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First Mononuclear Bis(sulphido) Molybdenum(IV) Complex of Crown Thioether trans-Mo(S)$_2$(syn-Me$_8$[16]aneS$_4$)

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Reaction of trans-Mo(N$_2$)$_2$(syn-Me$_8$[16]aneS$_4$) with S$_8$ gave trans-Mo(S)$_2$(syn-Me$_8$[16]aneS$_4$) (**1**), which was also obtained by treating the N$_2$ complex with t-BuSH through the C-S bond cleavage. The novel mononuclear structure of **1** was elucidated by an X-ray analysis.

Molybdenum sulphido complexes have received increasing interest in view of their structural diversities and biological and catalytic implications. Probably due to the strong propensity of sulphido ligand to bridge metals, most of them are multinuclear and the monomeric complexes containing Mo=S linkages are rather limited$^{1)}$ except hexavalent thiomolybdate anions. Particularly, mononuclear molybdenum bis(sulphido) complexes are extremely sparse and cis-Mo(S)$_2$(C$_5$H$_{10}$NO)$_2$ [C$_5$H$_{10}$NO=piperidine-N-oxido(-1)]$^{2)}$ may be the sole example characterized so far by an X-ray structural study. Herein we describe the first example of mononuclear bis(sulphido) complex of Mo(IV) containing a crown thioether trans-Mo(S)$_2$(syn-Me$_8$[16]aneS$_4$)(**1**) (Me$_8$[16]-aneS$_4$=3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane) with a MoS$_6$ coordination sphere.

Reaction of trans-Mo(N$_2$)$_2$(syn-Me$_8$[16]aneS$_4$)$^{3)}$ with an excess of S$_8$ in toluene at room temperature and subsequent chromatography [silica gel, eluant CH_2Cl_2-EtOH(9:1)] of the toluene soluble products afforded **1** as yellowish orange crystals (31%). Alternatively, **1** may be prepared by treating the dinitrogen complex with two equivalents of t-BuSH at ambient temperature in 51% yield. The fate of t-Bu group was not examined. A closely related C-S bond cleavage of bulky thiols has been observed in the preparation of $[Mo(t\text{-}BuS)_2PMe_2Ph]_2(\mu\text{-}S)_2$4) and $\{Mo(i\text{-}Pr)_3C_6H_2S(OMe)\text{-}PMe_2Ph\}_2(\mu\text{-}S)_2$5) from cis-$Mo(N_2)_2(PMe_2Ph)_4$ and the corresponding thiols. The N_2 complex of crown thioether, however, differs from the phosphine analogue in its ability to disrupt two C-S bonds per Mo atom affording the terminal sulphido complex. The presence of terminal sulphido ligands of **1** was confirmed by the observation of a strong ν(Mo=S) band at 436 cm^{-1}. A syn conformation of the coordinated $Me_8[16]aneS_4$ ligand was deduced from the observation of two Me (δ 1.18 and 1.53) and two CH_2 proton signals [δ 2.90(d, J=11.6 Hz) and 3.05(d, J=11.6 Hz)] in the ^1H NMR spectrum.

The discrete monomeric structure of **1** was elucidated by an X-ray structural analysis (Fig. 1).6) The geometry about Mo atom is slightly distorted octahedral with two sulphido ligands at the axial sites and four sulfur atoms of the crown thioether at the equatorial positions. The Mo atom is displaced by 0,031(5) Å from the 4S plane of syn-$Me_8[16]aneS_4$ toward the ring carbon atoms, the deviation of S atoms from the plane being 0.004(8) Å. The S_t=Mo=S_t moiety (S_t=terminal sulphide) is strictly linear [178.8(3)°]. Thus, the molecule possesses approximately C_{4v} symmetry. The Mo-S(thioether) distances [average 2.483(8) Å] is significantly longer than those found in trans-MoL_2(syn-$Me_8[16]aneS_4$) [L=N_2, 2.424(2);3) L=CO, 2.436(2);7) L=PhNC, 2.418(2) Å].8) The elongation in Mo-S distances compared to those of the zero-valent complexes may be ascribed to the reduced d_π-d_π interaction in Mo(IV)-S(thioether) bonds. Recently the π-acceptor ability of crown thioethers has been established by Schröder et al.9) Probably due to strong trans influence of terminal sulphido ligand, the Mo=S_t separations [average 2.238(9) Å] are considerably longer than those (2.126-2.129 Å) of $[MoS(S_4)_2]^{2-}$,1a) $[MoS(CS_4)_2]^{2-}$,1b) and

