(19) For previous stereochemical interpretations of lanosterol biosynthesis, see G. Stork and A. W. Burgstahler, *J. Am. Chem. Soc.*, 77, 5068 (1955); A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, 38, 1890 (1955).

(20) In many epoxide cyclization experiments, significant amounts of acyclic ketone resulting from simple rearrangement are formed, despite the greatly enhanced reaction rate due to the neighboring π bond.[6] As an explanation for this and other cyclization results, there may be generated with participation some type of partially cyclized intermediate cation common to all processes, reacting with external nucleophiles (or bases) to give acyclic and monocyclic material as well as with further double bonds to give polycyclics. As a particularly attractive feature, this hypothesis (proposed by Professor J. Brauman) accounts both for the rate acceleration in production of noncyclized material as well as the lack of extra acceleration in the rate of polycycle formation.

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Structural and Dynamic Stereochemistry of α-$Mo_8O_{26}^{4-}$

Sir:

Rational synthesis of novel, large polyoxoanions is virtually impossible due to a scarcity of experimental data from which principles governing reaction mechanism may be inferred. We report here the results of a dynamic ^{17}O NMR solution study and a solid-state x-ray diffraction study which, for the first time, provide experimental evidence for a simple structure-reactivity relationship and its more general implications.

When ^{17}O enriched α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ (**1**) is dissolved in acetonitrile containing a small amount of water, ^{17}O NMR spectra shown in Figure 1c–e are obtained as the temperature is lowered. Since infrared studies[1] have established an α-β $Mo_8O_{26}^{4-}$ equilibrium in acetonitrile and x-ray diffraction studies[2,3] have determined the structures of α- and β-$Mo_8O_{26}^{4-}$ (see Figure 1a, b), the resonances may be assigned by comparison with the spectrum of ^{17}O enriched β-$[(n\text{-}C_4H_9)_4N]_3KMo_8O_{26}\cdot 2H_2O$ (**2**) in acetonitrile, shown in Figure 1f, using the ^{17}O NMR chemical shift scale described elsewhere.[4] Although the spectra shown in Figure 1c–e are not of sufficient quality to allow quantitative interpretation, several distinctive features may be noted: (1) as the temperature increases, resonances for O_B and O_C in α-$Mo_8O_{26}^{4-}$ broaden significantly, while resonances for O_A and O_D do not, (2) the H_2O triplet is observed at 30 °C, and (3) the O_B resonance broadens more rapidly than the O_C resonance as the temperature increases. From these features, one may conclude that (1) the O_B and O_C resonances broadening is due to a nuclear site exchange process, not quadrupolar broadening, (2) the site exchange process does not involve water, and (3) the exchange process involves exchange between the O_B site (two oxygens) and the O_C site (six oxygens). A simple mechanism consistent with this site exchange scheme is reorientation of the tetrahedral molybdate unit within the α-$Mo_8O_{26}^{4-}$ structure, either inter- or intramolecularly. Such a mechanism involves breaking and subsequent re-forming of bonds between O_C and the octahedrally coordinated molybdenums (Mo_I) in α-$Mo_8O_{26}^{4-}$, and the rapid reaction rate implies their being weak bonds.

Detailed examination of the α-$Mo_8O_{26}^{4-}$ structure, obtained from single crystals of α-$[(n\text{-}C_3H_7)(C_6H_5)_3P]_4Mo_8O_{26}\cdot H_2O\cdot CH_3CN$ (**3**),[5] confirms the weakness of these bonds. Although the α-$Mo_8O_{26}^{4-}$ ion in **3** possesses only inversion symmetry, deviations from idealized D_{3d} symmetry are slight (see Table I). Three features of the structure indicate the weakness of the Mo_I–O_C bonds and the potential lability of the MoO_4^{2-} unit within the α-$Mo_8O_{26}^{4-}$ ion. First, the average Mo_I–O_C distance of 2.425 Å implies a bond order[6] of less than 0.1. Second, the significant variation of Mo_I–O_C distances, ranging from 2.369 (3) to 2.444 (3) Å, reflects the ease with which these bonds may be stretched.[7] Finally, the average Mo_{II}–O distance within the tetrahedral coordination sphere is 1.764 Å, which agrees, within standard deviations, with the average of 1.772 Å found in $Na_2MoO_4\cdot 2H_2O$.[8] Thus the MoO_4^{2-} unit could be reoriented with only a slight deformation of its geometry. As a result of these three considerations, α-$Mo_8O_{26}^{4-}$ may be accurately represented by the

