$]. IR [KBr, Nujol mull, ν in cm^{-1}]: 1602 (m), 1590 (m), 1460 (vs), 1420 (s), 1372 (m), 1260 (s), 1219 (vs), 1090 (m), 858 (s), 766 (m), 757 (s), 749 (s), 710 (s), 695 (s), 683 (m), 582 (m), 547 (m).

(16) X-ray diffraction data for **4**: crystal size; 0.20 × 0.30 × 0.50 mm; orange prisms; monoclinic, space group $P2_1/a$ with a = 15.098 (3) Å, b = 12.438 (2) Å, c = 16.459 (3) Å, β = 97.26 (1)°, Z = 4, V = 3064 (1) Å^3, and d_{calcd} = 1.24 g/cm^3; μ(Cu) = 31.5 cm^{-1}; F(000) = 1208; data were collected on a Nicolet R3m diffractometer with Cu radiation, λ = 1.541 78 Å; ω scan mode, scan speed = 3.91–29.3 (deg min^{-1}); scan width = 0.9°; T = 298 K; measured reflections, 4554; range of hkl = $\pm h,+k,+l$; (sin θ)/λ limit (Å^{-1}) = 0.544 ($2\theta_{max}$ = 114°); number of unique reflections, 4136; number of reflections used in analysis, 2606 [$I > 3\sigma(I)$]; structure solved by direct methods; all non-hydrogen atom positions were located and refined anisotropically; all hydrogen atom positions were calculated and refined isotropically; number of variables, 361; R = 0.051; R_w = 0.067, $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ with g = 0.00089; GOF = 1.503; largest remaining peak, 0.31 e/Å^3; largest shift/esd, final cycle, 0.008.

axial positions are occupied by two molecules of pyridine, while the three aryloxo groups lie in the equatorial plain. All of the bond angles and distances are normal, and no significant V–C contact has been detected within 3.6 Å. The magnetic moment $\mu_{eff} = 2.71\ \mu_B$ is in agreement with a V(III) d^2 high-spin configuration. A study on the reactivity of vanadium aryloxides is currently in progress.

Acknowledgment. This work has been supported by the University of Groningen Chemistry Department and by a NATO travel grant (0402/87). We are indebted to the generosity of the Chemistry Department, Columbia University.

Supplementary Material Available: Stereoview of complex **3** and tables of crystal data, anisotropic thermal parameters, positional parameters, bond distances, bond angles, torsional angles, and rms thermal vibration amplitudes for complex **3** and crystal data, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom parameters for complex **4** (25 pages); listings of calculated and observed structure factors for complexes **3** and **4** (42 pages). Ordering information is given on any current masthead page.

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(17) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Coordination Complexes of Polyoxomolybdate Anions. Characterization of a Tetranuclear Core from Reactions in Methanol: Syntheses and Structures of Two Polyoxomolybdate Alcoholates, $(MePPh_3)_2[Mo_4O_{10}(OCH_3)_6]$ and $(n\text{-}Bu_4N)_2[Mo_4O_{10}(OCH_3)_2(OC_6H_4O)_2]$, and Their Relationship to a General Class of Tetranuclear Cluster Types $[Mo_4O_x(OMe)_2(L)_y(LL)_z]^{2-}$

Sir:

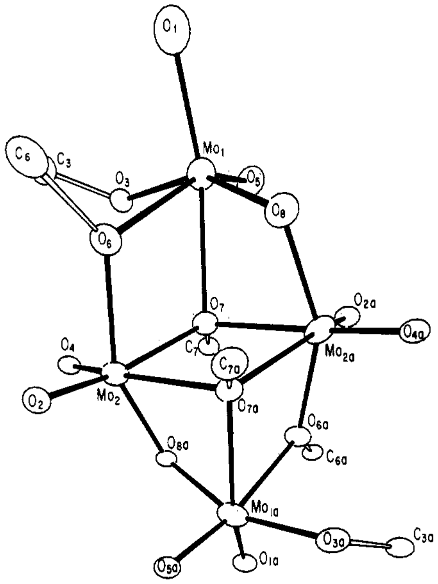

Figure 1. ORTEP view of the structure of $[Mo_4O_{10}(OCH_3)_6]^{2-}$, showing the atom-labeling scheme. Selected bond lengths (Å): Mo1–O1, 1.708 (2); Mo1–O3, 1.919 (3); Mo1–O5, 1.708 (2); Mo1–O6, 2.248 (2); Mo1–O7, 2.261 (2); Mo1–O8, 1.976 (2); Mo2–O2, 1.701 (3); Mo2–O4, 1.702 (2); Mo2–O6, 2.033 (2); Mo2–O7, 2.286 (2); Mo2–O7a, 2.415 (2); Mo2–O8, 1.870 (2).

