

A New Co-ordination Mode for a Tetrathia Crown Ether. Crystal Structure of $[\text{MoBr}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MoBr}_3(\text{CO})_4] \cdot \text{C}_6\text{H}_{14}$ ($\text{Me}_8[16]\text{aneS}_4 = 3,3,7,7,11,11,15,15$ -octamethyl-1,5,9,13-tetrathiacyclohexadecane)

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Equimolar quantities of $[\{\text{MoBr}(\mu\text{-Br})(\text{CO})_4\}_2]$ and 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane ($\text{Me}_8[16]\text{aneS}_4$) in CH_2Cl_2 at 20 °C gave the novel seven-co-ordinate cation-anion complex $[\text{MoBr}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MoBr}_3(\text{CO})_4]$ whose molecular structure shows the cation to have a 4:3 'piano-stool' geometry in which the Mo atom lies 1.488(2) Å above the plane of the four S atoms, the first example of this structural type.

Dinitrogen complexes of molybdenum with thiolate, thioether or sulfide co-ligands are of considerable interest as functional models for nitrogenase. To date, only one such complex with all-thioether co-ligands has been studied in depth, *i.e.* the sulfur macrocycle complex *trans*- $[\text{Mo}(\text{N}_2)_2(\text{Me}_8[16]\text{aneS}_4)]^\dagger$ reported by Yoshida *et al.*¹ This species was prepared by reduction of the dibromide *trans*- $[\text{MoBr}_2(\text{Me}_8[16]\text{aneS}_4)]$ **1**, obtained by reaction of $\text{Me}_8[16]\text{aneS}_4$ with $[\{\text{MoBr}(\mu\text{-Br})(\text{CO})_4\}_2]$ in toluene under reflux.² We find that the same combination of reagents in dichloromethane at 20 °C does not give **1**, but the novel ionic complex $[\text{MoBr}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MoBr}_3(\text{CO})_4] \cdot \text{C}_6\text{H}_{14}$ **2**‡ which has been characterised crystallographically. The iodo derivative of complex **2** and its tungsten analogue can also be prepared by the reaction of 2 equivalents of $[\text{MI}_2(\text{CO})_3(\text{MeCN})_2]$ (M = Mo or W) with 1 equivalent of $\text{Me}_8[16]\text{aneS}_4$.

† $\text{Me}_8[16]\text{aneS}_4 = 3,3,7,7,11,11,15,15$ -Octamethyl-1,5,9,13-tetrathiacyclohexadecane.

‡ Satisfactory elemental analyses (C,H,S) were obtained. Selected IR (Csl) ν/cm^{-1} : 2089s, 2023s, 1975s (br), 1899s, 895m, 880m, 532s and 482s. Conductivity (MeNO_2): $\Lambda_M = 82 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

§ Crystallographic data: $\text{C}_{22}\text{H}_{46}\text{BrMoO}_2\text{S}_4 \cdot \text{C}_4\text{Br}_3\text{MoO}_4 \cdot \text{C}_6\text{H}_{14}$, $M = 1174.5$, monoclinic, space group $F2/d$ (equivalent to no. 15), $a = 24.279(2)$, $b = 19.974(2)$, $c = 36.823(2)$ Å, $\beta = 92.428(6)^\circ$, $U = 17840.7$ Å³, $Z = 16$, $D_c = 1.749 \text{ g cm}^{-3}$, $F(000) = 9312$, $\mu(\text{Mo-K}\alpha) = 43.2 \text{ cm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å. Very dark green crystals; one, *ca.* $0.36 \times 0.26 \times 0.24$ mm, mounted in air on glass fibre; photographic examination showed very sharp diffraction spots; Enraf-Nonius CAD4 diffractometer (monochromated radiation) for accurate cell dimensions (from 25 reflections, each in four orientations, θ *ca.* 10.5°) and intensity measurements (to θ_{max} 22.5°). 5823 Unique reflections corrected for Lorentz-polarisation effects, deterioration, absorption and to eliminate negative intensities statistically. Structure determined by automated Patterson methods (program SHELXS³), refined (in extended version of SHELX⁴) to R 0.053, R_g 0.058⁴ for 3589 reflections (those with $I > 3/2\sigma_1$), weighted $w = (\sigma_F^2 + 0.00142F^2)^{-1}$. Hydrogen atoms included in calculated positions in the cation; all non-hydrogen atoms (except in disordered, unresolved hexane solvent molecule) anisotropic. Final difference peaks of $0.9 \text{ e} \text{ \AA}^{-3}$ close to Mo in both cation and anion.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

