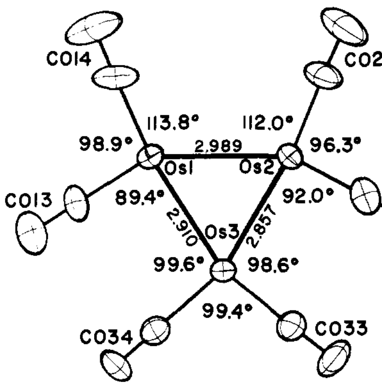
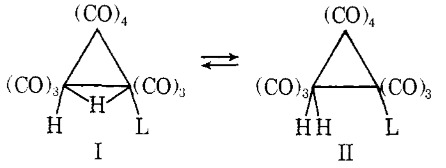


Figure 2. The equatorial plane of the $H_2Os_3(CO)_{11}$ molecule, showing angles (in deg) and Os–Os distances (in Å). The bridging hydride ligand is believed to lie between Os(1) and Os(2) near the intersection of lines extended from CO(13) → Os(1) and CO(24) → Os(2).

Os(2)—63.8 (11)% of the molecules have the geometry shown in Figure 1, whereas 36.2 (11)% have the axial CO and H ligands on Os(2) reversed.

While the hydride ligands were not located directly from the X-ray structural analysis, their positions may reliably be inferred from their effects on the geometry of the remainder of the molecule. (The virtue of this approach has already been demonstrated for $[H_2Re_3(CO)_{12}^-]$[9] and $H_2Ru_6(CO)_{18}$,[10] among others.) Thus, there are two abnormally large bond angles in the equatorial plane (see Figure 2), ∠Os(2)-Os(1)-CO(14) = 113.8 (6)° and ∠Os(1)-Os(2)-CO(23) = 112.0 (5)°; all other interligand angles lie in the range 89.4–99.6° and are more equitably distributed. Furthermore, the Os(1)-Os(2) distance of 2.9886 (9) Å is significantly longer than the bonds Os(1)-Os(3) and Os(2)-Os(3) (2.9097 (7) and 2.8574 (7) Å, respectively). Each of these observations suggests that the bridging hydride ligand lies in the equatorial plane, displaced outward from the Os(1)-Os(2) vector and near the intersection of lines extended from C(24) → Os(2) and C(13) → Os(1). The terminal hydride ligand may be assigned to an axial site on Os(2).

Mutual exchange of the bridging and terminal hydrides in $H_2Os_3(CO)_{10}L$ is evidenced by variable-temperature ^1H NMR spectra. The two limiting low-temperature hydride signals broaden as the sample temperature is raised, disappear completely into the baseline, then reappear at ca. 50° as a very broad coalesced resonance centered near the mean chemical shift. In this temperature region separate signals for coordinated and added free L are observed with **2**, **4**, and **5**, which precludes ligand dissociation as the cause of the dynamic behavior. Obtaining accurate line shapes at higher temperatures is complicated by concurrent decomposition. However, preliminary measurements of line broadening in the slow-exchange region provide an estimate of the barrier to exchange and reveal a slight dependence of the barrier upon the nature of L (**1**, $\Delta G^\ddagger{}_{237} = 12.4$ kcal mol^{-1}; **4**, $\Delta G^\ddagger{}_{219} = 10.9$ kcal mol^{-1}).[11] The probable intermediate (II) in this exchange process has both hydride ligands bound just to one osmium center.[12] This structure nicely conforms to the 18-electron rule for each osmium atom, but the fact that it is higher in energy than I indicates the extra stability associated with a bridging hydride ligand compared with a terminal one.



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(2) With the stronger donors the reaction is essentially complete upon mixing. For preparative purposes the reaction with CO is best conducte under 3–4 atm pressure at 25°. Higher temperatures and prolonge reaction times lead to $Os_3(CO)_{12}$. We are presently studying the kinetic of ligand uptake. NOTE ADDED IN PROOF. Compounds **1**, **3**, and **4** hav been described recently; A. J. Deeming and S. Hasso, *J. Organomet Chem.*, **88**, C21 (1975).

