other side by a $SMo(h^5-C_5H_5)(CO)_3$ ligand. A consequence of the necessity of electron-pair Re(1)–Re(2) and Re(1)–Mo(3) bonds is that each of the four metal atoms formally attains a noble-gas electronic configuration, in accord with the observed diamagnetism of the compound. The Re–Re bond length of 2.985 (1) Å is within the Re–Re single-bond range, while the Re–Mo bond length of 2.909 (2) Å is notably but not unexpectedly shorter than that of 3.12 Å reported[13] for $(OC)_5Re-Mo(h^5-C_5H_5)(CO)_3$. A prominent structural feature is the presence of the metal-coordinated, tetrahedral-like sulfur atom, S(2), linking the Re_2Mo cluster to Mo(4) by means of four σ bonds involving all six valence electrons of the sulfur atom. The other structurally characterized organometallic example of a similar sulfur atom tetrahedrally coordinated to four metal atoms is $[Fe_2(CO)_6(SMe)]_2S$.[5]

Each of the three metal atoms in the Re_2Mo cluster has a different coordination of ligands (with the metal atoms in this molecule assumed to occupy distinct coordination sites). Based on the premise that its cyclopentadienyl ring sterically fills three coordination sites, the localized environment about Mo(3) can be described as eight-coordinated with a configuration not unlike that found[14] about each Mo atom in both the neutral parent $[Mo(h^5-C_5H_5)(SR)_2]_2$ and its cationic 1+ offspring. The Re(1) atom is seven-coordinated, which, on the basis of quasiequivalence of its seven ligands (*viz.*, Mo(3), Re(2), S(1), S(2), and the three CO's), may be envisioned as a so-called 4:3 distribution of ligands,[15] with a resulting idealized fourfold axis (relating the two metal and two sulfur atoms to one another) approximately coincident with an idealized threefold axis (relating the three carbonyls to one another). The six-coordinated environment of Re(1), S(1), S(2), and the three carbonyl ligands about the Re(2) atom may be simply described as a distorted octahedron.

Originally we expected the bridged dimer $[Re(CO)_4(SMo(h^5-C_5H_5)(CO)_3)]_2$ to be formed along with Me_3SnCl by cleavage of the S–Sn bonds in $[Re(CO)_4(SSnMe_3)]_2$ upon reaction with $Mo(h^5-C_5H_5)(CO)_3Cl$. This dimer, which may be an intermediate before decarbonylation and condensation into **1**, has not yet been isolated. We feel that **1** represents an example of the kind of sulfur-bridged metal cluster complex which can be prepared by this synthetic method. Extensions of this preparative route hopefully should enable one to design metal–sulfur model systems including those of biological interest. The results communicated here will be reported in full upon completion of closely related work in progress.

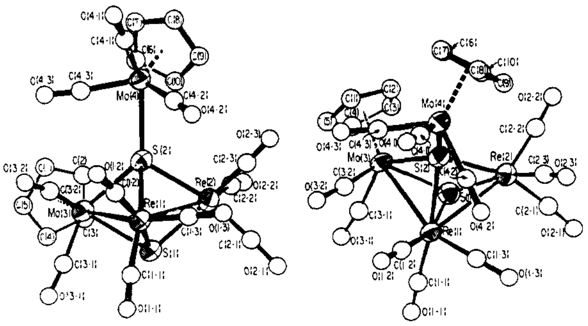

Figure 1. Molecular geometry of the (mixed metal)–sulfur cluster system $[Re_2Mo(h^5-C_5H_5)(CO)_8](S)[SMo(h^5-C_5H_5)(CO)_3]$ containing both a trimetal- and a tetrametal-coordinated sulfur atom. The anisotropically refined rhenium, molybdenum, and sulfur atoms are designated as 50% probability thermal ellipsoids. Important distances are Re(1)–Re(2), 2.985 (1); Re(1)–Mo(3), 2.909 (2); Re(2)···Mo(3), 3.927 (2); Re(1)–S(1), 2.448 (5); Re(1)–S(2), 2.473 (5); Re(2)–S(1), 2.410 (5); Re(2)–S(2), 2.453 (4); Mo(3)–S(1), 2.487 (5); Mo(3)–S(2), 2.523 (5); and Mo(4)–S(2), 2.550 (5) Å. The Re(2)–Re(1)–Mo(3) bond angle is 83.56 (4)°.

