Inorg. Chem. **1987**, *26*, 1889–1893 **1889**

Contribution from the Departments of Chemistry, University of Colorado, Boulder, Colorado 80309,
and The Open University, Milton Keynes MK7 6AA, England

Molybdenum-95 NMR Spectroscopy and Its Relation to the Structure and Reactivity of Sulfur-Bridged Cyclopentadienylmolybdenum Dimers

Carla J. Casewit,[†] M. Rakowski DuBois,[†] Ruth A. Grieves,[‡] and Joan Mason*[‡]

Received October 2, 1986

A range of 4000 ppm in molybdenum shift is observed for sulfur-bridged cyclopentadienylmolybdenum compounds, the shielding decreasing in the following sequence: cubane > [CpMo^{V}(=S)(μ-S)]$_2$ > [CpMo^{IV}(μ-S)(μ-SR)]$_2$ > [Mo^{III}(μ-SR)$_2$]$_2$. In tetrasulfur-bridged Mo(III) and Mo(IV) dimers the metal nucleus shifts are very sensitive to change in the organo substituents (R) on sulfur, over a range of nearly 2000 ppm, and strong deshielding of the carbon and protons confirms the delocalization of the Mo$_2$(organoS$_4$) core. Because of the small ligand field splitting, the nephelauxetism of the sulfur ligands does not dominate the metal nucleus shifts as it does for lower oxidation states. The molybdenum shielding is therefore determined by the core frontier orbitals, and correlations with the electronic spectra, electrode potentials, and reactivity are evident. The (reversible) addition of a hydrogen or other molecule to two bridging sulfurs, although a reductive process Mo(IV) → Mo(III), deshields the metal nucleus by adding electrons to the paramagnetic circulation. Strong deshielding is observed with conjugating organo substituents, as delocalization of p(S) electrons stabilizes ligand field LUMOs.

Introduction

The presence of ligating sulfur in molybdenum systems with important catalytic activity,[1-3] from molybdenum sulfide surfaces to molybdoenzymes, lends particular interest to the sulfur-bridged molybdenum dimers or small clusters that show related properties and can be studied under homogeneous conditions. Remarkable donor–acceptor reactivity has been discovered for cyclopentadienylmolybdenum dimers with four sulfur (sulfido or thiolato) bridges allowing homogeneous redox reactions, hydrodesulfurization, and other transformations of organic groups under mild conditions.[4-13] These dimers, like the related cubanes,[14] can sustain more than one reversible one-electron-redox process with continuity of structure,[4,12,15] as do electron-transport agents in redox proteins.[1c]

We recently described EPR studies on paramagnetic Mo(III)–Mo(IV) sulfur-bridged dimers[15] and now report ^{95}Mo NMR spectroscopic investigations of the diamagnetic Mo(V), Mo(IV), and Mo(III) dimers, to probe the structure in solution and the nature of the reactive site. The molybdenum NMR shifts are remarkably sensitive to change in organo substitution on the bridging sulfur. Together with the NMR properties of the organo groups, they demonstrate the extension of the delocalization of the Mo$_2$S$_4$ core to include the organic groups on sulfur and correlate with the unusual reactivity. Molybdenum NMR spectroscopy has recently been reviewed.[16]

Results and Discussion

Table I gives spectroscopic results for a range of cyclopentadienylmolybdenum sulfur-bridged dimers, with a related Mo(II) complex[17] and a molybdenum–sulfur cubane for comparison. The range of molybdenum shifts is nearly 2000 ppm for the quadruply bridged Mo(III) and Mo(IV) dimers, or 4000 ppm with inclusion of the open Mo(V) dimers and the cubane. The line widths, often below 100 Hz, are therefore small in relation to the dispersion of the shifts, and these clearly have considerable potential for the characterization of products of reaction at the sulfur bridges.

In the interest of sensitivity, the line widths have not been optimized. They may be reduced by an increase in the molecular tumbling rate[18] by warming of the sample or by use of a less viscous solvent, as shown by the reduction from 110 to 60 Hz with a change from CH$_2$Cl$_2$ to Et$_2$O solvent for [Mo(C$_5$H$_4$Me)(S)(SEt)]$_2$ (IVb). Line widths are reduced also if substitution of the cyclopentadienyl ring is avoided, particularly by branched alkyl groups, cf. the line width of 550 Hz observed for the isopropyl derivative (VIIIb). On the other hand, such substitution improves the solubility of the complex. As found for other η^5-cyclopentadienyl complexes,[19] the line widths are often small compared with those for other complexes of similar molecular volume and apparent symmetry, the electronic distribution of the *polyhapto*cyclopentadienyl group producing a particularly small electric field gradient at the transition-metal nucleus.[20]

Two lines are resolved in molybdenum as well as proton resonance for two isomers of the mercapto complex (IVa), but not for the allene adduct (VII), although doubling of the carbon resonance shows the presence of two forms. These are likely to result from different orientations of the dithiolate ligands.

