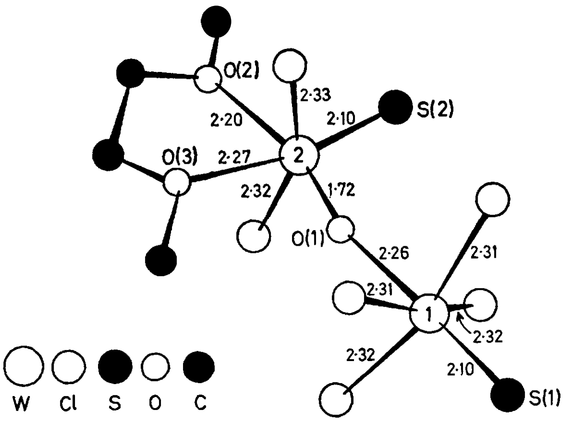
Crystal Structure of a Complex Containing Tungsten(VI) Sulphide Oxide Dichloride

By D. Britnell, M. G. B. Drew, G. W. A. Fowles,* and D. A. Rice
(*Department of Chemistry, University of Reading, Whiteknights, Reading* RG6 2AD)

Summary The reaction of $WSCl_4$ with 1,2-dimethoxyethane (dme) results in oxygen abstraction and the formation of a complex that a single-crystal study shows may be formulated as $WSCl_4,WOSCl_2$,dme; the $WSCl_4$ and $WOSCl_2$,dme units are linked through the oxygen atom of the $WOCl_2$ unit, both tungsten atoms having a distorted octahedral environment.

It is known that tungsten(VI) chloride reacts with oxygen-containing ligands to give the oxide chlorides $WOCl_4$ and WO_2Cl_2 or complexes of these halides.[1,2] We have found that tungsten(VI) sulphide tetrachloride ($WSCl_4$) undergoes a similar reaction with ether ligands, so that 1,2-dimethoxyethane (dme) produces a brown crystalline benzene-soluble complex of stoicheiometry $C_4H_{10}Cl_6O_3S_2W_2$. The crystals are monoclinic, $a = 17{\cdot}852(12)$, $b = 9{\cdot}931(8)$, $c = 9{\cdot}582(8)$ Å, $\beta = 93{\cdot}80(17)^\circ$, $U = 1695{\cdot}7$ Å^3, $M = 750{\cdot}9$, $D_c = 2{\cdot}94$, $Z = 4$, $D_m = 2{\cdot}94$, space-group $P2_1/a$. The intensities of 1055 independent reflections ($2\theta < 40^\circ$) above background were recorded using Zr-filtered Mo-K_α radiation on a G.E. XRD 5 manual diffractometer by the stationary-crystal–stationary-counter method. The structure was solved by Patterson and Fourier methods and refined (W anistropic; S, Cl, O, C isotropic) to R 0·06. The structure (see Figure; standard deviations W–Cl and W–S 0·01, W–O 0·02 Å) shows that the complex is interpreted best as a $WOSCl_2$,dme species bonded unsymmetrically through oxygen to a $WSCl_4$ species, the dimensions of which are relatively unchanged from those found in $WSCl_4$ itself.[3]



Figure

Both tungsten atoms have distorted octahedral environments. The two entities contain a terminal W=S multiple bond (2·10 Å), but as the W–O bonds in the bridge are quite different in length (2·26, 1·71 Å), we can represent the molecule as (A). Of the two tungsten-oxygen bridging

$$S{=}W(Cl_4){\leftarrow}O{=}W(S)Cl_2,\text{dme} \qquad (A)$$

bonds, W(2)–O(1) is shorter than the comparable bonds in $[WO_4]^{2-}$ (1·79 Å)[4] and $WOCl_4$ (1·80 Å)[5], and thus has substantial multiple bond character, while the longer W(1)–O(1) bond, represented as W←O, is of similar length to those between W(2) and the oxygen atoms of the complexing dme ligands (2·20 and 2·27 Å). It should be noted that the shorter of these two bonds is *trans* to W=O, while the other is *trans* to W=S. The formation of the oxygen bridge rather than a sulphur bridge is comparable with the presence of bridging oxygen in polymeric $WOCl_4$[5] and terminal sulphur in monomeric $WSCl_4$.[3]

The near planarity of the S(1), W(1), O(1), W(2), S(2), O(2), and O(3) atoms (average deviation 0·03 Å) suggests a degree of π bonding throughout the molecule. The staggering of the two octahedra relative to the W · · · W axis can be attributed to intramolecular forces, as can the fact that the W–O–W angle (161·2°) is less than 180°. A similar but smaller deviation (171·6°) is found in the Mo–O–Mo bridge in $MoOBr_3$[6] where the Mo–O distances are also quite different.

The preparative method employed ensured that the oxygen atom in the $WOCl_2$ unit could only arise *via* oxygen abstraction from the dimethoxyethane.

(*Received, 2nd February* 1972; *Com.* 152.)

---

[1] G. W. A. Fowles and J. Frost, *J. Chem. Soc.* (*A*), 1967, 671.
[2] B. Brisdon, *Inorg. Chem.*, 1967, **6**, 1791.
[3] M. G. B. Drew and R. Mandyczewsky, *J. Chem. Soc.* (*A*), 1970, 2815.
[4] N. M. Kools, A. S. Koster, and G. D. Rieck, *Acta Cryst.*, 1970, **B26**, 1974.
[5] H. Hess and H. Hartung, *Z. anorg. Chem.*, 1966, **344**, 157.
[6] M. G. B. Drew and I. B. Tomkins, *Acta Cryst.*, 1970, **B26**, 1161.