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Organometallic Chalcogen Complexes. XXIV. Synthesis, Structure, and Bonding of $[Mo_3(h^5-C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$ Containing a Triangular Molybdenum(IV) Cluster Cation with Doubly and Triply Bridging Sulfur Atoms[1]

Sir:

A systematic investigation in our laboratories of the reactions between thio derivatives of trialkyltin and various organo(transition metal) halides for the purpose of obtaining certain desired metal cluster complexes has led to the isolation and stereochemical characterization of the salt $[Mo_3(h^5-C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$. Besides representing a new kind of metal–chalcogen cluster system with the unprecedented feature of containing both doubly and triply bridging sulfur atoms, the $[Mo_3(h^5-C_5H_5)_3S_4]^+$ cation generates interest from a bonding viewpoint in its particular mode of nonconformity to the noble-gas configuration for each metal atom. An additional incentive for our exploration of the unusual structural and electronic properties of cyclopentadienylmolybdenum–sulfur complexes stems from possible biochemical implications with respect to the unknown metal–ligand coordinated units in molybdenum–sulfur enzymes.

$[Mo_3(h^5-C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$ was obtained as one of the products from the reaction of $Mo(h^5-C_5H_5)(CO)_3Cl$ in 1,2-dimethoxyethane with $[Sn(CH_3)_3]_2S$.[2]

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(1) Previous paper in this series: P. J. Vergamini, H. Vahrenkamp, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6326 (1971).

(2) Yield >50% based on S. *Anal.* Calcd for $Mo_3S_4Cl_2SnC_{18}H_{24}$: Mo, 34.02; S, 15.16; C, 25.55; H, 2.86. Found: Mo, 35.20; S, 17.54; C, 26.48; H, 2.73; mp, 230° dec.

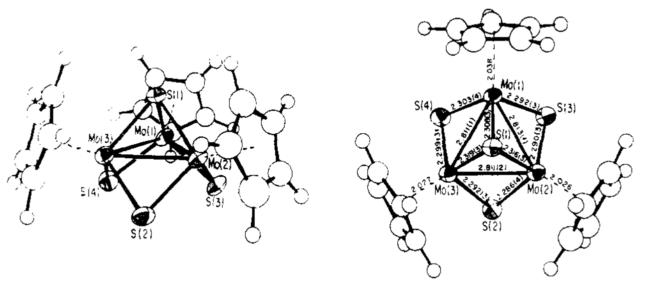

Figure 1. Stereochemistry of the $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ cation which ideally conforms to a C_{3v}-$3m$ geometry (based on assumed cylindrical symmetry for each cyclopentadienyl ring). The anisotropically refined molybdenum and sulfur atoms and isotropically refined carbon atoms are shown as 50% probability thermal ellipsoids.

The diamagnetic character of this air-stable compound was established from a magnetic susceptibility measurement[3] and from a proton nmr spectrum which showed in methanol solution only one sharp peak at 6.20 ppm (external TMS as standard) due to the cyclopentadienyl hydrogens. Recrystallization from CH_2Cl_2 solution gave dark green needle-like plates which an X-ray diffraction analysis showed to belong to the triclinic system. Unit cell dimensions are a = 11.887 (1), b = 12.485 (1), c = 9.526 (1) Å, α = 101.642 (3), β = 97.022 (3), γ = 107.819 (3)°. The experimental density (flotation) of 2.2 ± 0.1 g cm^{-3} agrees with a calculated value of 2.18 g cm^{-3} for $Z = 2$. The structure was solved from interpretations of Patterson–Fourier maps computed with data collected with Mo Kα radiation on a General-Electric full-circle diffractometer by the θ–2θ scan technique. Full-matrix least-squares refinement, performed under $P\bar{1}$ symmetry on 2579 absorption-corrected data for which $|F_o| \geq 4.0\sigma(F_o)$, yielded an R_1 value of 5.6%. In this refinement, rigid-body constraints were applied to each C_5H_5 ring (*viz.*, D_{5h} geometry) and to each CH_3 group; the isotropically assigned temperature factors for the hydrogen atoms were not varied, while all carbon atoms were refined isotropically and all other atoms anisotropically.[4]

Crystalline $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$ is comprised of discrete cations and anions. The $[Sn(CH_3)_3Cl_2]^-$ anion can be considered as an axially distorted trigonal-bipyramidal structure of C_{3v}-$3m$ symmetry with the three methyl groups located at equatorial sites and the two chlorine atoms at axial sites. The three Sn–CH_3 bond lengths are all within 0.01 Å of the average value of 2.12 (1) Å, whereas the two Sn–Cl bond lengths of 2.572 (4) and 2.696 (3) Å are distinctly dissimilar, with the latter value being the longest such bond reported for a direct Sn–Cl interaction. A detailed discussion of the stereochemistry and bonding of the anion will be presented elsewhere.

