The Crystal Structure of an Oxidation Product from the Reaction between Tungsten(V) Chloride and Trichloroacetonitrile

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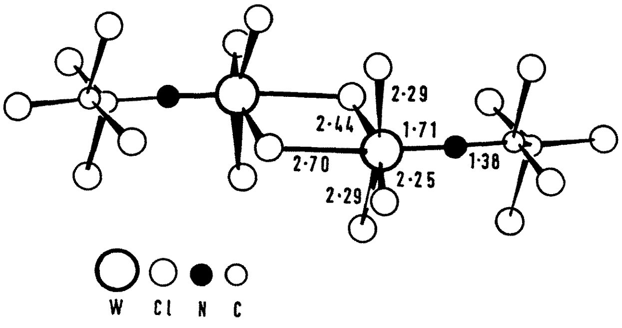
Summary During the reaction of tungsten(V) chloride with trichloroacetonitrile addition across the cyanide bond occurred to give di-μ-chloro-bis[tetrachloro(pentachloroethylnitrido)tungsten(VI)] which contains a tungsten–nitrogen multiple bond of length 1·71(2) Å.

THE oxidation of certain lower-valent metal chlorides by CCl_3CN has been previously reported;[1] of particular interest is the oxidation of tungsten(V) chloride to give a tungsten(VI) compound, corresponding, on analysis, to $WCl_6,2CCl_3CN$. Slow crystallisation (several weeks) of the latter from dichloromethane yielded orange–yellow crystals of analysis WCl_6, CCl_3CN.

X-Ray studies show crystals of $W_2Cl_{18}C_4N_2$ (M = 1081·86) to be monoclinic with the space group $P2_1/n$, $a = 6{\cdot}54(1)$ Å, $b = 20{\cdot}21(2)$ Å, $c = 9{\cdot}11(1)$ Å, $\beta = 90{\cdot}0(1)°$, $Z = 2$, $U = 1204{\cdot}8$ Å^3 and $D_c = 2{\cdot}98$ g cm^{-3}. The intensities of 2111 independent reflections ($2\theta < 50°$) were recorded, using zirconium-filtered Mo-K_α radiation on a GE XRD-5 manual diffractometer by the stationary crystal–stationary counter method. The structure was solved by Patterson and Fourier methods, and least-squares refinement on the 1200 non-zero reflections has reached a conventional R factor of 0·06.

Each tungsten atom can be considered to be in a distorted octahedral environment (see Figure). Standard deviations for the bond distances are W–Cl 0·01, W–N 0·02, and N–C 0·03 Å. Units of WCl_4, CCl_3CCl_2N are linked through chlorine bridges. Thus two of the chlorine atoms are bonded to carbon of the CN group rather than to tungsten. The W–N bond length of 1·71(2) Å is shorter than those previously found for tungsten(VI)–oxygen multiple bond lengths, which lie in the range 1·8—1·9 Å, [1·79 in K_2WO_4,[2] 1·81 in $WOCl_4$,[3] and 1·89 Å in the seven-co-ordinate $WOCl_4(As_2C_{10}H_{16})$[4]]. In the $W(NMe_2)_6$[5] structure, the W–N distances are 2·03(3) Å and it is suggested that the estimated single bond and double bond distances lie in the range (2·04—2·07 Å) and (1·92—1·95 Å) respectively.



FIGURE

Because of the short W–N distance and the almost linear W–N–C skeleton (the angle = 177(2)°) and the valence requirements, the bond can be formally considered as triple ($\mathrm{W}\overset{\leftarrow}{=}\mathrm{N}$), with p_{π}–d_{π} bonding incorporating the nitrogen lone pair. A double (W=N) bond would require a W–N–C angle of about 120° and molecular models indicate that this would give considerable steric hindrance between the CCl_2 and WCl_4 groups.

The WCl_4 unit is not quite planar, the tungsten atom being 0·32 Å above the plane of the four chlorine atoms with N–W–Cl angles close to 98°. The average length of the three W–Cl non-bridging bonds is 2·28 Å, which is similar to bond lengths found in the molecules $WOCl_4$[3] and $WSCl_4$.[6] The two W–Cl bridging distances, *cis* and *trans* to N, are respectively 2·44(1) and 2·70(1) Å.

The chlorination of the CN group was not expected, although the reaction between acetonitrile, phosphorus(v) chloride and chlorine is said to give a similar result.[7] At present we cannot be sure whether the chlorination occurred during the original reaction or during the course of the slow recrystallisation from dichloromethane. Careful thermal decomposition of $WCl_6,2CCl_3CN$ also yields a compound of composition WCl_6,CCl_3CN, which has an identical i.r. spectrum (4000—250 cm^{-1}) to the compound recrystallised from dichloromethane, but the *X*-ray powder patterns of the two compounds are not the same. Further work is being done to establish the mode of chlorination of the cyanide group.

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