to **5c** is due to hydrogen reversion from a triplet biradical such as **5b**, since if this were the case, we would expect racemization of recovered optically active **5** from partially photolyzed solutions.

Acknowledgment. The authors thank Professor P. J. Wagner for graciously communicating his results on the photochemistry of α-ketopropiophenones.

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Organometallic Chalcogen Complexes. XIX. Stereochemical Analyses of a Tetramercapto-Bridged Molybdenum(III) Dimer, $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$, Containing a Strong Molybdenum–Molybdenum Interaction, and of Its Corresponding Paramagnetic Cation

Sir:

Our interest in the systematic preparation and characterization of a large assortment of organo-(transition metal) cluster systems has been focused on the stereochemical consequences caused by the addition or removal of valence electrons. A major objective of these studies is to obtain a better understanding of the detailed nature of metal–metal interactions in transition metal cluster systems in that from the observed changes in molecular parameters due to the change in the number of valence electrons it has proven possible to deduce qualitatively the topological nature of the MO containing the least stable valence electrons.[1-9] The drastic influence of valence electrons on molecular geometry has been previously demonstrated from X-ray crystallographic measurements for metal cluster complexes in which the number of valence electrons has been varied by replacement with either different metal atoms and/or different ligands.[1-9] In the first of a series of papers dealing with structural studies of metal cluster systems in which the number of valence electrons has been altered by oxidation (or reduction), we wish to report the chemical synthesis and characterization of the cationic complex $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2^+$, together with a characterization of its neutral parent $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$. The stereochemical relationship of this neutral and oxidized molybdenum(III)–mercapto complex is of special interest not only in connection with the different modes of coordination and stereochemical behavior of reduced Mo(V)–oxidized Mo(VI) species in a number of sulfydryl enzymes,[10] but also with respect to providing a better understanding of the function of molybdenum in the catalysis of several oxidation–reduction reactions in biochemical systems. This investigation has established the detailed geometry of this type complex and together with a comparison of the structural features of the neutral and oxidized iron–sulfur dimer, $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^n$ ($n = 0, +1$),[11] has revealed that the particular molecular architecture (and especially the nature of the bridging ligands) has a dominant influence with respect to possible alteration of geometry due to a gain or loss of electrons.

The neutral $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$ complex was obtained from the reaction of $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$ with dimethyl disulfide by the method of King,[12] who, from the compound's diamagnetic character (indicated from the proton nmr spectrum and confirmed by him from magnetic balance measurements), proposed a dimeric tetramercapto-bridged structure containing an electron-pair Mo–Mo bond. Crystals of this neutral complex form from $CHCl_3$ solution as orange-brown needle-like plates in the orthorhombic space group $P2_12_12_1$ (D_2^4, No. 19). The unit cell containing four dimeric molecules has dimensions $a = 15.608\ (2)$ Å, $b = 14.767\ (2)$ Å, $c = 7.878\ (1)$ Å. The structure was determined from conventional methods based on data collection with a General Electric four-circle diffractometer by the θ–2θ scan technique with Mo Kα radiation. Least-squares refinement, in which each cyclopentadienyl ring was rigidly constrained as a regular pentagon (with C–C and C–H bond lengths of 1.405 and 1.08 Å, respectively), yielded an unweighted R_1 value of 4.2% for 1220 observed reflections. The four bridging sulfur atoms in the crystallographically independent dimeric molecule were found to be disordered such that there are two sets of four sulfur atoms experimentally weighted 4:1. However, each methyl carbon atom was treated as nondisordered in that the positions of the two methyl carbon atoms of each disordered pair of sulfur atoms were assumed to be coincident; no attempt was made to locate the presumably disordered methyl hydrogen atoms.

The monocation was chemically synthesized as the hexafluorophosphate salt by the oxidation of $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$ in methylene chloride with $AgPF_6$ in ethanol. This reaction leads to the formation of a deep purple solution from which, on addition of ether, a purple solid is deposited. Crystals of $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2PF_6$ suitable for X-ray investigation were obtained by recrystallization from hot acetonitrile solution. Acetone or acetonitrile solutions of this compound are moderately stable to air, but reduction of the cation to the neutral species slowly occurs in solution. More rapid reduction may be effected by the addition of $NaBH_4$. The formulation of this new compound was substantiated by elemental analysis and conductivity measurements in acetone. $[Mo(h^5\text{-}C_5H_5)\text{-}$

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(1) Previous paper in this series: C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, 93 (1969).