The $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ cation (Figure 1) consists of three $Mo(h^5\text{-}C_5H_5)$ moieties positioned at the vertices of an equilateral triangle and linked to each other by a triply bridging sulfur atom, S(1), and three doubly bridging sulfur atoms as well as by direct Mo–Mo interactions. The cyclopentadienyl ring attached to each molybdenum atom has its corresponding centroid equidistant from the two adjacent doubly bridging sulfur atoms and the one triply bridging sulfur atom. On the basis of assumed cylindrical symmetry for each cyclopentadienyl ring, the cation experimentally conforms to a C_{3v}-$3m$ geometry. The framework of the entire cation can be visualized as arising from a cubane-like $Mo_4(h^5\text{-}C_5H_5)_4S_4$ architecture[5] by the formal removal of one $Mo(h^5\text{-}C_5H_5)^-$ group. The resulting $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ cation is isostructural with the $[Mn_3(h^5\text{-}C_5H_5)_3(NO)_4]$ molecule[6] (where NO ligands occupy the sulfur positions). The same basic geometrical unit can be formally derived from the β-Nb_3X_8 type structure (where X = Cl, Br, I)[7] if the three halogen atoms coordinated to each niobium atom of a given Nb_3X_4 cluster are replaced by a cyclopentadienyl ring.

The presence of a formal oxidation state of 4+ for each Mo (corresponding to a d^2 electronic configuration) in the $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ cation enables an electron-pair coupling between each pair of Mo(IV). In analogous fashion, there is a great tendency for Mo(V) complexes to form dimeric sulfur- or oxygen-bridged species with spin pairing of the d^1 electrons of the two Mo(V)'s. Definitive evidence for strong electron-pair interactions in $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ is provided by its short Mo–Mo distances of average value 2.812 Å which parallel that of 2.894(5) Å in the sulfur-bridged $[MoO(h^5\text{-}C_5H_5)S]_2$ dimer for which a direct Mo–Mo interaction was proposed[8] between the two Mo(V)'s. In $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ the average distance from the doubly bridging sulfur atoms to the Mo(IV) is 2.293 Å compared to the similar average value of 2.314 Å for the distances from the triply bridging sulfur atom to the Mo(IV). These Mo–S bond lengths are also analogous to those of 2.317 (3) Å (average) in $[MoO(h^5\text{-}C_5H_5)S]_2$,[8] but are considerably shorter than the Mo–S bond lengths in other complexes[9–11] and the estimated[11] normal Mo(V)–S single-bond distance of 2.487 (7) Å. Considerable π bonding was propounded[8] to exist in the four-membered Mo_2S_2 ring bridging system of $[MoO(h^5\text{-}C_5H_5)S]_2$ to account for the observed Mo–S bond shortening. The Mo–S–Mo bond angles subtended at the triply bridging sulfur atom range from 74.7 (1) to 74.9 (1)°, with an average value of 74.8°, while those subtended at the doubly bridging sulfur atoms range from 75.3 (1) to 75.8 (1)°, with an average value of 75.6°.

In contrast to other molybdenum cyclopentadienyl complexes, in $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ and in $[MoO(h^5\text{-}C_5H_5)S]_2$ each Mo is deficient by two electrons from attaining a so-called closed-shell electronic configuration. Qualitative MO symmetry arguments[12] based on C_{3v} symmetry indicate that the nine metal symmetry orbital com-

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(3) Kindly performed by Dr. Michael Camp *via* the Faraday method.

(4) For computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(5) Although to our knowledge $Mo_4(h^5\text{-}C_5H_5)_4S_4$ has not as yet been synthesized, it, as well as the corresponding $Cr_4(h^5\text{-}C_5H_5)_4S_4$ tetramer, prepared by K. Ulm (Ph.D. Dissertation, Ludwig-Maximilians-Universität, Munich, 1961), should possess T_d-$\bar{4}3m$ geometry.

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binations ($2a_1 + a_2 + 3e$) available for direct metal–metal interactions (as well as for π bonding with the S ligands) develop into four *bonding* ($2a_1 + e$) and five *antibonding* ($a_2 + 2e$) delocalized trimetal orbitals (relative to the energies of the isolated AO's of each metal atom). Furthermore, in order to account for the diamagnetism of $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$, it is presumed from orbital overlap considerations that the six electrons available for direct Mo–Mo interactions occupy $a_1 + e$ bonding combinations, with the remaining a_1 trimetal bonding combination being empty. The application of this same MO scheme to the isostructural, diamagnetic $Mn_3(h^5\text{-}C_5H_5)_3(NO)_4$ molecule, for which each Mn conforms to the noble-gas rule, indicates that the 12 electrons available for placement into the 9 trimetal orbitals inhabit, in addition to the a_1 and e bonding levels (filled in $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$), the other a_1 bonding level along with a doubly degenerate antibonding e one. Complete occupation of these least two levels would tend to cancel each other in terms of metal–metal interactions, and therefore from a localized valence-bond viewpoint both the $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$ cation and the $Mn_3(h^5\text{-}C_5H_5)_3(NO)_4$ molecule possess electron-pair metal–metal bonds.