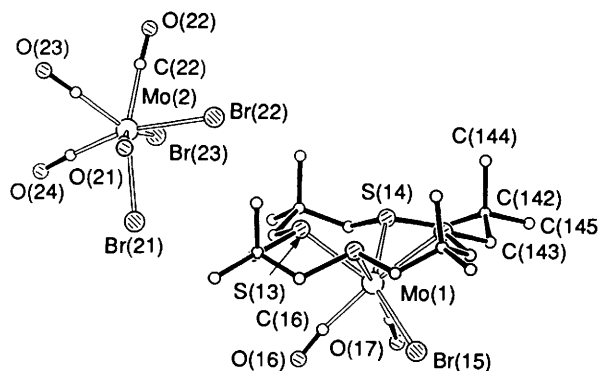


Fig. 1 Molecular structure of $[\text{MoBr}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MoBr}_3(\text{CO})_4] \cdot \text{C}_6\text{H}_{14}$ **2**. Hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths and angles: in the cation, Mo(1)-Br(15) 2.580(2), mean values for Mo-S 2.586(16), Mo-C 1.97(2), C-O 1.134(16), S-C 1.828(4), S...S 2.99(2) Å. S-Mo-S 70.7(4), Mo-S-C 109.3(7), C-S-C 99.3(9)°; in the anion, mean values excluding those involving C(23): Mo-Br 2.650(5), Mo-C 2.041(8), C-O 1.101(9) Å, Br-Mo-Br 90.8(5), Br-Mo-C 76.0(6), C-Mo-C 112.9(19)°; also Mo(2)-C(23) 1.959(14), C(23)-O(23) 1.156(17) Å, mean C(23)-Mo-C 74.2(7) and C(23)-Mo-Br 124.8(7)°

The molecular structure of **2**§ is illustrated in Fig. 1, together with selected bond distances and angles. Both the anion and cation contain seven-co-ordinate Mo^{VI} and the distribution of the bromide ligands suggests that the dimeric starting material $[\{\text{MoBr}(\mu\text{-Br})(\text{CO})_4\}_2]$, which is thought to contain two bridging bromides⁵ (such a structure has been determined crystallographically for the tungsten analogue⁶), has undergone asymmetric cleavage.

The structure of the cation of **2** shows the first example of a 'piano-stool' type of co-ordination geometry for a four-sulfur macrocyclic ligand. The Mo atom in the cation of **2** is located 1.488(2) Å above the mean plane of the square of the four sulfur atoms, which are co-planar to within 0.057(4) Å. The co-ordination environment of molybdenum may be described as a 4:3 'piano stool' arrangement with an S₄ seat and the three legs occupied by the bromide and two carbonyl ligands. In a projection of the ion onto the S₄ plane, the bromide lies in a staggered position midway between S(11) and S(12), while the

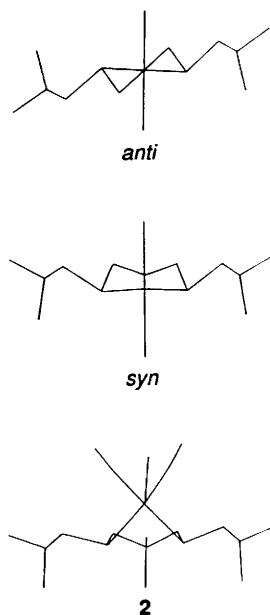
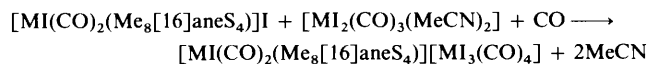
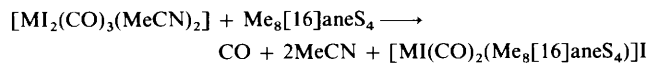


Fig. 2 Known conformations for complexes of $\text{Me}_8[16]\text{aneS}_4$. Some methyl groups have been omitted for clarity

two carbonyl groups lie more closely under the Mo–S(13) and Mo–S(14) bonds. We did, in fact, locate a second, disordered bromide ligand (occupancy 0.054) in a similar position between S(12) and S(13) [the angle Br(15')–Mo(1)–C(16) is $23.2(7)^\circ$], but did not find the corresponding carbonyl groups.