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(5) E.g., $H_2Os(CO)_4$, 18.73; $H_2Os_2(CO)_8$, 20.11; $HOs_3(CO)_{10}(SEt)$, 27.5 $HOs_3(CO)_{12}^+$, 29.1.[8]

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(7) For $H_2Os_3(CO)_{11}$ in CH_2Cl_2, ν_{Os-H} appears as a very weak band at 193 cm^{-1}. However, the substantial shifts of some carbonyl bands fro $H_2Os_3(CO)_{11}$ to $D_2Os_3(CO)_{11}$ imply an interaction between hydride an carbonyl stretching modes.

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(12) The following pathway is suggested for the preparation $H_2Os_3(CO)_{10}$[13]: $Os_3(CO)_{12} \rightarrow Os_3(CO)_{11} \rightarrow H_2Os_3(CO)_{11}$ (II) – $H_2Os_3(CO)_{11}$ (I) → $H_2Os_3(CO)_{10}$. This implies that oxidative addition H_2 occurs at just one metal center.

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(14) After Sept 1, 1975, please address correspondence to this author the Department of Chemistry, State University of New York at Buffal Buffalo, New York 14214.

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A New Type of Heteropoly Anion. Tetramolybdo Complexes of Dialkyl- and Diarylarsinates[1]

Sir:

We wish to report the synthesis and structure[2] of a nove type of heteropoly oxometalate complex that contains covalently attached organic groups. The structure exhibits number of unusual features including a localized, nontitra table proton.

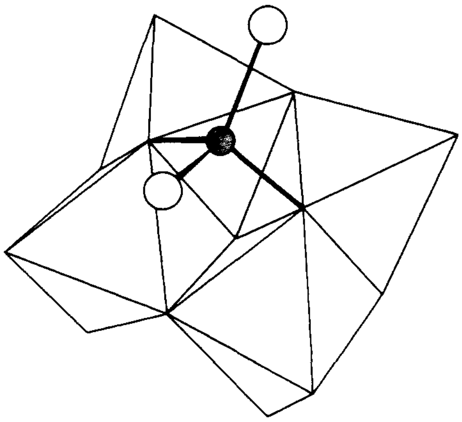

Figure 1. Structure of $[(CH_3)_2AsMoO_{14}OH]^{2-}$: ○, CH_3; ●, As; octahedra represent MoO_6 groups.

As part of a program to explore and develop the chemistry of organic derivatives of heteropoly complexes,[3] we have synthesized some molybdate complexes of dialkyl and diaryl arsinic acids. The complexes have the general formula $[R_2AsMo_4O_{14}(OH)]^{2-}$ with R = CH_3, C_2H_5, and C_6H_5. Ten salts, with sodium, potassium, guanidinium, tetramethyl-, and tetrabutylammonium counterions have been crystallized and characterized by elemental analysis and uv, ir, and NMR measurements. Salts of the dimethyl derivative appear to have been prepared earlier by Rosenheim and Bilecki[4] but were not investigated further.

The heteropoly complexes are readily prepared from stoichiometric quantities of sodium molybdate and the appropriate arsinic acid at pH 4–5. The anions thus formed are stable within the pH range 2–6 according to uv spectra (maximum at ca. 250 nm).

The guanidinium salt, $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O$, crystallizes as large monoclinic blocks with the following crystal data (Mo $K\alpha_1$, λ 0.70926 Å): space group $P2_1/c$; $Z = 4$; $a = 8.531$ (2), $b = 8.527$ (2), $c = 30.129$ (5) Å; $\beta = 95.49$ (2)°; $\rho_{calcd} = 2.65$, $\rho_{obsd} = 2.62$ (2) g cm^{-3}. X-Ray intensity data were collected by automated diffractometer and the solution and refinement of the structure were carried out by standard methods. The final conventional unweighted R based on 2519 observed reflections was 0.045. The details of the structure determination will appear in a later publication.