Rationale of the Metal Nucleus Shielding. In a ligand field atom-in-a-molecule formulation, the chemical shift of a metal nucleus with an open d shell is dominated by paramagnetic dπ → dσ^* circulations.[21] The coordination sphere of the metal in cyclopentadienylmolybdenum with three or four sulfur ligands

---

(1) (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. (b) Newton, W. E.; Otsuka, S., Eds. *Molybdenum Chemistry of Biological Significance*; Plenum: New York, 1979. (c) Hughes, M. N. *The Inorganic Chemistry of Biological Processes*, 2nd ed.; Wiley: Chichester, England, 1981. (d) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley-Interscience: New York, 1985.

(2) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(3) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(4) Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

(5) Miller, D. J.; Rakowski DuBois, M.; *J. Am. Chem. Soc.* **1980**, *102*, 4925.

(6) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

(7) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(8) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429. DuBois, D. L., unpublished observations.

(9) Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710.

(10) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(11) Miller, W. K.; Haltiwanger, R. C.; VanDerveer, M. C.; Rakowski DuBois, M. *Inorg. Chem.* **1983**, *22*, 2973.

(12) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

(13) Miller, D. J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Proceedings of 4th International Conference on the Chemistry and Uses of Molybdenum*; Barry, H. F., Ed.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; p 384.

(14) Bandy, J. A.; Davies, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395.

(15) Casewit, C. J.; Rakowski DuBois, M. *Inorg. Chem.* **1986**, *25*, 74.

(16) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

(17) Le Gall, J.-Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

(18) Boeré, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 319.

(19) (a) Dysart, S.; Georgii, I.; Mann, B. E. *J. Organomet. Chem.* **1981**, *213*, C10. (b) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1981**, *20*, 4183.

(20) Akitt, J. W.; McDonald, W. S. *J. Magn. Reson.* **1984**, *58*, 401.

(21) Mason, J. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 199. Mason, J. *Chem. Rev.*, in press. Jameson, C. J.; Mason, J. *Multinuclear NMR*; Plenum: New York, 1987; Chapter 3.

[†] University of Colorado.

[‡] The Open University.

0020-1669/87/1326-1889$01.50/0 © 1987 American Chemical Society

Table I. NMR and Other Spectral Parameters for Sulfur-Bridged Molybdenum Dimers and Related Compounds

	Mo oxidn			$W_{1/2}$,[d]	$E_{1/2}$,[e] V			$\delta(^{13}C)$ $(\delta(^{1}H))$[f]			UV-vis[g]				X-ray
compd[a]	no.	solvent[b]	$\delta(^{95}Mo)$[c]	Hz	redn	oxidn	ref	Cp	*Me*Cp	SR	solvent	λ, nm	$10^{-3}\epsilon$	ref	ref
$[Mo(C_5H_4\text{-}i\text{-}Pr)(\mu_3\text{-}S)]_4$ (I)		bz–tol	−1643	60		−0.33	14								
$[Mo(C_5H_5)(CO)_2(S_2CNEt_2)]$ (II)	II	$CHCl_3$	−544[h]	171				94.2							
trans-$[Mo(C_5H_4Me)(O)(\mu\text{-}S)]_2$ (IIIa)	V	$CHCl_3$	−489	120				104.1	14.4						*m*
								101.8							
cis-$[Mo(C_5H_4Me)(O)(\mu\text{-}S)]_2$	V	$CHCl_3$	−332	75				104.7	14.4						*m*
								100.9							
$[Mo(C_5Me_5)(S)(\mu\text{-}S)]_2$ (IIIb)	V	$CHCl_3$	475	400				113.9	12.5		$CHCl_3$	335	10.25	28	7
												446	5.98		
												485	2.47 sh		
$[Mo(C_5H_4Me)(\mu\text{-}S)(\mu\text{-}SH)]_2$ (IVa)	IV	CH_2Cl_2	389[i]	45				96.7	17.5	(−1.60), H	$CHCl_3$	310	sh	6	
			400	40				99.3		(−1.53)		390	1.7		
												510	3.9		
												700	2.5		
$[Mo(C_5H_4Me)(\mu\text{-}S)(\mu\text{-}SEt)]_2$ (IVb)	IV	CH_2Cl_2	497	110	$\underbrace{-1.43\quad -0.57}_{-0.86^{j}}$		12	98.7	17.0	27.7, CH_3	$CHCl_3$	320	sh	6	6[j]
		Et_2O	513	60				96.2		31.9, CH_2		398	1.6		
												514	3.9		
												687	2.1		
$[\{Mo(C_5H_4Me)\}_2(\mu\text{-}S)(\mu\text{-}SMe)(\mu\text{-}SCH_2S)]I$ (V)	IV	CH_2Cl_2	536	50	$\underbrace{-0.34\quad -1.39^{k}}_{-1.05}$		12	102.0	17.0	19.0, CH_3	CH_2Cl_2	477	1 sh	15	12
								104.0		49.8, CH_2		537	1.2		
										(4.8)		855	2.2		
$[Mo(C_5H_4Me)(\mu\text{-}S)]_2(\mu\text{-}SCH_2S)$ (VI)	IV	CH_2Cl_2	601	40	$\underbrace{-1.30\quad -0.27}_{-1.03}$		12	97.6	16.9	33.5, CH_2	THF	498	0.86	15	
								100.6		(2.6)		598	2.1		
								117.9				727	2.4		
$[Mo(C_5H_5)\{\mu\text{-}SCH_2C(=CH_2)S\}]_2$ (VII)	III	CH_2Cl_2	476	80		−0.24		91.6		37.2, CH_2					13
										37.6					
										108.1, $=CH_2$					
										153.9, $>C=$					
										154.1					
$[Mo(C_5H_5)(\mu\text{-}SMe)_2]_2$ (VIIIa)	III	toluene	937	70		0.15	12	(5.1)			CH_2Cl_2	460	0.5 sh	15	33
$[Mo(C_5H_4\text{-}i\text{-}Pr)(\mu\text{-}SMe)_2]_2$ (VIIIb)	III	toluene	1010	550				(5.1)							
$[Mo(C_5H_4Me)(\mu\text{-}SMe)]_2(\mu\text{-}SCH_2S)$ (IX)	III	CH_2Cl_2	1273	45		−0.04	12	87.5	16.2	22.3, CH_3					10
								93.2		74.6, CH_2					
								(5.1)		(6.2)					
$[Mo(C_5H_4Me)_2(\mu\text{-}SC_2H_2S)\{\mu\text{-}SC(S)S\}]$ (X)	III	CH_2Cl_2	1283	23				96.1	16.2	147.6, $-CH=CH-$					
								98.8							
								(5.1)							
$[Mo(C_5H_4Me)]_2(\mu\text{-}SC_2H_2S)(\mu\text{-}SCH_2S)$ (XI)	III	CH_2Cl_2	1925	60		−0.12	12	90.1	16.4	92.3, CH_2	CH_2Cl_2	368	sh		10
										(6.2)					
								95.4		147.4, $-CH=CH-$					
								(5.1)							
$[Mo(C_5H_4Me)(\mu\text{-}SC_2H_2S)]_2$ (XII)	III	CH_2Cl_2	2327	550		−0.15	12	93.2		147.7, $-CH=CH-$					11
								97.2		(6.5)					

