

Tungsten(v) Oxytrichloride

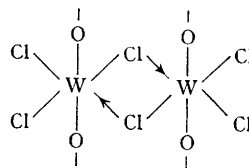
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THE oxytrichlorides of quinquevalent vanadium, niobium, and tantalum are well established, and Zalkin and co-workers¹ have shown that the niobium compound is polymeric with Nb_2Cl_6 units linked through Nb-O-Nb bridges. The analogous molybdenum compound, MoOCl_3 , has been prepared recently,² and we now report the preparation and characterisation of the tungsten derivative. This was obtained by reduction of tungsten(vi) oxytetrachloride with aluminium powder in a sealed tube at 100–140°C. Aluminium(III) chloride and excess of tungsten(vi) oxytetrachloride were mostly removed by sublimation at 225°C, leaving the required compound as an olive-green solid which was finally purified by washing with dichloromethane in an all-glass vacuum apparatus.

The tungsten(v) oxytrichloride so prepared is only slightly paramagnetic (χ'_m , 60×10^{-6} c.g.s.), and its infrared spectrum shows a single strong broad peak at 796 cm^{-1} . These data indicate a

structure analogous to that of niobium(v) oxytrichloride, since the low magnetic susceptibility would result from pairing of the electrons on adjacent tungsten atoms in W_2Cl_6 units and the peak at 796 cm^{-1} corresponds to W-O-W rather than W=O bonds.



Further support for this hypothesis is provided by the X-ray powder photograph, the indexing of which reveals a tetragonal unit cell of dimensions $a = 10.7$ and $c = 3.84$ Å; these dimensions agree

closely with the reported¹ values for NbOCl_3 , $a = 10.87$ and $c = 3.96$ Å. The diffuse reflectance spectrum of the compound shows a peak at $13,100 \text{ cm.}^{-1}$ and a pronounced shoulder at $24,400 \text{ cm.}^{-1}$

As would be expected from the proposed polymeric structure, tungsten(v) oxytrichloride is insoluble in the usual organic solvents (*e.g.*, C_6H_6 and CH_2Cl_2) but slowly dissolves in donor solvents with the formation of complex compounds. The latter appear to be of two types, of empirical formula $\text{WOCl}_3\cdot\text{L}$ and $\text{WOCl}_3\cdot 2\text{L}$. Thus reaction

with pyridine at room temperature yields a navy-blue solid $\text{WOCl}_3\cdot\text{C}_5\text{H}_5\text{N}$ which is slightly paramagnetic (χ'_m , 248×10^{-6} c.g.s.). With methyl cyanide under reflux, however, $\text{WOCl}_3\cdot 2\text{CH}_3\text{CN}$ is formed as a dark blue-green solid, and the infrared spectrum of this compound shows a single strong peak at 994 cm.^{-1} , suggesting the presence of a terminal $\text{W}=\text{O}$ bond rather than $\text{W}-\text{O}-\text{W}$ bridging. Investigations of these two classes of compound which form with a range of monodentate ligands are proceeding, as also are attempts to prepare tungsten(v) oxytribromide.

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¹ A. Zalkin, D. E. Sands, and R. E. Elson, *Acta Cryst.*, 1959, **12**, 21.

² D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1198.