

π system due to their *axial* nature, which is apparent from the $J_{9a,1(4)}$ and $J_{9s,1(4)}$ values.¹⁴ As can be expected from the molecular conformation of **5**, the ρ values for the methyl protons, H_{9a} , and H_{9s} were very small.

In conclusion, it is suggested that the sign of the hfsc of a proton with a $p\pi$ orbital across the W-plan arrangement is the same as the sign of the π spin density.

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Organometallic Chalcogen Complexes. XXIII. Preparation and Structural Characterization of a Mixed Transition Metal Cluster Complex, $[\text{Re}_2\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3](\text{S})[\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3]$, Containing Triply and Quadruply Bridging Sulfur Atoms. A New Synthetic Route to Highly Clustered Metal-Sulfur Systems¹

Sir:

The extreme versatility of sulfur in atomic form in its various modes of coordination in organometallic cluster systems has been established directly from crystallographic studies which have shown a "bare" sulfur atom linked to transition metals as (1) a doubly bridging, two-electron σ -donating ligand;² (2) a triply bridging, four-electron σ -donating ligand;³ (3) a quadruply bridging, four-electron σ -donating ligand;⁴ and (4) a quadruply bridging six-electron σ -donating ligand.⁵ Similar metal linkages have also been found for atomic selenium and tellurium. Although a variety of reactions have been used to prepare such organometallic chalcogen complexes, in many cases they are obtained mostly in low yields from rather unusual and sometimes unpredicted reactions. In an effort to acquire them in a more designed fashion, we are carrying out reactions by which reactive organometallic chalcogen intermediates can be isolated and then brought by further reaction to produce desired metal cluster chalcogen species.

Abel and coworkers⁶ first studied the reactions of organotin-mercaptopto complexes of the types $\text{R}_3\text{SnSR}'$ and $\text{R}_2\text{Sn}(\text{SR}')_2$ with organometallic halides to produce compounds containing the mercaptan as a ligand, the driving force being the formation of a metal-sulfur bond and an organotin halide. It was subsequently shown by Schumann and coworkers⁷ that the chalcogen atom in $(\text{Me}_3\text{Sn})_2\text{X}$ (where X = S, Se, Te) is sufficiently basic to displace a carbonyl ligand from $\text{M}(\text{CO})_6$

(where M = Cr, Mo, W) to form $\text{M}(\text{CO})_5(\text{X}(\text{SnMe}_3)_2)$ (where X = S, Se, Te). We have undertaken a systematic study of the reactions of $(\text{Me}_3\text{Sn})_2\text{S}$, both in the free state and bound to a metal as a Lewis base adduct, with a variety of organometallic halides. In order to illustrate the diversity and scope of this method, including the means of preparing mixed metal-sulfur clusters, we report here the synthesis and structural analysis of one of the first mixed metal-sulfur complexes, $[\text{Re}_2\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3](\text{S})[\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ (**1**), which is of special interest in its hitherto unknown feature of possessing both triply bridging, four-electron σ -donating and quadruply bridging, six-electron σ -donating sulfur atoms.

The reaction of $(\text{Me}_3\text{Sn})_2\text{S}$ with $\text{Re}(\text{CO})_5\text{Cl}$ was previously reported by one of us to go smoothly to a bridged dimeric species, $[\text{Re}(\text{CO})_4(\text{SSnMe}_3)]_2$.⁸ This Me_3SnS -bridged dimer reacts with $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}$ in either 1,2-dimethoxyethane or benzene at 75° with loss of carbonyl to form **1**. This air-stable compound, which is only slightly soluble in polar solvents, was shown from a magnetic susceptibility measurement⁹ to be diamagnetic. Its stoichiometry¹⁰ as well as atomic arrangement were ascertained from a crystallographic investigation.

Crystals of **1** suitable for X-ray diffraction were taken from the reaction product and were found from photographic data to belong to the monoclinic system. The unit cell of centrosymmetric symmetry $P2_1/c$ contains four molecules. The lattice parameters obtained from application of a diffractometric method¹¹ are $a = 9.364$ (1), $b = 30.256$ (3), $c = 11.015$ (1) Å, $\beta = 122.52$ (1)°. The structure was determined by conventional Patterson and Fourier techniques from intensity data collected with Mo $K\alpha$ radiation by the θ - 2θ scan technique on a General Electric full-circle, Datex-controlled diffractometer. A mixed anisotropic-isotropic, full-matrix, least-squares refinement based on 2224 absorption-corrected data with $|F| > 4\sigma(F)$ yielded an unweighted R_1 value of 4.3%. In this refinement, each of the two cyclopentadienyl rings was constrained as a rigid regular D_{5h} pentagon with C-C and C-H bond lengths of 1.405 and 1.09 Å, respectively. Anisotropic thermal parameters were utilized for the metal and sulfur atoms and isotropic ones for all other atoms, with those of the hydrogen atoms not varied throughout the refinement.¹²

The molecular geometry (Figure 1) of **1** consists of a nonlinear trinuclear metal framework with $\text{Re}(1)$ of the central $\text{Re}(\text{CO})_3$ fragment forming electron-pair metal-metal bonds with a $\text{Re}(\text{CO})_3$ group and a $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_2$ group. The three metal atoms of this open triangular system are all bridged on one side of their plane by a "bare" sulfur atom, S(1), and on the

(8) H. Vahrenkamp, *Chem. Ber.*, **103**, 3580 (1970).