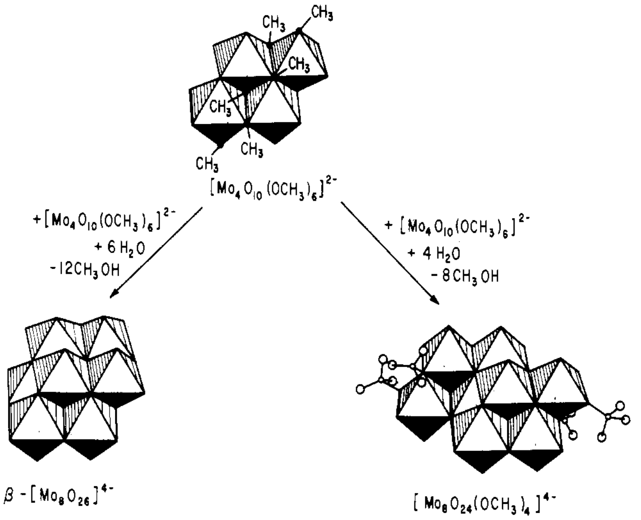

Figure 2. Idealized polyhedron representation of the structure of $[Mo_4O_{10}(OCH_3)_6]^{2-}$ and of the formal relationship to the structures of β-$[Mo_8O_{26}]^{4-}$ and of $[Mo_8O_{24}(OCH_3)_4]^{4-}$. Condensation of two $[Mo_4O_{10}(OCH_3)_6]^{2-}$ units by sharing of four edges of each unit and loss of CH_3OH produces the β-$[Mo_8O_{26}]^{4-}$ structure while the $[Mo_8O_{24}(OCH_3)_4]^{4-}$ structure results either from shearing of $[Mo_4O_{13}]^{2-}$ asymmetric units of β-$[Mo_8O_{26}]^{4-}$ parallel to one other or from condensation of two $[Mo_4O_{10}(OCH_3)_6]^{2-}$ units along two edges of each unit and partial loss of CH_3OH.

Organic derivatives of isopolymolybdate anions are of fundamental chemical interest as models for the interactions of substrates with metal oxide surfaces and in the photooxidation of organic compounds.[1,2] In recent years a variety of oxygen-[3–7] or nitrogen-containing[8–13] organic derivatives of polyoxomolybdate anions have been synthesized and structurally characterized. In the specific case of the selective oxidation of methanol to formaldehyde over molybdate catalysts, the molybdenum oxy-methoxide complex $[Mo_2O_5(OCH_3)_2]$[6] and the methoxy-isopolymolybdate complex $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8CH_3OH$[5] provide adequate chemical models and structural information relevant to surface coordination geometry.[7] Furthermore, isopolymolybdate

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(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.
(2) Ioannidis, I.; Papaconstantinou, E. *Inorg. Chem.* **1985**, *24*, 439. Hill, C. L.; Renneke, R. *J. Am. Chem. Soc.* **1986**, *108*, 3528.
(3) Adams, R. D.; Klemperer, W. G.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1979**, 256.
(4) Day, V. W.; Frederick, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491. Day, V. W.; Thompson, M. R.; Day, C. S.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1980**, *102*, 5973.
(5) McCarron, E. M., III; Harlow, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 6179.
(6) McCarron, E. M., III; Staley, H. H.; Sleight, W. *Inorg. Chem.* **1984**, *23*, 1043.
(7) McCarron, E. M., III; Sleight, A. W. *Polyhedron* **1986**, *5*, 129.
(8) McCarron, E. M., III; Whitney, J. F.; Chase, D. B. *Inorg. Chem.* **1984**, *23*, 3276.
(9) Hsieh, T.-C.; Zubieta, J. *Inorg. Chem.* **1985**, *24*, 1287.
(10) Hsieh, T.-C.; Zubieta, J. *Polyhedron* **1986**, *5*, 309.
(11) Hsieh, T.-C.; Zubieta, J. *Polyhedron* **1986**, *5*, 1655.
(12) Shaikh, S. N.; Zubieta. *Inorg. Chem.* **1986**, *25*, 4613.
(13) Hsieh, T.-C.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1749.

0020-1669/87/1326-4303$01.50/0