In all of the ten or so mononuclear complexes of $\text{Me}_8[16]\text{aneS}_4$ and the unmethylated macrocycle $[16]\text{aneS}_4$ which have been structurally characterised to date,^{1,2,7–9} the macrocycle takes up four equatorial co-ordination sites and the metal lies in or close to ($<0.11 \text{ \AA}$) the mean plane of the four sulfur atoms. This arrangement theoretically allows for four conformational variants, depending on the relative orientations of the hydrocarbon chains in the macrocycle. Of these, only three have been demonstrated by X-ray crystallography. The two more common conformations are designated *syn* (or 'all-up') and *anti* (or 'up-up-down-down') by the disposition of the non-co-ordinating sulfur lone pairs (Fig. 2). There is only one example of the third type (designated 'up-down-up-down'), found in the complex $[\text{Hg}([16]\text{aneS}_4)(\text{ClO}_4)_2]$.⁸

The mean Mo–S bond length in **2** is $2.59(2) \text{ \AA}$, rather longer than the values for molybdenum complexes of $\text{Me}_8[16]\text{aneS}_4$ in the equatorial *syn* and *anti* geometries ($2.42\text{--}2.44 \text{ \AA}$).^{1,2,7,9} The angles between the normals to the CSC planes and the Mo–S bonds are, however, only slightly more acute than in other complexes (mean 30.5° in **2** compared to 34.2° in **1**⁷). The macrocycle achieves this angle by varying the degree of puckering in the hydrocarbon backbone, as illustrated in Fig. 2. This results in a flatter conformation, in which the mean distance between adjacent sulfur lone pairs is $2.99(2) \text{ \AA}$. This is considerably shorter than the contacts found in the equatorially-co-ordinated conformations of this ligand (e.g. 3.44 \AA for **1**⁹), and shorter even than the typical values for ethylene-bridged macrocycles such as $[14]\text{aneS}_4$ (1,4,8,11-tetrathiacyclotetradecane) and $[9]\text{aneS}_3$ (1,4,7-trithiacyclononane) (typically $3.1\text{--}3.3 \text{ \AA}$).⁷ A still greater contrast lies in the distorted equatorial conformation of the closely related ligand $[16]\text{aneS}_4$ in the complex $[\text{Hg}([16]\text{aneS}_4)(\text{ClO}_4)_2]$,⁸ in which the mean inter-



Scheme 1

sulfur contact is 3.75 \AA . These variations underline the conformational flexibility of sulfur macrocycles.

The $[\text{MoBr}_3(\text{CO})_4]^-$ anion, which to our knowledge has not previously been structurally characterised, has the expected capped octahedral structure and is isostructural with its tungsten analogue.¹⁰ The carbonyl of O(23) is the capping ligand and lies on a pseudo three-fold symmetry axis through this ion.

The reaction of 2 equivalents of $[\text{MI}_2(\text{CO})_3(\text{MeCN})_2]$ ($\text{M} = \text{Mo}$ or W) with $\text{Me}_8[16]\text{aneS}_4$ in CH_2Cl_2 at 20°C gives $[\text{MI}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MI}_3(\text{CO})_4]$ ($\text{M} = \text{Mo}$ or W)¹¹ in good yield. Likely steps in this reaction are shown in Scheme 1. It should also be noted that heating **2** in toluene at 60°C gives compound **1**; therefore **2** can be regarded as an intermediate in the formation of **1**. We are currently studying the reactions of $[\text{MI}_2(\text{CO})_3(\text{MeCN})_2]$ and $[\{\text{WBr}(\mu\text{-Br})(\text{CO})_4\}_2]$ with other S_4 macrocycles.

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