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The Crystal Structure of an Adduct of Trichlorosulphidotungsten(V)

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The sulphidohalides of molybdenum and tungsten have received far less attention than the analogous oxohalides and while for molybdenum the majority of the studies concern the lower oxidation states those involving tungsten concern almost exclusively tungsten(VI) [1]. Accordingly we have been investigating the chemistry of lower oxidation state sulphidohalides of tungsten and now report the first structure of a species containing a tungsten(V) sulphidohalide moiety. The tungsten(VI) sulphidochloride WCl_4S was allowed to react with a $CHCl_3$ solution of $CH_3SCH_2CH_2SCH_3$ (1:1 molar ratio) for three weeks at room temperature. The product was isolated by vacuum line filtration and washed with dry $CHCl_3$. Crystals suitable for X-ray crystallography were obtained by recrystallisation of the product from $CHCl_3$.

Crystal Data

$C_4H_{10}Cl_3S_3W$, M = 444.63, monoclinic, space group $P2_1/c$ a = 14.925(10), b = 13.308(10), c = 6.936(5) Å, β = 121.9(1)°, Z = 4, U = 1377.6 Å^3, d_m = 2.46, d_{calc} = 2.52 g cm^3. The intensities of 2048 independent reflections with $2\theta < 50°$ were recorded using zirconium filtered Mo-Kα 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 a least squares refinement on 1429 non-zero reflections reached R = 0.068.

The asymmetric unit contains a $WCl_3S\cdot CII_3SCH_2CH_2SCH_3$ molecule in which the tungsten atom is six co-ordinate (see Fig. 1 for atomic numbering scheme). The structure is distorted from that of a regular octahedron by the presence of the sulphur–tungsten multiple bond and the chelating ligand whose two sulphur atoms subtend an angle of 80.0(5)° at the tungsten atom.

The tungsten–sulphur multiple bond (2.146(11) Å) is significantly longer than that reported for WCl_4S (2.098(8) Å) [2] and those in adducts of WCl_2OS (2.10(1) Å) [3] and WCl_4S (2.10(1) Å) [3] and WCl_4S (2.07(1) Å [4]. The lengthening of the tungsten–sulphur bond on going from tungsten(VI) to tungsten(V) reflects the increase in effective ionic radius of the metal on decrease in oxidation state (W(VI) 0.60, W(V) 0.62 Å) [5]. Documented evidence on the change in bond length of a W=X bond on going from tungsten(VI) to tungsten(V) is sparse but for molybdenum this variation in the oxidation state is said to cause a change of between 0.02 and 0.04 Å in the Mo=O bond length [6, 7].

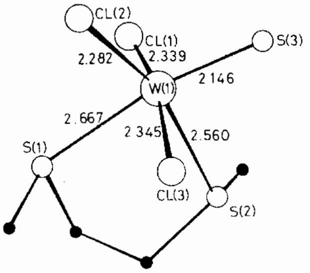

Fig. 1. The structure of $WCl_3S\cdot CH_3SCH_2CH_2SCH_3$. Standard deviations on bond lengths are *ca.* 0.008 Å.

The presence of the multiply bonded moiety W=S increases the S(3)–W–Cl(1)(2)(3) angles above 90° and thus raises the tungsten atom 0.32 Å above the approximate plane formed by S(2)Cl(1)Cl(2) and Cl(3). The presence of the W=S bond also gives rise to variation in the W–S (ligand) distances so that W–S(1) (*trans* to W=S) (2.668(9) Å) is longer than W–S(2) (*cis* to W=S) (2.560(6) Å).

These values for the distance of the tungsten atom above the equatorial plane (0.32 Å) and the length of the W–S bond *trans* to W=S (2.668(9) Å) can be used to characterise the *trans* effect of the W(V)=S bond. Comparable values in the tungsten(VI) compound $2WCl_4S\cdot CH_3SCH_2CH_2SCH_3$ are 0.36, 2.79 Å and 0.38, 2.81 Å for the two independent tungsten atoms. Thus the *trans* effect of the W=S bond is noticeably strengthened on going from W(V) to W(VI) consistent with the decrease in bond length.

The compound reported here is paramagnetic (μ = 1.45 B.M.), exhibits a broad e.s.r. signal, and in its infra-red spectrum has a band at 528 cm^{-1} that is attributed to ν(W=S), this value being some 20–30 cm^{-1} less than that observed for ν(W=S) in tungsten compounds.

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