[a] Structures are given in Chart I. [b] bz-tol is a 1:1 mixture by volume of benzene and toluene. All solvents were deuteriated. [c] $\delta(^{95}Mo)$ relative to 1 M Na_2MoO_4(aq) at pH 11, high frequency positive. [d] Line width at half-height, not optimized. [e] Redox potentials vs. SCE. All cyclovoltammograms are reversible or quasi-reversible unless otherwise described. [f] $CDCl_3$ solution. [g] sh = shoulder. [h] Reference 17. [i] Anti and syn compounds, ratio of peak areas 1.86:1. [j] $(SMe)_2$ compound. [k] Irreversible. [l] Both signals broad. [m] Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M., unpublished results.

resembles that of (d^6) piano-stool compounds of cobalt,[22] in which (as in the corresponding sandwich compounds)[22,23] the metal nucleus is deshielded by circulation of d_{z^2} and $d_{xy},d_{x^2-y^2}$ nonbonding ($d\pi$) electrons in d_{xz}^*, d_{yz}^* LUMOs, where z is the principal axis of the molecule. The paramagnetic term σ_P (which as a shielding term is opposite in sign to the chemical shift δ) is given by[22]

$$\sigma_P = -K(1/\Delta E_1 + 1/\Delta E_2)\langle r^{-3}\rangle \qquad (1)$$

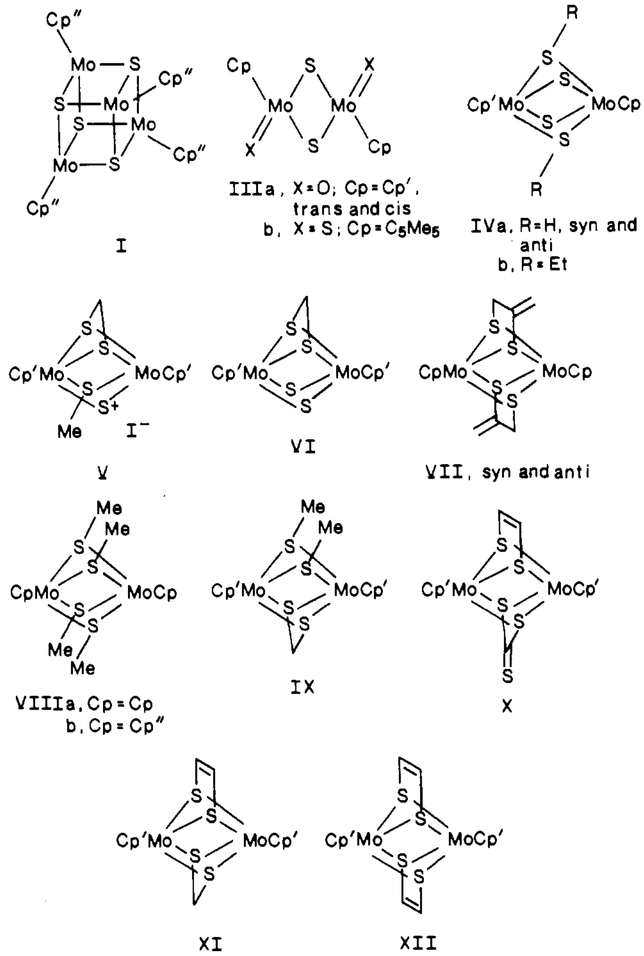
where ΔE_1 and ΔE_2 are the ligand field excitation energies for the d_{z^2} and $d_{xy},d_{x^2-y^2}$ orbitals, respectively, and r is the valence d electron radius. The coefficient K contains the angular momentum terms and increases with imbalance of charge in the valence shell. The K and ΔE values are dependent on the coordination geometry and so are likely to be affected by distortion of the Mo_2S_4 framework, as discussed below.

