Synthesis and Structure of Mo_3O_9.4DMSO (DMSO = dimethyl sulphoxide): a Novel Chain Structure

E. M. McCarron III and R. L. Harlow I

Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898, U.S.A.

The reaction of $MoO_3.2H_2O$ with DMSO (dimethyl sulphoxide) in a DMSO–H_2O solution produces the crystalline compound Mo_3O_9.4DMSO which has been shown by *X*-ray diffraction to consist of infinite chains of molybdenum–oxygen polyhedra; the chemical repeat unit of the chain contains one tetrahedron $[Mo(O_t)_2(O_b)_2]$ which bridges two octahedra $[Mo\{cis(O_t)_2\}(O_b)_2(DMSO)_2]$, where O_t and O_b represent terminal and bridging oxo-ligands, respectively.

Schöllhorn *et al.*[1] reported that interlayer water molecules in layer-type molybdenum oxide bronzes could be displaced by molecules of DMSO (DMSO = dimethyl sulphoxide) with consequential expansion of the layer spacing. Since $MoO_3.2H_2O$ has a layer structure (with one H_2O bound to each molybdenum and one H_2O intercalated), an analogous displacement of one H_2O by DMSO was expected. Interestingly, $MoO_3.2H_2O$ was observed to dissolve in DMSO at room temperature to form a yellow solution with a maximum concentration of approximately 1.7 M. Because of its potential usefulness in making a wide variety of MoO_3 complexes, the MoO_3–DMSO system was investigated in some detail.

Workup of the DMSO solution of $MoO_3.2H_2O$ led to the identification of four $MoO_3.n$DMSO solid phases. Stirring of a concentrated solution for 48 h at 22 °C produced an amorphous precipitate of MoO_3.2DMSO. Washing of this precipi-

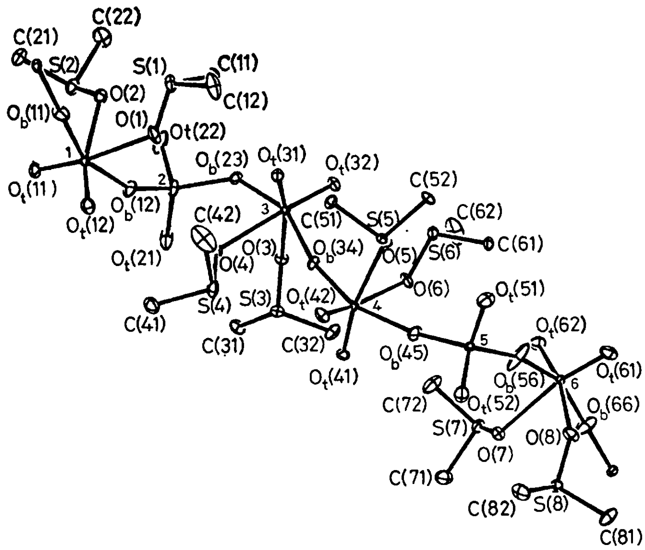

Figure 1. Asymmetric unit of Mo_3O_9.4DMSO. Oxygen atoms $O_b(11)$ and $O_b(66)$ are located on crystallographic centres of symmetry. Two of the DMSO ligands [those containing S(4) and S(7)] suffer from serious disorder problems; for clarity, only the atoms with the highest occupation factors are shown.

tate with acetone caused the removal of some of the DMSO and gave a MoO_3.1.33DMSO crystalline product. Rapid concentration of the DMSO solution *in vacuo* led to the formation of a MoO_3.DMSO glass. When this glass was subsequently dissolved in a DMSO–H_2O mixture and gently heated at *ca.* 80 °C for 24 h, colourless parallelepiped crystals of MoO_3.1.33DMSO were produced. Removal of the crystals from the mother liquor resulted in loss of DMSO to give a polycrystalline material with approximately the same composition as the glass *i.e.* 1 : 1 MoO_3 : DMSO.

Thermogravimetric analysis was used to determine the MoO_3 : DMSO ratio in the various phases. In all cases, heating liberated DMSO and left a residue of orthorhombic MoO_3.†

The structure of MoO_3.1.33DMSO was determined by *X*-ray diffraction and was found to consist of $[-O-MoO_2(DMSO)_2-O-MoO_2-O-MoO_2(DMSO)_2-]_n$ infinite chains. Two such Mo_3O_9.4DMSO species as shown in Figure 1 make up an asymmetric unit. The molybdenum exists in both octahedral and tetrahedral co-ordinations which repeat as (–oct–tet–oct–oct–tet–oct–)$_n$. The infinite nature of the 'core structure' [2] which can be represented as $[-O_bMo\{cis(O_t)_2\}-O_bMo(O_t)_2O_bMo\{cis(O_t)_2\}-]_n$ is at present unique among organic oxo-molybdenum complexes; all such structures published to date have contained discrete ions or molecules.