(2) Single-crystal X-ray and esr studies of the paramagnetic complexes $Co_3(CO)_9X$ (X = S, Se) and their diamagnetic analogs $Co_2Fe(CO)_9X$ (X = S, Se, Te)[1,3] and X-ray measurements of the paramagnetic complex $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ and its diamagnetic analog $Ni_2Co(h^5\text{-}C_5H_5)_3(CO)_2$[4] have shown that electrons in excess of the closed-shell electronic configuration of each metal atom in these triangular metal cluster systems occupy primarily the *antibonding* metal σ orbitals.[5]

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$(\mathrm{SCH_3})_2]_2\mathrm{PF_6}$ is paramagnetic with a solid-state magnetic moment of 1.69 ± 0.05 B.M. at ambient room temperature.[13] The esr spectral parameters of g = 2.009 and ΔH = 32 G, measured in $\mathrm{CH_2Cl_2}$ solution, are in close agreement with those found by Dessy, *et al.*,[14] for the monocation electrochemically generated from $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2$. There is no evidence at room temperature for hyperfine splitting due to the $^{95}\mathrm{Mo}$ (15.72%; $I = {}^5/_2$) or $^{97}\mathrm{Mo}$ (9.46%; $I = {}^5/_2$) nuclei.

X-Ray data showed the reddish-purple needles of $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2\mathrm{PF_6}$ to be tetragonal with four formula species in a unit cell of dimensions $a = b$ = 12.386 (3) Å and c = 11.664 (3) Å. Systematic absences of intensities are consistent with the three probable space groups $I4cm$ ($C_{4v}{}^{10}$, No. 108), $I\bar{4}c2$ ($D_{2d}{}^{10}$, No. 120), and $I4/mcm$ ($D_{4h}{}^{18}$, No. 140). The structure was eventually solved and refined in the latter centrosymmetric space group; its symmetry requires each of the four dimeric cations to possess crystallographic site symmetry D_{2h}-$2/m2/m2/m$ which in turn demands twofold-disordered sulfur atoms and twofold-disordered cyclopentadienyl rings with one twofold crystallographic axis coincident with the Mo–Mo bond and each of the other two perpendicular twofold axes passing though two methyl carbon atoms. The four $\mathrm{PF_6}^-$ anions also lie on special positions in the unit cell corresponding to site symmetry D_4-422. The R_1 value based on rigid-body least-squares refinement is 8.4% for 341 observed maxima obtained by diffractometry means (described above).

Both the neutral and oxidized $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2{}^n$ complexes (n = 0, +1) (Figure 1) exist as discrete species in which the two $\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})$ moieties are linked to each other by four symmetrically positioned bridging mercapto ligands. The sulfur-attached methyl carbon atoms are oriented such that with the assumption of cylindrical symmetry for each cyclopentadienyl ring the entire dimer (except for the undetermined methyl hydrogen atoms) conforms experimentally to C_{4h}-$4/m$ geometry. The horizontal mirror plane which bisects the two halves of the dimer passes through the four sulfur and four methyl carbon atoms. For the diamagnetic neutral species a *direct* metal–metal bond rather than electron-pair coupling through an exchange mechanism *via* the bridging ligands is in accord not only with the short Mo–Mo distance of 2.603 (2) Å but also is completely compatible with the four Mo–S–Mo bridging angles of sharply acute values of range 63.6 (1)–63.9 (1)° rather than near the tetrahedral value.[15]

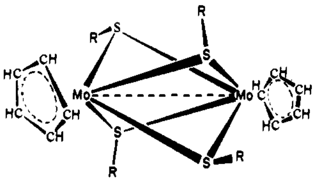
$[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SR})_2]_2^n$ ($\mathrm{R{=}CH_3}$; n=0,+1)

Figure 1. Geometry of the neutral and oxidized $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2{}^n$ dimers (n = 0, +1).