As shown by eq 1, the metal shielding increases with increase in the ligand field splittings ΔE, and also with increased nephelauxetic effect of the ligands, through decrease in the radial term $\langle r^{-3}\rangle$.[21] In these molybdenum dimers the energy term in eq 1 is evidently dominant: despite the greater nephelauxetism of the sulfur ligands, the molybdenum is strongly deshielded as compared with sandwich or carbonyl half-sandwich compounds. Thus ^{95}Mo shifts (relative to molybdate) are −1362 ppm for the benzene sandwich[23] and −1856 and −2120 ppm for the tricarbonyl piano-stool compounds $[Mo(C_5H_5)(CO)_3]_2$ and $[Mo(C_5H_5)(CO)_3]^-$, respectively;[19] cf. −1856 ppm for $[Mo(CO)_6]$.[16] Similarly, the presence of the relatively strong cyclopentadienyl ligand in the dimers tends to increase the metal shielding relative to that in molybdenum(VI) thiometalates such as MoS_4^{2-}, with δ 2259; the Mo(V) doubly bridged dimer (IIIb) (with δ 475) can be compared with a corresponding site in the trinuclear $(\mu\text{-S})_2$ oxothiomolybdates (with δ 1680) in this respect.[24] Further testimony to the secondary role played by nephelauxetic effects in the dimers is the general decrease in molybdenum shielding with decrease in oxidation number. The more common trend observed for main-group nuclei or transition metals (particularly in lower oxidation states) is for the shielding to decrease with increase in positive atomic charge or oxidation number, because of increase in the $\langle r^{-3}\rangle$ term.[21]

Thus the weak ligand field of the sulfur more than compensates for the increased nephelauxetism, which dominates when ligand field splittings are larger. The Mo(V) compounds (III) in Table I follow the example of the 4-coordinate metalates, in which the metal nucleus shielding increases in the sequence of the spectrochemical series, Se < S < O;[16] cf. S < O observed also for trinuclear $(\mu\text{-S})_2$ oxothiomolybdates.[24] In the formally d^0 tetraoxo compounds the ^{17}O deshielding,[25] like the temperature-independent paramagnetism of permanganate and related complexes,[26] was shown to be mediated by paramagnetic circulations of oxygen ($\sigma + \pi$) electrons in the low-lying d orbitals, and these must dominate the deshielding of the metal nuclei also. Both the oxygen and the metal shielding decrease as some of the oxygen is replaced by sulfur.[27]

Overall, the decrease in shielding of the metal nucleus in Table I parallels the decrease in ligand field strength in the sequence CO > Cp > O > S. In the series of Mo(II) piano-stool compounds $[MoCp(CO)_2(S\frown S)]$[17] the molybdenum shielding is higher than in the dimers and increases with the π-donor ability of the group attached to sulfur, e.g., from the dithiophosphate with δ −340 to the diethyldithiocarbamate (II) with δ −544. In the cyclopentadienylmolybdenum dimers, similarly, the metal shielding increases from the $(SR)_4$, Mo(III) to the $S_2(SR)_2$, Mo(IV) compounds. Within the Mo(IV) series the shielding is highest with hydrido substituents on sulfur, and within the Mo(III) series it tends to increase from the compounds with π-acceptor organic substituents on sulfur to those with saturated organic groups, over a remarkable range of nearly 2000 ppm, as discussed below.

Chart I. Structures of Compounds in Table I^a



^{a}Cp is η-C_5H_5, Cp′ is η-C_5H_4Me, and Cp″ is η-C_5H_4-i-Pr, unless otherwise described.

As to changes in the cyclopentadienyl ring, some deshielding (by 73 ppm) is observed for the $[MoCp(\mu\text{-SMe})_2]_2$ compound (VIII) when an isopropyl substituent is present. Similarly in sandwich and piano-stool compounds methylation of the arene reduces the metal shielding, often incrementally, as it favors the forward bonding and disfavors the back-bonding.[23] Thus higher metal shielding is expected for $[MoCp(S)(\mu\text{-S})]_2$ than for the C_5Me_5 compound (IIIb) that was measured.

