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Preliminary communication

The X-ray Structure of Tetraethylammonium μ-Pentachlorothiophenolato-*bis*{pentacarbonyltungstate(O)}.

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SUMMARY

$[NEt_4][W_2(CO)_{10}SC_6Cl_5]$ has been synthesised via the mononuclear pentacarbonyl species and characterised by elemental, IR and X-ray analyses; the bridging W-S-W angle in the dinuclear anion is 132.1°

Tetraethylammonium μ-pentachlorothiophenolato-*bis*{pentacarbonyltungstate(O)}, $[NEt_4][W_2(CO)_{10}SC_6Cl_5]$,(I), is prepared in good yield at room temperature by the reaction of tetraethylammonium chloropentacarbonyltungstate(O) with thallium(I) pentachlorothiophenolate and silver tetrafluoroborate (molar ratio 2:1:1), in tetrahydrofuran (THF), under an atmosphere of nitrogen. This method also provides a simple route to the previously reported [1] complex $[W_2(CO)_{10}SC_6H_5]^-$. The IR spectrum of (I) in THF has distinct carbonyl stretching bands at 2073(w), 2062(m), 1977(m,sh), 1941(vs) 1916(s), and 1876(s) cm^{-1} which by analogy with the spectrum of $[Cr_2(CO)_{10}I]^-$ (II) is consistent with a bent W-S-W bridge [1,2,3].

The crystals of (I), $C_{24}Cl_5H_{20}NO_{10}SW_2$, $M = 1059.5$, are triclinic, spacegroup $P\bar{1}$, $\underline{a} = 13.682$, $\underline{b} = 11.699$, $\underline{c} = 10.597$ Å, $\alpha = 91.71$, $\beta = 100.31$, $\gamma = 92.20^\circ$, $\underline{V} = 1666.5$ Å^3, $\underline{D}_c = 2.11$ g cm^{-3}

for $\underline{Z} = 2$. A Philips PW1100 four circle diffractometer was used, with graphite crystal monochromatised Mo-$\underline{K}_\alpha$ radiation, to collect 2770 reflections with $I/\sigma(I) \geqslant 3$. Full matrix refinement of the atomic parameters (W, S and Cl anisotropic) has given an R-value of 0.036. The structure of the anion is shown in Fig.1.

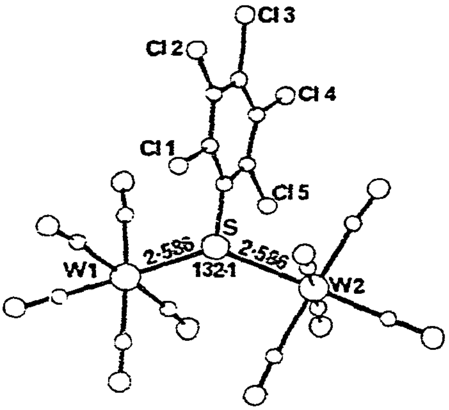

Fig.1. The structure of the complex anion $[W_2(CO)_{10}SC_6Cl_5]^-$ with the bridging bond lengths (Å) and angle (°).

The two tungsten atoms are bridged by the sulphur atom of the pentachlorothiophenolate ligand with a large W(1)-S-W(2) angle of 132.1(1)°. In contrast the Cr-I-Cr angle in (II) is only 117.9(1)°; this is also greater than the value expected for sp^3 hybridisation of the bridging atom. The only sulphur-bridged ditungsten X-ray structure previously reported [4], $(\pi\text{-}C_5H_5)_2W(\mu\text{-}SC_6H_5)_2W(CO)_4$, has two bridging sulphur atoms, with equal W-S-W angles of 104.9(3)° and approximately pyramidal sulphur coordination geometries. It seems probable that the size of the bridging angle (M-L-M), in complexes with two $M(CO)_5$ groups, is largely determined by minimisation of contacts between carbonyl groups on the two halves of the bridged complex. The M-L distances are considerably shorter in (I) than in (II); in (I) the W-S distances are both 2.585(4) Å and in (II) the mean Cr-I distance is 2.789(5) Å.

Consequently the opening out of the W-S-W angle in (I) to 132.1° results in a W-W distance of 4.73 Å which is very similar to the Cr-Cr distance of 4.78 Å in (II) and the closest intramolecular carbonyl oxygen-oxygen contacts in the two complexes are also similar, 3.19 in (I) and 3.01 Å in (II).

The equatorial tungsten-carbonyl bond lengths (*cis* to the bridging thiol ligand), mean 2.002(6) Å, are significantly longer than the corresponding *trans* bonds, mean 1.935(12) Å. The longer W-C bonds may be attributed to competition of the mutually *trans* carbonyl ligands for π-electron density from the tungsten atoms which would reduce the W-C bond order. It may be deduced that any π-bonding from the tungsten to the bridging sulphur atom is much weaker than that to the carbonyls.

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