Table I. Average Distances (Å) and Average Bond Angles (deg)

	$[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})\text{-}(\mathrm{SCH_3})_2]_2{}^{a,b}$	$[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})\text{-}(\mathrm{SCH_3})_2]_2\mathrm{PF_6}{}^b$
Mo–Mo	2.603 (2)	2.617 (4)
Mo–S	2.46	2.44
S···S	2.96	2.90
$\mathrm{S{-}CH_3}$	1.84	1.82
$\mathrm{Mo{-}C_5H_5}$ (centroid)	1.97	1.97
$\mathrm{Mo{-}C_5H_5}$ (carbon)	2.30	2.30
∠Mo–S–Mo	64	65
∠S–Mo–S	116	115
$\angle\mathrm{Mo{-}S{-}CH_3}$	116	118

[a] Crystal disordered model (80% weighted orientation). [b] *Individual* bond distances and interbond angles have the following esd's: Mo–S, 0.005; S···S, 0.009; $\mathrm{S{-}CH_3}$, 0.018 Å; Mo–S–Mo, 0.2; S–Mo–S, 0.2; $\mathrm{Mo{-}S{-}CH_3}$, 0.7°.

Unlike the drastic change in geometry[11] between the neutral and oxidized mercapto-bridged iron dimers, $[\mathrm{Fe}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{SC_6H_5})]_2$ and $[\mathrm{Fe}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{SCH_3})]_2{}^+$, the most notable feature between the mercapto-bridged molybdenum dimers revealed from Table I is the lack of any conspicuous stereochemical change between the neutral and oxidized forms other than a difference in the nonbonding S···S distances which may be attributed to greater repulsion among the presumably more negatively charged sulfur atoms in the neutral species. It was expected prior to these results that the $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2{}^+$ cation would probably have a shorter Mo–Mo bond length in accord with our prejudice that some metal–metal multiple bond character would be achieved by the removal of an electron from an MO which is antibonding in a dδ–dδ fashion with respect to the two molybdenum atoms in the neutral species.[16] The occurrence of multiple

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(13) We are grateful to Mr. Michael Camp for carrying out a Faraday magnetic measurement.

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(16) Our prejudice that the highest occupied MO in the neutral parent molecule involves an antibonding combination of molybdenum dδ orbitals is based on the following qualitative bonding representation which is similar to those previously employed[1-9] to describe the nature of metal–metal bonding in other metal atom cluster systems. If local right-handed coordinate systems are chosen at each molybdenum atom with the z axes directed along the internuclear Mo–Mo line, the nine valence orbitals of each molybdenum atom may be classified relative to the metal–metal axis with the 5s, $5p_z$, and $4d_{z^2}$ orbitals of σ symmetry, with the $5p_x$, $5p_y$ and $4d_{xz}$, $4d_{yz}$ pairs of π symmetry, and with the $4d_{x^2-y^2}$, $4d_{xy}$ pair of δ symmetry. For each Mo(III) it is reasonable to set aside one σ and two π orbitals for binding with its attached cyclopentadienyl ring and to assign one σ, two π, and one δ orbital for localized electron-pair σ bonding with the four bridging mercapto sulfur atoms. This leaves one σ and one δ orbital per Mo(III) to be considered for direct Mo–Mo interactions. On the basis of overlap considerations the σ orbitals are presumed to interact considerably with each other to give strongly bonding and antibonding orbital energies (relative to the energy of each isolated σ orbital), while the more weakly interacting δ orbitals should produce a relatively small separation between the bonding and antibonding energy levels. In this view the available six electrons (*i.e.*, three electrons from each Mo(III)) will occupy the bonding σ and both the bonding δ and antibonding δ* metal symmetry orbitals (effectively nullifying any δ contribution to the metal–metal bond) to give a resulting electron-pair Mo–Mo σ bond for the parent $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2$ molecule. Oxidation of this neutral molecule to give the monocation is therefore presumed to result in a removal of one electron from the weakly antibonding δ* metal orbital combination, which (in the absence of any constraints of the bridging mercapto ligands) would be expected to give rise to a small δ-bond stabilization of the Mo–Mo interaction. One underlying assumption (which we feel is a valid one) in this qualitative description of the nature of the metal–metal bonding in the $[\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{SCH_3})_2]_2{}^n$ (n = 0, +1) complexes is that the bonding metal–ligand MO's are of much lower energy and the empty antibonding metal–ligand MO's are of higher energy than the occupied metal σ and δ