Molecular Orbital Interpretations of the ^{95}Mo Shielding in the Sulfur-Bridged Dimers. Figure 1 is an MO diagram derived from extended Hückel calculations[7,8] on a series of dimers (shown in Chart I), from the doubly bridged compound $[MoCp(S)(\mu\text{-S})]_2$ (IIIb) to the quadruply-bridged $[MoCp(\mu\text{-S})_2]_2$, with $[MoCp(\mu\text{-S})(\mu\text{-SH})]_2$ and $[MoCp(\mu\text{-SH})_2]_2$, respectively, modeling Mo(IV) and Mo(III) dimers with σ-only substituents. The bis(ethenedithiolate) compound (XII) represents Mo(III) dimers with unsaturated substituents in conjugation with the bridging sulfurs. The orbitals are labeled for C_{2h} or D_{4h} symmetry, as appropriate.

Important to the NMR shielding, as to the reactivity, are the small ligand field splittings: the frontier orbital gap for the Mo(V) dimer (IIIb) was calculated as 1.3 eV. Unusually, the $\delta^*(x^2-y^2)$ (b_{1u}) LUMO in the $(\mu\text{-S})_4$ compound lies below its $\delta(x^2-y^2)$ (b_{2g}) counterpart, because of destablization of the δ orbital by interaction with sulfur $p_{x,y}$ orbitals; it turns out that such interactions of sulfur lone-pair electrons are influential in the NMR spectral relationships. The successive addition of two pairs of hydrogen atoms, representing organic radicals, contributes an

---

[22] Lucken, E. A. C.; Noack, K.; Williams, D. F. *J. Chem. Soc. A* **1967**, 148.

[23] Green, J. C.; Grieves, R. A.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1313; manuscripts in preparation.

[24] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2827.

[25] Figgis, B. N.; Kidd, R. G.; Nyholm, R. S. *Proc. R. Soc. London, A.* **1962**, *269*, 469.

[26] Carrington, A. *Mol. Phys.* **1960**, *3*, 271.

[27] Do, Y.; Simhon, E. D.; Holm. R. H. *Inorg. Chem.* **1985**, *24*, 1831.

[28] Bruce, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 3433.

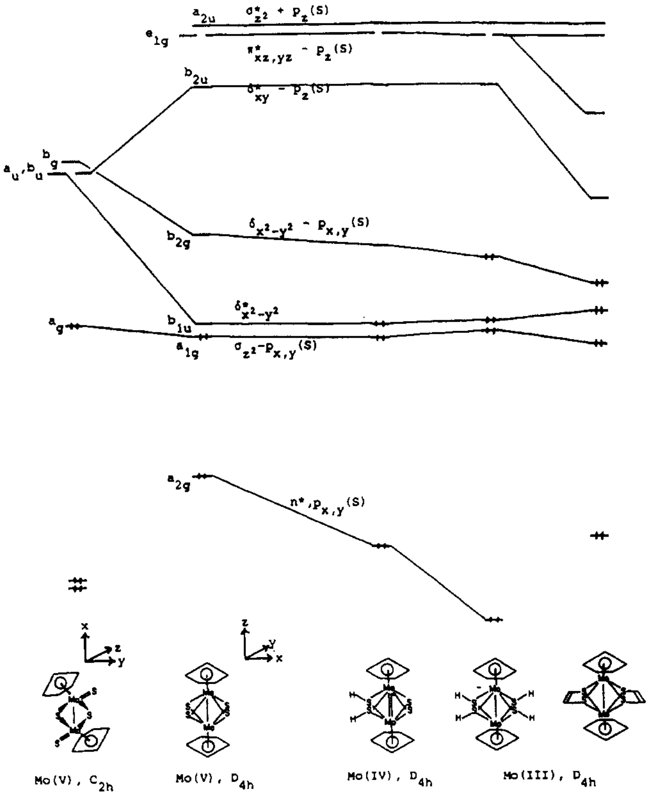


Figure 1. Frontier molecular orbitals for sulfur-bridged cyclopentadienylmolybdenum dimers (taken from ref 7 and 8).

electron pair to each of these δ* and δ LUMOs (low-lying unoccupied MOs) in turn, with relatively small changes in the orbital energies,[8] as shown in Figure 1. In each case the LUMOs are largely metal-centered ligand field orbitals,[8,15,29] and the orbitals above and below those shown in Figure 1 are well out of range of the frontier orbital set.