The remarkably compact and symmetrical anion consists of a ring of four alternately face- and edge-shared MoO_6 octahedra capped by the $(CH_3)_2AsO_2$ tetrahedron as shown in Figure 1. The structure represents only the second example[5] of a heteropoly complex containing face-shared octahedra. The metal-to-oxygen bond distances are similar to those found in other heteropoly molybdates and can be classified into distinct groups according to the type of oxygen involved. Metal–oxygen distances for each group range as follows: (1) terminal oxygens, 1.689 (8)–1.721 (8) Å, (2) oxygens bridging two metals, 1.901 (7)–1.940 (7) Å, (3) oxygens bridging two metals and an arsenic, 2.267 (7)–2.339 (7) Å. The unique basal oxygen is asymmetrically located. Three molybdenum–oxygen distances are 2.375 (7), 2.341 (7), and 2.393 (7) Å while the fourth is 2.542 (7) Å. The unique oxygen lies 0.725 (7) Å below the 3.16 × 3.36 Å rectangular plane formed by the metals.

The stoichiometry of all the salts prepared indicates that the anion contains a proton which is not directly revealed by the X-ray data. Although potentiometric titrations with sodium hydroxide show only a single well-defined end point corresponding to the reaction

$$R_2AsMo_4O_{14}(OH)^{2-} + 7OH^- \rightarrow R_2AsO_2^- + 4MoO_4^{2-} + 4H_2O$$

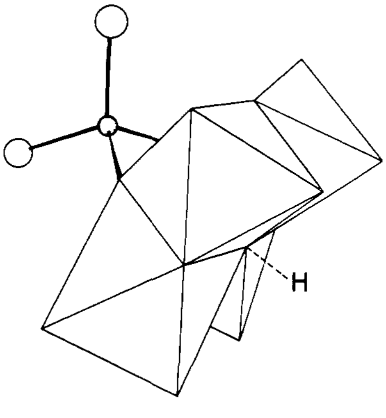

Figure 2. View of the $[(CH_3)_2AsMoO_{14}OH]^{2-}$ structure showing probable location of the hydrogen atom: ○, CH_3; ●, As; octahedra represent MoO_6 groups.

the presence of the proton is confirmed by a narrow line at 1.98 ppm in the NMR spectrum of $(Bu_4N)_2[(CH_3)_2AsMo_4O_{14}(OH)]$ in dichloromethane and by a sharp infrared absorption at 3615 cm^{-1} in a Nujol mull of the same salt. The integrated intensity of the NMR line is one-sixth that of the $As(CH_3)_2$ protons, which occurs at 2.19 ppm. The chemical shift of the OH proton is some 4 ppm upfield from that of the "internal" protons[6] in the metatungstate ion, $H_2W_{12}O_{40}{}^{6-}$ and indicates absence of hydrogen bonding in the molybdoarsinate case. The 1.98 ppm resonance disappears when methanol is added to the solution, showing that the proton is labile. The most probable location of the proton is the unique basal oxygen of the Mo_4O_{15} group as shown in Figure 2. This position is consistent with the X-ray data for the guanidinium salt which show a tightly bound water of hydration 2.8 Å from the oxygen in question. The asymmetric location of the basal oxygen mentioned above presumably accommodates this hydrogen bonding arrangement. That a proton attached to the exterior of a heteropoly oxoanion should be effectively nonacidic in aqueous solution is highly unusual. Many possibilities exist for the further derivatization of such complexes.

References and Notes

(1) Supported by the Office of Naval Research through Contract No. N00014-69-A-0220-0009.

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The Thermal Isomerization of 5-Acetyl-5-methylbicyclo[2.1.0]pentane. Endo–Exo Stereomutation and Cyclopropyl-Allylic Rearrangement of the Endo Ketone on Separate Potential Energy Surfaces

Sir:

The concurrent thermal endo-exo stereomutation of 5-acetylbicyclo[2.1.0]pentanes and rearrangement to 3-acetyl-1-cyclopentenes have been described previously by ourselves[1] and by Jorgenson,[2] and the cyclopropyl-allylic rearrangement, e.g., **1** → **3**, was shown to involve 1,2-migration