This MO model, which focuses primary attention on the metal cluster bonding,[13] predicts (1) the possibility of reduction of the $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$cation; (2) the feasibility of attempting to prepare the unknown molecule (or cations) of $M_3(h^5\text{-}C_5H_5)_3S_4$ (where M = Ru, Os); (3) the possibility of oxidation of $Mn_3(h^5\text{-}C_5H_5)_3(NO)_4$. In fact, a cyclic voltammogram of the $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$ salt in CH_2Cl_2 gives a one-electron reduction wave at −0.55 V (*vs.* sce). Further studies are being carried out to substantiate these predictions, and full details of our communication presented here will be reported upon completion of this work.

Acknowledgments. We are indebted to the National Science Foundation (No. GP-4919 and GP-19175X) for their financial support of this work. H. V. expresses his gratitude to the Deutsche Forschungsgemeinschaft for a traveling grant. The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made possible by partial support from the National Science Foundation and the Wisconsin Alumni Research Foundation, administered through the University Research Committee. We also thank Fraulein G. Fortuna for her assistance.

[13] The qualitative symmetry arguments and resulting predictions are assumed to be valid despite extensive mixing, which no doubt occurs among metal–ligand and trimetal symmetry orbitals belonging to a given representation.

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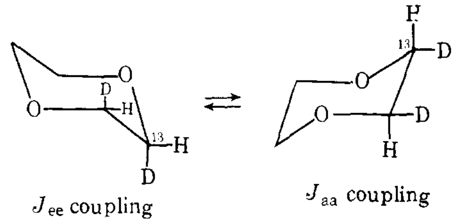
Ring Inversion Barrier of 1,4-Dioxane

Sir:

Whereas the nmr spectrum of cyclohexane[1] separates from a singlet into a multiplet at −65°, the 1,4-dioxane protons appear as a sharp singlet even at −160° with a width at half-height comparable to that of TMS.[2,3] This anomalous behavior has three possible explanations. First, the chair-to-chair inversion barrier may be lower than ~5 kcal/mol ($\Delta G^{\ddagger}$). Second, dioxane may exist predominantly in a boat form which pseudorotates with a low energy barrier. Third, a coincidence of the axial and equatorial resonances may exist at low temperatures.

In examining the proton spectrum of 1,4-dioxane, it was noted that the ^{13}C side bands appear as multiplets. The multiplet structure of the side band has been the textbook example[4,5] of chemical shift nonequivalence induced by coupling with the natural-abundance ^{13}C nucleus. The multiplet observed is a time-average spectrum resulting from rapidly interconverting forms of dioxane.[6] It was therefore hypothesized that at a temperature sufficiently low to cause the inversion process to be slow on the nmr time scale, significant changes would occur in the coupling in the ^{13}C side bands. With this idea in mind, the ^{13}C side-band proton spectrum of dioxane was investigated at low temperatures. A change is observed at approximately −90°. However, the peaks are broad and overlap and hence are difficult to analyze.

In order to simplify the ^{13}C side bands, a specifically deuterated dioxane was synthesized. For this purpose 2,3,5,6-dioxane-d_4, in which the relationship of the deuterium atoms of the –OCHDCHDO– moiety is trans, was prepared.[7] This isomer was selected because at low temperature in the ^{13}C side bands, the individual J_{ee} and J_{aa} couplings are expected to be observed (eq 1),



(1)

and the side band is expected to consist of a pair of doublets. At room temperature, each side band is expected to exist as a doublet with $J = {}^1/_2(J_{aa} + J_{ee})$.

Spectra of the trans-trans compound were obtained in a solvent mixture of 10% TMS, 37% CH_2Cl_2, 37% $CH_2{=}CHCl$, and 16% dioxane-d_4 (volume %). At room temperature, the expected spectrum for the upfield side band consisting of a doublet of 6.5 Hz was observed. (The low-field side band was not investigated owing to the nearness to side bands of the solvents.) At −103°, the spectrum of the upfield side band consisted of a doublet (J_{aa} = 11.7 Hz) and an unresolved doublet (J_{ee} = *ca.* 1 Hz) (Figure 1). However, the J_{ee} doublet is not centered within the J_{aa} doublet as was expected. The reason for this lack of symmetry is explained below.

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(7) The synthesis of this compound will appear in a forthcoming paper.