Since low-energy d–d excitations are expected to dominate the molybdenum shielding, the rather similar shieldings ($\delta(^{95}\mathrm{Mo})$ 400–600) of the doubly bridged $[\mathrm{Mo^{V}(S)(\mu\text{-}S)}]_2$ dimers and the quadruply bridged $[\mathrm{Mo^{IV}(\mu\text{-}S)(\mu\text{-}SR)}]_2$ dimers can be seen as a resultant of two factors that are evident in Figure 1. The increase in ligand field splitting from the Mo(V) to the Mo(IV) dimers, tending to increase the shielding, is offset by the filling of the $\delta^*(x^2 - y^2)$, a_{1g} LUMO in the Mo(IV) dimers, providing further electrons for the paramagnetic circulation. The further decrease in shielding observed for the $[\mathrm{Mo^{III}(\mu\text{-}SR)_2}]_2$ dimers with σ-only organo substituents is then linked with the filling of the $\delta(x^2 - y^2)$, (b_{2g}) LUMO. A comparable observation in reverse is the increase by 450 ppm in molybdenum shielding[30] on protonation of the bent sandwich dihydride

$$[\mathrm{MoCp_2H_2}],\ d^2 \rightarrow [\mathrm{MoCp_2H_3}]^+,\ d^0$$

as this removes the low-energy paramagnetic circulation of the dπ electron pair, which is strongly stabilized on bond formation. An analogue in main-group chemistry is the well-known increase in shielding of nitrogen in a delocalized system (as in pyridine) on protonation, since this removes the low-energy n(N) → π* circulation.[31]

Because of the small ligand field splittings, small changes in the frontier orbital energies have a proportionately large effect. Figure 1 shows a significant lowering, by 1 eV or so, of ligand field δ* and π* LUMOs in the Mo(III) dimers when each pair of sulfurs is bridged by a (CH=CH) group, compared with σ-only substituents; Table I shows a deshielding of 1350 ppm from the $(\mathrm{SMe})_4$ compound (VIII) to the $(\mathrm{SCH{=}CHS})_2$ compound (XII). As indicated in Figure 1, the changes in the d orbital energies depend on the interactions with the p(S) electrons, which are strongly influenced by the organo substituents; thus, the b_{2g} $\delta(x^2 - y^2)$ orbital is destabilized by $p_{x,y}(\mathrm{S})$ electrons, but less so for thiolate compared with sulfide and much less so when there is full conjugation with the organic cross-link. The b_{2u} and e_{1g} LUMOs are not very different as between the Mo(IV) and Mo(III) dimers with saturated ligands, and the sizable stabilization in the compound with ethenedithiolate cross-links results from reduction of the destabilization by $p_z(\mathrm{S})$ electrons, as they can delocalize in pπ*(C) orbitals. The importance of this extension of conjugation is shown by the remarkable difference between the molybdenum shifts, 2327 and 470 ppm, respectively, in the ethene- and 2,3-propenedithiolate compounds XII and VII. The ethenedithiolate ligand is a noninnocent ligand in the Jørgensen classification,[32] as it can be formulated as $^-$S—CH=CH—S$^-$, S=CH—CH—S$^-$, or S=CH—CH=S, S=CH—CH=S, with corresponding changes in the metal oxidation state.

Also important, of course, are the changes in steric effects in the four- or five-membered rings formed by the organo cross-links, as they affect the orbital overlaps.

Correlation of Molybdenum Shielding with Angular Distortion and Reactivity. Cross-linking of two bridging sulfurs by a methylene group reduces the molybdenum shielding in both the Mo(IV) and the Mo(III) series, as in compounds V, VI, IX, and XI, and this may be related to distortion of the $\mathrm{Mo_2S_4}$ framework by the small bite of the methanedithiolate ligand.[10,11] In the $(\mathrm{SCH_2S})(\mathrm{SMe})_2$ compound (IX) the dithiolate S–Mo–S angle (66.1°) and intraligand S··S distance (2.67 Å) are markedly smaller than the corresponding values in the $\mathrm{Mo(SMe)_2}$ group (70.3° and 2.82 Å) or between the dithiolate and monothiolate in IX (79.1° and 3.12 Å);[10] cf. 74° and 2.96 Å for the $(\mathrm{SMe})_4$ compound (VIIIa);[33] indeed, the S··S distance within the methanedithiolate ligand is short enough for S–S bonding interaction.[10] The deshielding may thus be linked with destabilization of the ligand field HOMOs by interaction with $p_{x,y}(\mathrm{S})$ electrons. Distortions of metal interbond angles commonly reduce the metal shielding, as when a 4-membered chelating diphosphine ring [Mo(dppm)] replaces a 5-membered ring [Mo(dppe)].[34] The deshielding is related to the decrease in local symmetry, increasing the angular momentum terms in eq 1, and to the removal of orbital degeneracies.

In sandwich and half-sandwich compounds in general, deshielding of the metal nucleus correlates with reduction in the strength of binding of the ring to the metal (e.g. with increase in ring size or from closed to open π systems) and thus with increase in reactivity of the complex.[23] Corresponding correlations of cobalt shift with catalytic activity have been observed for organocobalt complexes.[35] In the tetrasulfur-bridged molybdenum dimers, also, frontier orbitals that determine the metal nucleus shielding are important to the chemical activity at the bridging sulfur. Thus the b_{2g} frontier orbital plays a vital part in the Mo(IV) ↔ Mo(III) interconversions: it is the HOMO in the Mo(III) dimers that reacts dissociatively,[8] and in the Mo(IV) dimers with cis sulfido ligands it is a vacant site for coordination of π(C=C) or σ(C≡N) electrons (with back-donation from the a_2 sulfur orbital into the π* orbital of the incoming group). The presence of a methanedithiolate group, as well as deshielding the metal nucleus, enhances the reactivity of the other two sulfido bridges in Mo(IV) dimers[9,10,12] and of the other two substituents in Mo(III) dimers.[10] In this way we can see correspondences of chemical shift and reactivity in these series also.