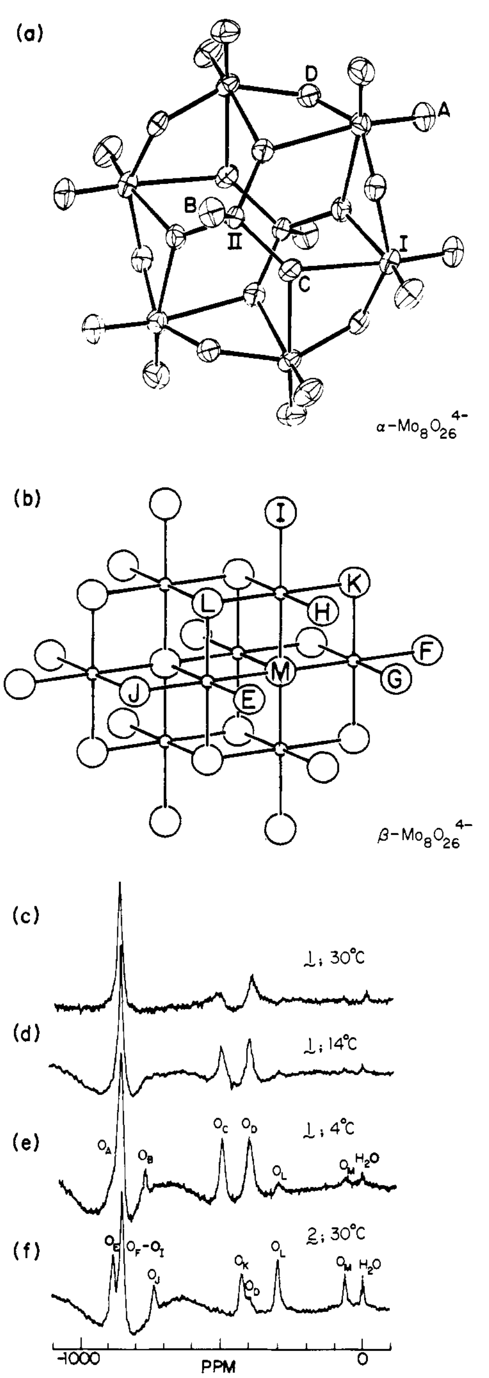

Figure 1. (a) ORTEP drawing of α-$Mo_8O_{26}^{4-}$ as observed in **3**. All atoms are represented by thermal vibration ellipsoids of 50% probability. Assuming idealized D_{3d} symmetry, nonequivalent oxygen atoms are labeled with letters and nonequivalent molybdenum atoms are labeled with numerals. (b) C_{2h} idealized view of β-$Mo_8O_{26}^{4-}$, where small circles represent molybdenum atoms, and large circles represent oxygen atoms. Nonequivalent oxygen atoms are labeled with letters. All molybdenum coordination polyhedra are drawn as idealized octahedra. (c)–(e) ^{17}O FT NMR spectra of 25 atom % ^{17}O enriched α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ (**1**) in hydrated acetonitrile, [Mo] = 0.16 M. (f) ^{17}O FT NMR spectrum of 34 atom % ^{17}O enriched β-$[(n\text{-}C_4H_9)_4N]_3KMo_8O_{26}\cdot 2H_2O$ (**2**) in acetonitrile, [Mo] = 0.05 M. Pure water at 30 °C is assigned a chemical shift of 0 ppm on the scale shown at the bottom of the figure.

Table I. Average Molybdenum–Oxygen Distances for the α-$\mathrm{Mo_8O_{26}}^{4-}$ ion in α-$[(n\text{-}\mathrm{C_3H_7})(\mathrm{C_6H_5})_3\mathrm{P}]_4\mathrm{Mo_8O_{26}{\cdot}CH_3CN{\cdot}H_2O}$

Type[a]	Distance,[b] Å
$\mathrm{Mo_I{-}O_A}$	1.696 (3, 2, 3)
$\mathrm{Mo_I{-}O_D}$	1.904 (3, 4, 9)
$\mathrm{Mo_I{-}O_C}$	2.425 (3, 19, 56)
$\mathrm{Mo_{II}{-}O_C}$	1.783 (3, 3, 5)
$\mathrm{Mo_{II}{-}O_B}$	1.708 (3)

[a] See Figure 1a for labeling scheme. [b] The first number in parentheses following an average value is the root mean squared value of the estimated standard deviation for an individual datum. The second and third numbers, when given, are the mean and maximum deviations from the averaged value, respectively.

formula $(\mathrm{MoO_4}^{2-})_2(\mathrm{Mo_6O_{18}})$ which characterizes the weak interactions between the two $\mathrm{MoO_4}^{2-}$ ions and a ring of six distorted $\mathrm{MoO_4}$ tetrahedra sharing corners.[9] This representation is also in accord with the existence of stable rings $(\mathrm{MoO_3})_n$, $n = 3, 4$, and 5, studied in the vapor phase by Berkowitz et al.