The structure of Mo_3O_9.4DMSO is in fact more closely related to a number of purely inorganic compounds. $Na_2Mo_2O_7$ [3] and $K_2Mo_2O_7$ [4] for example contain infinite chains of MoO_4 tetrahedra and MoO_6 octahedra although the modes of linkage in each of the three cases are quite different. The Mo–O bond distances and O–Mo–O bond angles of the DMSO complex (Figure 2) agree closely with those of the sodium salt.

The structure of MoO_3.1.33DMSO suggests that MoO_3.2DMSO consists of chains containing all octahedral $[-O-MoO_2(DMSO)_2-]$ units while MoO_3.DMSO contains

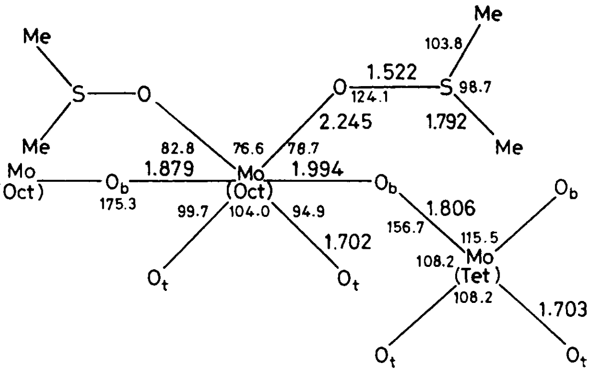

Figure 2. Average bond distances and angles for the four octahedral and two tetrahedral units which make up the asymmetric unit. Values affected by the disorder of the DMSO ligands have not been included. The deviation from any average is generally small except for the Mo(oct)–O_b–Mo(tet) angles which vary from 137.7 to 169.2°.

chains with octahedral $[-O-MoO_2(DMSO)_2-]$ and tetrahedral $[-O-MoO_2-]$ units in a ratio of 1 : 1. Unfortunately single crystals which would be suitable for *X*-ray analysis could not be obtained for these complexes.

Crystal data: $Mo_3O_9.[(CH_3)_2SO]_4$, $C_8H_{24}Mo_3O_{13}S_4$, M = 744.35, triclinic, space group $P\bar{1}$; at −100 °C, a = 15.563(2), b = 19.224(3), c = 8.391(1) Å, α = 100.85(1), β = 90.94(1), γ = 112.36(1)°; U = 2270 Å^3; Z = 4; Syntex $P3$ diffractometer, graphite monochromator, Mo-K_α radiation, λ = 0.710 69 Å; ω-scans of 1.0°, $4 < 2\theta < 55°$, 10 388 reflections. An empirical absorption correction based on ψ-scan data was applied; transmission factors ranged from 0.906 to 1.000. The structure was solved by direct methods and refined by full-matrix least-squares techniques: 8220 reflections with $I > 2\sigma(I)$ were used and there were 575 variables (anisotropic thermal parameters for all non-hydrogen atoms; occupancy factors were refined for the atoms of the disordered DMSO ligands; hydrogen atoms were not included); R = 0.039, R_w = 0.040.[5]‡

Two of the DMSO groups were badly disordered. The disorder of the ligand containing S(4) was modelled by including two sulphur atoms [S(4), S(4P)] and three carbon atoms [C(41), C(42), C(43)]. The disorder of the S(7) ligand required two oxygen atoms [O(7), O(7P)], three sulphur atoms [S(7), S(7P), S(7PP)], and three carbon atoms [C(71), C(72), C(73)]. The final difference Fourier showed one peak near S(4) (2.1 e Å^{-3}), indicating that the model was less than perfect. Other peaks, (1.0—1.83 e Å^{-3}), represented density from other disordered sites or residual density near the Mo atoms.

Received, 6th September 1982; Com. 1070

References

1 R. Schöllhorn, R. Kuhlmann, and J. O. Besenhard, *Mater. Res. Bull.*, 1976, **11**, 83.
2 C. Knobler, B. R. Penfold, W. T. Robinson, C. J. Wilkins, and S. H. Yong, *J. Chem. Soc., Dalton Trans.*, 1980, 248.
3 M. Seleborg, *Acta Chem. Scand.*, 1966, **20**, 2195.
4 S. A. Magarill and R. F. Klevtsova, *Sov. Phys.-Crystallogr.*, (*Engl. Transl.*), 1972, **16**, 645.
5 Computation details may be found in the following reference: W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1979, **18**, 2030.

† The observed and calculated weight losses at 600 °C are as follows: MoO_3.2DMSO, 53.7 and 52.1%; MoO_3.1.33DMSO, 43.4 and 42.0%; MoO_3.DMSO glass, 37.5 and 35.2 (elemental analysis for CHN: obs. 11.21/2.78/0; calc. 10.81/2.70/0); polycrystalline MoO_3.DMSO, 37.8 and 35.2.

‡ 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.