---

(29) Bruce, M. R. M.; Bruce, A. E.; Tyler, D. R. *Polyhedron* **1985**, *4*, 2073.
(30) Grieves, R. A.; Mason, J. *Polyhedron* **1986**, *5*, 415.
(31) Mason, J. *Chem. Rev.* **1981**, *81*, 205.
(32) Jørgensen, C. K. *Inorg. Chim. Acta, Rev.* **1968**, *2*, 65. Müller, A.; Diemann, E.; Jørgensen, C. K. *Struct. Bonding (Berlin)* **1973**, *14*, 23.
(33) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470.
(34) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W.; Grim, S. O. *J. Chem. Soc., Dalton Trans.* **1982**, 2353.
(35) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R.; von Philipsborn, W.; Egolf, T. *J. Organomet. Chem.* **1984**, *272*, 231. Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics*, **1985**, *4*, 2214.

Delocalization in the Mo_2(organoS_4) Chromophore. Unusual deshielding in the bridging organo-substituents bears witness to the extension of the delocalization of the Mo_2S_4 core to include the organic group. Alkene, polyene, or aromatic carbon normally have shifts in the range 125–135 ppm, which are little affected by sulfur substitution, inductive effects being small. The carbon in the ethenedithiolate cross-link is significantly deshielded, with δ 147–148 in compounds X, XI, and XII. In the 2,3-propenedithiolate cross-link the carbon bonded to sulfur is further deshielded, with δ 154 in VII, although this correlates with relatively high shielding for the molybdenum. There is even pronounced deshielding of cross-linking saturated carbon and the attached protons, showing their participation in the low-lying excited states. A methylene group next to sulfur or between two sulfurs in an organic compound would normally have proton shifts of about 3.5 ppm and a carbon shift of 20–35 ppm, which may be reduced by angle strain in a four-membered ring; cf. δ 18.7 in thietane. However, the methanedithiolate carbons have shifts of 33–50 ppm in the Mo(IV) dimers V and VI and 75–92 ppm in the Mo(III) dimers IX and XI, and the proton shifts increase to 6 ppm or more. Particularly interesting is the sensitivity of the shifts on one pair of sulfurs to changes in the other, in view of the changes in reactivity already noted; thus, the methanedithiolate carbon is deshielded by 40 ppm (and the protons by 3.6 ppm) when the other two sulfurs are methylated, and by a further 18 ppm if the two methyl substituents are replaced by an ethene (CH=CH) cross-link.

The mercapto protons in IVa are shielded by about 2 ppm compared to protons in thiols.

Correlation of Molybdenum Shielding with Electronic Spectra. In parallel with the decrease in shielding there is a general red-shifting in the electronic spectrum from the Mo(V)[28] to the Mo(IV)[6,15] dimers, and within the Mo(IV) series (with some overlap of the series as before). Similarly, in the near-IR absorption observed for the corresponding mixed-valence (delocalized) Mo(III)/Mo(IV) dimers, the transition energy decreases in the same sense as the molybdenum shielding in the diamagnetic compounds, being lowest for complexes with the methanedithiolate ligand. The visible spectra of the Mo(III) compounds show little beyond the tail of the strong UV absorption.[15] In the spectra of the Mo(IV) and the Mo(III)/Mo(IV) dimers the lowest energy absorption is largely $\delta^* \rightarrow \delta$ (with little magnetic dipole character). The δ LUMO (which corresponds to the HOMO in the Mo(III) dimers) is sensitive to substituents on the sulfur, being destabilized by interaction with $p_{x,y}$(S) orbitals, and a corresponding sensitivity is likely for the *xy*, *xz*, and *yz* LUMOs, which are destabilized by the p_z(S) orbitals. The parallelisms observed in the NMR and the optical spectra thus support the MO interpretation of the shielding.

Correlation of Molybdenum Shielding with Electrode Potentials. Deshielding of a transition metal nucleus, in favorable circumstances, may correlate with algebraic decrease in $(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}})$, as this may be related (on a one-electron model) to a HOMO–LUMO gap for rotationally allowed (d–d) excitations, ΔE in eq 1. As shown in Table I, deshielding of molybdenum in the $Mo^{III}(SR)_4$ dimers correlates with algebraic decrease in $E_{1/2}^{\text{ox}}$, with the exception of the 2,3-propenedithiolate (VII), for which unexpectedly high shielding was observed. In the $Mo^{IV}S_2(SR)_2$ dimers deshielding correlates with algebraic increase in $E_{1/2}^{\text{red}}$ and decrease in $(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}})$.