metal–metal bonds in a number of other molybdenum oligomers[17] lends weight to our hypothesis. The observed essential invariance of the Mo–Mo bond length in the neutral dimer to oxidation may be ascribed to the least stable MO being primarily nonbonding with respect to the two molybdenum atoms. However, a much more plausible explanation (still consistent with our hypothesis of some metal–metal multiple bond character in the oxidized complex) emerges after it is noted that the bridging Mo–S–Mo angles in the neutral dimer are as small as those found in any doubly bridging mercapto system. Hence, it is proposed that these already angularly strained bridging ligands effectively prevent any possible shortening of the Mo–Mo distance on oxidation. These results have a generalized stereochemical importance in ligand-bridged metal–metal bonded systems. The essential invariance of the metal–metal distance in the oxidized form need not imply that there is no increase in multiple bond character between the metal atoms in the oxidized species. The lack of appreciable geometrical change may be due primarily to the particular steric constraints of the bridging ligands in a given architecture.

This study represents the first complete structural determination of this type of binuclear metal complex.[18–22] Our conclusions have prompted a structural investigation of the weakly temperature-dependent paramagnetic vanadium analog $[V(h^5\text{-}C_5H_5)(SCH_3)_2]_2$,[23] which hopefully will provide a further assessment of the interrelationship of the nature of the bridging ligands to the metal–metal distance in a complex apparently containing considerable metal–metal interaction.

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symmetry combinations. It should be noted that one referee has suggested that the narrow esr resonance at room temperature with no apparent hyperfine structure in the $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2^+$ cation may signify that this cation is best regarded as a radical cation with the unpaired electron density located mainly on the sulfur atoms. Low-temperature esr measurements are in progress in an attempt to clarify this possibility.

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(18) The analogous metal dithiolene complexes $[M(h^5\text{-}C_5H_5)(SCCF_3)]_2$ (M = V, Mo) were prepared and characterized from nmr, ir, and room-temperature magnetic susceptibility data by King,[12,19] who proposed the existence of a Mo–Mo single bond to account for the observed diamagnetism of the molybdenum dimer and a V–V bond of partial double-bond character in the vanadium derivative to explain the observed small magnetic moment. A preliminary X-ray analysis of the molybdenum dimer was carried out by Cox and Baird[20] who, in spite of difficulties encountered in unsuccessful attempts to refine the structure, nevertheless ascertained the gross tetramercapto-bridged geometry proposed by King.[12] A comparison of their determined bond length of 2.62 (2) Å with that of 2.603 (2) Å found for $[Mo(h^5\text{-}C_5H_5)(SCH_3)_2]_2$ makes it likely that the detailed geometries of the corresponding methylthio and dithiolene metal complexes are closely related to each other. Cox and Baird[21] also concluded from similar crystal data (including lattice parameters and space group assignments) that the molybdenum and vanadium dithiolene dimers are isostructural. The corresponding chromium complex, $[Cr(h^5\text{-}C_5H_5)(SCCF_3)_2]_2$, was surprisingly found from an X-ray analysis[21] to have a disulfur-bridged rather than a tetrasulfur-bridged structure. Two derivatives of the same molecular formula $[Mo(h^5\text{-}C_5H_5)S_2C_6H_{10}]_2$, prepared by Treichel and Wilkes,[22] presumably are geometrical isomers with tetrasulfur-bridged and/or disulfur-bridged structures.

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Organometallic Chalcogen Complexes. XX. Stereochemical Characterization of an Oxidized Iron–Sulfur Dimer, $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$. A Paramagnetic Cation Effectively Containing a One-Electron Metal–Metal Bond[1]

Sir:

As part of a systematic investigation of redox effects on the geometries of various types of organometallic oligomers which gain and/or lose electrons without rupture of their atomic frameworks,[1] we wish to report the structural characterization of an $[Fe(h^5\text{-}C_5H_5)(CO)(SR)]_2^+$ cation (R = CH_3) which, in conjunction with the known architectures of the neutral phenylmercapto analog[2] and other stereochemically related complexes,[3–10] provides definitive evidence that the iron–iron interaction in the above cation can be essentially described as a *one-electron metal–metal bond.* These results are of particular importance in that they imply the possibility that the geometries of the plant-like or bacterial-type ferredoxins, which have been shown to possess either *dimeric* or one (or two) *tetrameric* iron–sulfur systems,[11] may be markedly different with regard to the iron–iron distances in the oxidized and reduced forms.

This work was greatly stimulated by the extensive electrochemical studies of Dessy and coworkers[12] who

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