

Crystal data: $C_{66}H_{68}B_2Mo_2S_4$, M 1203.0, triclinic, $a = 11.362(1)$, $b = 11.860(1)$, $c = 13.246(2)$ Å, $\alpha = 68.38(1)^\circ$, $\beta = 64.70(1)^\circ$, $\gamma = 62.92(1)^\circ$, $U = 1402.9$ Å³, $D_m = 1.44$ g cm⁻³ (by flotation), $Z = 1$, $D_c = 1.42$ g cm⁻³, space group $P\bar{1}$. 4324 independent reflections were measured by four-circle diffractometry using Mo- K_α radiation ($\lambda = 0.71069$ Å). The structure was solved by Patterson and Fourier methods and refined by large block least-squares. Hydrogen atoms were located from difference syntheses, but were positioned geometrically. The final R -value is 0.026 (R' 0.032).†

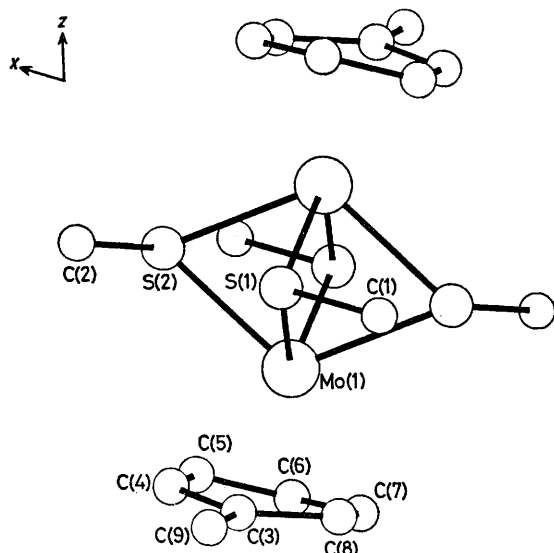


FIGURE. Structure of $[(\eta\text{-MePh})Mo(\mu\text{-SMe})_4Mo(\eta\text{-MePh})]^{2+}$.

The unit cell contains one cation with the structure shown in the Figure, together with two tetraphenylborate anions. The cation exists as a discrete dimeric species of crystallographic point-group symmetry C_i , the centre of symmetry being situated midway between the Mo atoms. The two $(\eta\text{-MePh})Mo$ species are linked to each other by four symmetrically positioned bridging methanethiolato ligands [Mo-S distances range from 2.451(1)—2.462(1) Å] and the molecular structure is very similar to those of the $[(\eta\text{-C}_5\text{H}_5)Mo(SMe)_2]_2^n$ complexes ($n = 0$ or $+1$).⁴

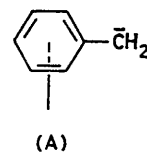
It is suggested that there is a direct metal-metal bond between the Mo atoms, and this is in accord with the short Mo-Mo distance of 2.614(1) Å, the acute Mo-S-Mo bridging angles of 64.39(2) and 64.27(2)°,⁵ and the observed diamagnetism of the cation.

While the Mo-C distances [2.287(3)—2.416(3) Å] and the ring C-C distances [1.381(7)—1.451(6) Å] are normal⁶ it is

interesting to note that the $\eta\text{-MePh}$ ligand is significantly non-planar and is folded with 9.6° about the C(3)···C(6) vector.

The compounds (II) are redox active. Cyclic voltametry studies at a Pt wire electrode in acetonitrile solution show a reversible 1-electron oxidation wave at +1.4 V vs. S.C.E. for the toluene derivative ($Bu_4^+N^+PF_6^-$ was used as supporting electrolyte). An irreversible reduction wave is observed at ca. -1.0 V vs. S.C.E. in acetonitrile solution. Zinc amalgam reduction of compound (II) in 1-methylimidazole-acetonitrile solution yields, after air oxidation, a green, weakly paramagnetic compound of stoichiometry $[Mo_2(SMe)_3(C_5H_3N_2Me)_6][PF_6]_3$ ($\mu_{eff} = 1.45$ B.M.) in 30% yield. Conductivity measurements and the observation of singlet resonances for each of the three aromatic protons as well as for both methyl groups in the n.m.r. spectrum indicate the centrosymmetric, dimeric structure shown in the Scheme.‡ The ready expulsion of a thiolate group in the above reaction is unusual and the reaction is under further investigation.

The compounds (II) are very stable and can be recovered unchanged from concentrated H_2SO_4 or 5 M HNO_3 after 24 h. A 10% solution of the toluene derivative (bisulphate salt) in saturated $Na_3PO_4\text{-}D_2O$ buffer (pD = 11) undergoes complete H-D exchange at the toluene methyl position within 12 h at 25 °C. The exchange was followed by observing the disappearance of the singlet methyl resonance at τ 7.3 in the n.m.r. spectrum. The SMe and aromatic protons resonances remained unchanged. The exchange rate is dependent on the base concentration. At a pD of 9 complete H-D exchange of a 5% solution of (II) in saturated $Na_2B_4O_7\text{-}D_2O$ buffer requires ca. 3 days at 60 °C. The i.r. spectrum of the deuteriated derivative (hexafluorophosphate salt) shows a weak C-D stretch at 2120 cm⁻¹.



Transition metal catalysed H-D exchange of hydrocarbons has often been observed with 'electron rich' complexes.⁷ The mechanism is believed to involve an oxidative addition of a C-H bond to the metal atom. However, the chemistry and stereochemistry of compound (II) makes it unlikely that such a mechanism is involved here. The easy H-D exchange observed above (comparable H-D exchange rates for free toluene require very strong bases such as lithium cyclohexylamide in cyclohexylamine solution)⁸ is presumably due to strong electron withdrawal from the aromatic rings by the Mo atoms

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ It is likely that the well defined resonances observed for this paramagnetic complex are due to a rapid spin relaxation mechanism (see, for example, A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970).

causing enhanced stabilization of the carbanion (A) thereby rendering the methyl groups kinetically acidic.

All of the above compounds have been characterized by elemental analyses, conductivity measurements, and i.r. and ^1H n.m.r. spectra.

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