(9) We gratefully thank Dr. Michael Camp for this measurement at room temperature by the Faraday method.

(10) Yield >60% based on S. *Anal.* Calcd for $\text{Re}_2\text{Mo}_2\text{O}_2\text{S}_2\text{C}_{21}\text{O}_{11}\text{H}_{10}$: Mo, 17.99; S, 6.02; C, 23.65; H, 0.94. Found: Mo, 17.30; S, 5.98; C, 24.23; H, 1.00; mp, 290° dec.

(11) A. S. Foust, Ph.D. Thesis, University of Wisconsin, Madison, Wis., Jan 1970.

(12) 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.

(1) Previous paper in this series: C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6032 (1971).

(2) (a) D. L. Stevenson and L. F. Dahl, *ibid.*, **89**, 3721 (1967); (b) A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969).

(3) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969), and references cited therein.

(4) C. H. Wei and L. F. Dahl, to be published.

(5) J. M. Coleman, A. J. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(6) E. W. Abel, A. M. Atkins, B. C. Crosse, and G. V. Hutson, *J. Chem. Soc. A*, 687 (1968), and references cited therein.

(7) (a) H. Schumann, O. Stelzer, and W. Gick, *Angew. Chem., Int. Ed. Engl.*, **8**, 271 (1969); (b) H. Schumann and R. Weis, *ibid.*, **9**, 246 (1970).

other side by a $\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3$ ligand. A consequence of the necessity of electron-pair $\text{Re}(1)\text{-Re}(2)$ and $\text{Re}(1)\text{-Mo}(3)$ 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 reported¹³ for $(\text{OC})_5\text{Re-Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3$. 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 $[\text{Fe}_2(\text{CO})_6(\text{SMe})_2]\text{S}$.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 found¹⁴ about each Mo atom in both the neutral parent $[\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{SR})_2]$ 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 $[\text{Re}(\text{CO})_4(\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3)]_2$ to be formed along with Me_3SnCl by cleavage of the S-Sn bonds in $[\text{Re}(\text{CO})_4(\text{SSnMe}_3)]_2$ upon reaction with $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}$. 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.

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(15) (a) L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, **2**, 1067 (1963); (b) C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965).

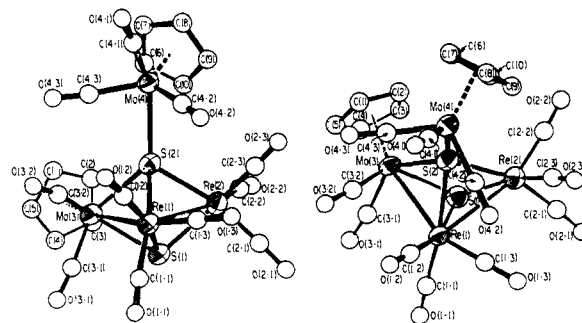


Figure 1. Molecular geometry of the (mixed metal)-sulfur cluster system $[\text{Re}_2\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_6(\text{S})[\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3]]$ containing both a trimetal- and a tetrametal-coordinated sulfur atom. The anisotropically refined rhenium, molybdenum, and sulfur atoms are designated as 50% probability thermal ellipsoids. Important distances are $\text{Re}(1)\text{-Re}(2)$, 2.985 (1); $\text{Re}(1)\text{-Mo}(3)$, 2.909 (2); $\text{Re}(2)\cdots\text{Mo}(3)$, 3.927 (2); $\text{Re}(1)\text{-S}(1)$, 2.448 (5); $\text{Re}(1)\text{-S}(2)$, 2.473 (5); $\text{Re}(2)\text{-S}(1)$, 2.410 (5); $\text{Re}(2)\text{-S}(2)$, 2.453 (4); $\text{Mo}(3)\text{-S}(1)$, 2.487 (5); $\text{Mo}(3)\text{-S}(2)$, 2.523 (5); and $\text{Mo}(4)\text{-S}(2)$, 2.550 (5) Å. The $\text{Re}(2)\text{-Re}(1)\text{-Mo}(3)$ bond angle is 83.56 (4)°.

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Organometallic Chalcogen Complexes. XXIV. Synthesis, Structure, and Bonding of $[\text{Mo}_3(h^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+[\text{Sn}(\text{CH}_3)_3\text{Cl}_2]^-$ Containing a Triangular Molybdenum(IV) Cluster Cation with Doubly and Triply Bridging Sulfur Atoms¹

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 $[\text{Mo}_3(h^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+[\text{Sn}(\text{CH}_3)_3\text{Cl}_2]^-$. Besides representing a new kind of metal-chalcogen cluster system with the unprecedented feature of containing both doubly and triply bridging sulfur atoms, the $[\text{Mo}_3(h^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$ 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 cyclopentadienyl-molybdenum-sulfur complexes stems from possible biochemical implications with respect to the unknown metal-ligand coordinated units in molybdenum-sulfur enzymes.

$[\text{Mo}_3(h^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+[\text{Sn}(\text{CH}_3)_3\text{Cl}_2]^-$ was obtained as one of the products from the reaction of $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}$ in 1,2-dimethoxyethane with $[\text{Sn}(\text{CH}_3)_3]_2\text{S}$.²

(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 $\text{Mo}_3\text{S}_4\text{Cl}_2\text{SnC}_{15}\text{H}_{24}$: 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.