Relation of the Molybdenum Shielding to Metal–Metal Bond Order and Metal–Sulfur Connectivity. For comparable ligands, without steric constraints, molybdenum shielding may be expected to decrease steadily with increase in the metal–metal bond order, i.e. as 1 > 2 > 3 > 4,[23,30] in contrast to the well-known 1 > 3 > 2 sequence in carbon shielding. This sequence for a transition metal accords with the decrease in overlap and splitting from σ to π to δ orbitals and the increase in imbalance of charge in the valence shell; the high shielding observed for alkyne carbon results from free diamagnetic circulation about the (linear) bond axis, which is not possible for the higher coordination numbers of transition metals. The Mo(V), Mo(IV), and Mo(III) dimers in Table I have formal metal–metal bond orders of 1, 2, and 1 respectively, the metal–metal distances being short enough for bonding interaction. In these compounds, therefore, the decrease in shielding in the sequence Mo(V) > Mo(IV) > Mo(III) follows the increase in the number of high-lying shared electron pairs, as might be expected, rather than the formal bond order. In any case the metal–metal distances are constrained to a very small range by the sulfur bridges.

In the compounds with comparable coligands the metal shielding decreases with decrease in the number of metal centers bridged by the sulfur, i.e. as (μ_3-S) > (μ_2-S) > terminal S. This has been observed in other sulfide complexes, as in ^{93}Nb resonance in the highly symmetric $[Nb_6S_{17}]$ cage,[36] and can be traced, ultimately, to the position in the spectrochemical series.[32]

Conclusion. NMR spectroscopy of the metal nucleus and the organosubstituents affords a sensitive probe of bond type and active sites in the extensive range of sulfur ligand systems. The ^{95}Mo deshielding in the sulfur-bridged dimers relative to the cubane and the 2000 ppm shifts range in the Mo(III) dimers can be accounted for in terms of small ligand field splittings and delocalization in the Mo_2(organoS_4) core. The frontier orbitals for the paramagnetic circulation, which also mediate the donor–acceptor reactivity of the complexes, are unusually sensitive to the organo substituents, as they interact with the sulfur lone-pair electrons, which contribute to the ligand field. The Mo(IV) range is understandably smaller in the absence of unsaturated ligands, and with less contribution of the p(S) orbitals to the HOMOs.

After this work was completed, molybdenum shifts were reported[37] for some sulfur-bridged compounds related to those we have studied, including some interesting extensions of the substituent effects we have discussed; thus, in Mo(V) dimers $[Mo(C_5Me_5)(O)(\mu\text{-}X)]_2$ the ^{95}Mo shielding decreases as S > Se. The ethenedithiolate compound $[Mo(C_5H_5)(\mu\text{-}SC_2(CF_3)_2S)]_2$ has δ 2301, close to that of XII. Effects of methylation in the compounds IIIa are evident in the shift of −93 ppm reported for $[Mo(C_5Me_5)(O)(\mu\text{-}S)]_2$.[37]

Experimental Section

Syntheses. Mo(V)[7], Mo(IV),[6,10,12] and Mo(III)[4,12,33] compounds were made by published methods.

NMR Methods. Hydrocarbon and ether solvents were dried by refluxing over potassium or sodium, CH_2Cl_2 was dried by distillation from P_2O_5, and all solvents were deoxygenated before use. Air-sensitive solutions were handled under inert atmosphere and transferred through stainless-steel tubes under a positive pressure of nitrogen. Samples were normally prepared under nitrogen in a 10-mm NMR tube fitted with a screw cap and a rubber septum. If the solution was very air- or moisture-sensitive the tube was flamed out before being filled and then frozen in liquid nitrogen and sealed under vacuum.

^{95}Mo spectra were obtained on a JEOL FX90Q spectrometer or, if higher sensitivity was required, on a Bruker WH400 instrument; with poorly soluble compounds, line width was sacrificed for more rapid data accumulation.

Acknowledgment. We thank Dr. D. L. DuBois for unpublished information on the (extended Hückel) orbital energies of the ethenedithiolate compound (XII), Dr. Damian Rodgers for samples of cubane I and dimer VIIIb, the Science and Engineering Research Council for the provision of high-field NMR facilities, Drs. Oliver Howarth and Eirian Curzon for the 400-MHz spectra run at Warwick University, and Gordon Howell for spectra run at The Open University. We thank the National Institutes of Health, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. M.R.D. thanks the John Simon Guggenheim Foundation for a fellowship (1984–1985).

Registry No. I, 89389-51-5; II, 32984-93-3; *trans*-IIIa, 107870-61-1; *cis*-IIIa, 107870-62-2; IIIb, 75901-60-9; IVa, 75675-65-9; IVb, 75901-57-4; V, 99510-48-2; VI, 85565-70-4; VII, 88690-28-2; VIIIa, 11077-57-9; VIIIb, 107799-55-3; IX, 103202-47-7; X, 86163-43-1; XI, 86163-40-8; XII, 75675-70-6; ^{95}Mo, 14392-17-7.

---

[36] Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706.

[37] Young, C. G.; Minelli, M.; Enemark, J. H.; Miessler, G.; Janietz, N.; Kauermann, H.; Wachter, J. *Polyhedron* **1986**, *5*, 407.