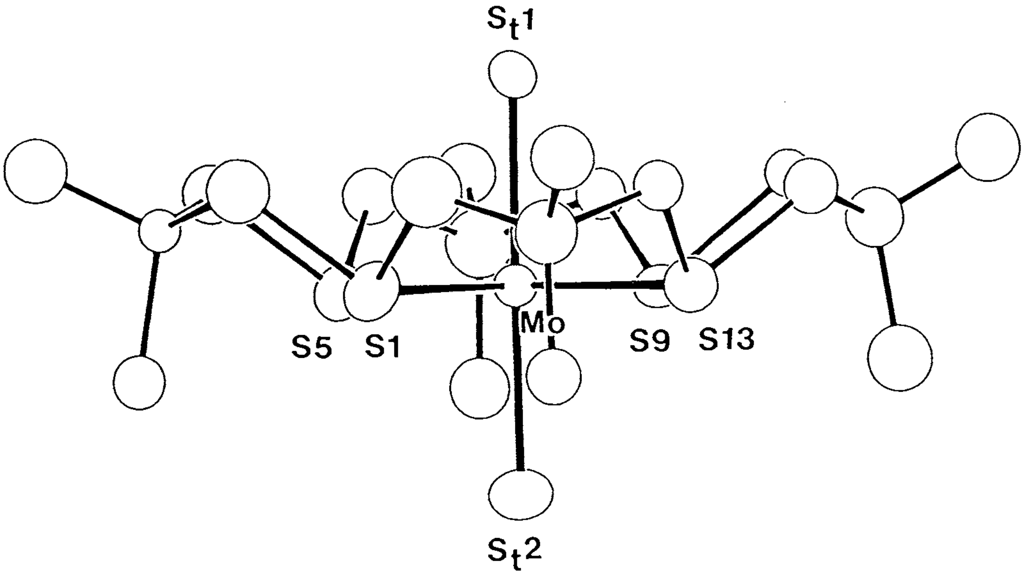

Fig. 1. Molecular structure of **1**. Selected bond distances (Å) and angles (deg.): Mo-S_t(1) 2.245(8), Mo-S_t(2) 2.232(9), Mo-S(1) 2.486(8), Mo-S(5) 2.469(9), Mo-S(9) 2.480(8), Mo-S(13) 2.498(8); S_t(1)-Mo-S_t(2) 178.8(3), S_t(1)-Mo-S(1) 91.0(3), S_t(1)-Mo-S(5) 91.2(3), S_t(1)-Mo-S(9) 90.2(3), S_t(1)-Mo-S(13) 90.4(3), S(1)-Mo-S(5) 90.4(3), S(5)-Mo-S(9) 89.9(3), S(9)-Mo-S(13) 90.1(3), S(1)-Mo-S(13) 89.6(3), S(1)-Mo-S(9) 178.8(3), S(5)-Mo-S(13) 178.4(3).

$MoS(S_2CNEt_2)\{HB(Me_2pz)_3\}$ (pz=pyrazoyl).[1d] The trans influence of terminal sulphide, however, is not so strong as η^1-oxo ligand since the Mo=S_t length [2.415(7) Å] found in trans-Mo(S)(O)(dppe)$_2$[1e] is longer than that of **1**.

The cyclic voltammogram of **1** measured in CH_2Cl_2 (0.1 M n-Bu_4BF_4, sweep rate 100 mV/s) shows three quasi-reversible redox couples [$E_{1/2}$=-0.96 (ΔE=80 mV), -0.62 (ΔE=60 mV), -0.42 V vs. SCE (ΔE=60 mV)] and two irreversible oxidation processes (E_p^{ox}= +0.22 and +0.66 V vs. SCE). The quasi-reversible electron transfer series may encompass four species in a rather narrow voltage range of 0.54 V from the neutral molecule to the trianion, $[\mathbf{1}]^{3-} \rightleftharpoons [\mathbf{1}]^{2-} \rightleftharpoons [\mathbf{1}]^{-} \rightleftharpoons \mathbf{1}$.

Finally it is worth noting that the success in synthesizing the novel mononuclear bis-sulphido complex of molybdenum(IV) can be ascribed to the tight coordination of the tetradentate $Me_8[16]aneS_4$ adopting syn conformation, which prevents the generation of coordinatively unsaturated species through partial dissociation of the thioether ligands and then the formation of polynuclear μ-sulphido complexes.

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6) Crystal data: $C_{20}H_{40}S_6Mo$, M=568.9, orthorhombic, space group $P2_12_12_1$, a= 16.746(9), b=14.298(9), c=10.825(7) Å, V=2592 Å^3, Z=4, Dc=1.46 g cm^{-3}, μ(Mo-Kα)=9.16 cm^{-1}. A total of 2725 reflections ($2\leq 2\theta \leq 50°$) were collected, of which 1021 with $|F_0| \geq 3\sigma(F)$ were used for structure determination. The final $R(R_w)$ is 0.075(0.064). The space group is acentric, however, refinement on the other enantiomer produced no change in R_w.

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