The simple relationship between kinetic lability and low bond order established here is consistent with previous exchange studies[12] and may be extended in an attempt to predict the kinetic behavior of other polyoxomolybdates. Several heteropolyanions may be viewed as structurally related to the α-$\mathrm{Mo_8O_{26}}^{4-}$ ion and represented as $(\mathrm{AsO_4}^{3-})_2(\mathrm{Mo_6O_{18}})$,[13] $(\mathrm{C_6H_5AsO_3}^{2-})_2(\mathrm{Mo_6O_{18}})$,[13] $(\mathrm{PO_4}^{3-})_2(\mathrm{Mo_5O_{15}})$,[14] $(\mathrm{CH_3PO_3}^{2-})_2(\mathrm{Mo_5O_{15}})$,[15] and $((\mathrm{CH_3})_2\mathrm{AsO_2}^-)(\mathrm{OH}^-)(\mathrm{Mo_4O_{12}})$,[16] which in turn implies potential lability with respect to dissociation of $\mathrm{AsO_4}^{3-}$, $\mathrm{C_6H_5AsO_3}^{2-}$, $\mathrm{PO_4}^{3-}$, $\mathrm{CH_3PO_3}^{2-}$, and $(\mathrm{CH_3})_2\mathrm{AsO_2}^-$, respectively. One may speculate further into the more general case where a large polyoxomolybdate cluster may be dissected into smaller clusters by breaking only weak bonds. For example, β-$\mathrm{Mo_8O_{26}}^{4-}$ may be accurately represented by $((\mathrm{O}^{2-})(\mathrm{Mo_4O_{12}})_2$ since the β-$\mathrm{Mo_8O_{26}}^{4-}$ cluster can be dissected into two $(\mathrm{O}^{2-})(\mathrm{Mo_4O_{12}})$ subunits by breaking only bonds whose lengths exceed 2.22 Å[17] and hence have bond orders less than 0.2.[6] This fact points toward a mechanistic pathway for the reaction of $((\mathrm{O}^{2-})(\mathrm{Mo_4O_{12}})_2$ with $(\mathrm{CH_3})_2\mathrm{AsO_2H}$ to form the $((\mathrm{CH_3})_2\mathrm{AsO_2}^-)(\mathrm{OH}^-)(\mathrm{Mo_4O_{12}})$ ion mentioned above. We are currently attempting to verify some of these speculations using dynamic $^{17}\mathrm{O}$ NMR techniques.

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(5) Compound **3** crystallizes in the centrosymmetric monoclinic space group, $C_{2/c}$–$C_{2h}{}^6$ (No. 15) with $a = 28.096\ (6)$ Å, $b = 14.313\ (2)$ Å, $c = 27.116\ (5)$ Å, $\beta = 121.32\ (1)°$, and $Z = 4$ (formula units as given above). Diffracted intensities were measured on a spherical crystal having $\mu r = 0.28$ for 12 892 independent reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 59°$ (the equivalent of 1.2 limiting Cu $K\bar{\alpha}$ spheres) on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffractometer using Nb-filtered Mo $K\bar{\alpha}$ radiation and θ–2θ scans. The four molybdenum atoms of the asymmetric unit were located using direct methods (MULTAN) and the remaining atoms by standard difference Fourier techniques. The resulting structural parameters have been refined to convergence ($R = 0.031$ for 4611 independent reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 43°$ (the equivalent of 0.50 limiting Cu $K\bar{\alpha}$ sphere) and $I > 3\theta(I)$) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement is continuing with those reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 59°$.

(6) F. A. Schroeder, *Acta Crystallogr., Sect. B*, **31**, 2294 (1975).

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(9) Kihlborg[10] in his study of $\mathrm{MoO_3}$ was apparently the first to note that certain molybdate structures containing octahedrally coordinated molybdenum with marked off-center displacement toward an octahedral edge may be best viewed as containing tetrahedral units. In the case of $\mathrm{MoO_3}$, he described infinite chains of corner sharing, distorted $\mathrm{MoO_4}$ tetrahedra which are only weakly associated to yield six-coordinate molybdenums.

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(18) Camille and Henry Dreyfus Teacher–Scholar.

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Intercalate of Xenon Tetrafluoride with Graphite

Sir:

The compounds xenon hexafluoride[1] and xenon oxide tetrafluoride[2] have previously been shown to intercalate in graphite. While these compounds react directly with graphite, xenon difluoride reacts only in the presence of hydrogen fluoride to yield an intercalate of variable composition.[3] We have now found that xenon tetrafluoride also forms intercalates with graphite.

Weighed quantities of graphite and excess $\mathrm{XeF_4}$ were allowed to react in preweighed Kel-F reaction vessels for periods of up to 3 weeks at room temperature. Reactions were generally complete after about 10 days, their slowness probably due to the low vapor pressure of $\mathrm{XeF_4}$. The excess $\mathrm{XeF_4}$ was then pumped off until the reactor attained constant weight or did not lose weight at rates exceeding 2 mg/h. Stoichiometries were calculated on the assumption that total weight gains were due to $\mathrm{XeF_4}$. The latter were extrapolated back to zero pumping time.

The graphite used was either BDH powder or GTA grade Grafoil from Union Carbide Co. Considerable variations in stoichiometry were observed. The results with powder based on nine different reactions were $\mathrm{C_{28.3\pm2.4}XeF_4}$, while those with Grafoil were $\mathrm{C_{41\pm1}XeF_4}$ based on four experiments. In one case, however, a stoichiometry of $\mathrm{C_{17.8}XeF_4}$ was obtained even after pumping for 27 h. Neither xenon nor carbon fluorides were liberated during the course of the reaction, and samples showed no visible changes. Fluorine analyses (Table I) correspond roughly to stoichiometries obtained from weight