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Tungsten Pentachloride

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Abstract. WCl_5, monoclinic, $C2/m$ (No. 12); a = 17·438 (4), b = 17·706 (4), c = 6·063 (1) Å, β = 95·51 (2)°, V = 1863·3 (6) Å^3, Z = 12, D_c = 3·86 g cm^{-3}. Crystals were grown by sublimation. The compound, isomorphous with $MoCl_5$ and $NbCl_5$, contains two crystallographically independent but essentially identical W_2Cl_{10} molecules each consisting of two distorted WCl_6 octahedra sharing an edge. The W atoms in the molecular units are 3·814 (2) Å apart.

Introduction. Tungsten pentachloride was prepared by reacting 1·00 g reagent grade WCl_6 with 0·05 g aluminum foil in a sealed, evacuated Pyrex tube (14 mm o.d. × 15 cm long). During the 48 h reaction period the end of the tube containing the aluminum was maintained at 475 °C while the WCl_6-containing end was kept at 225 °C. Upon cooling the reaction tube to room temperature, green-black needles of WCl_5 were found in what had been the cool end of the tube. The reaction tube was opened in an inert atmosphere, and dry, degassed mineral oil was poured over the crystals, thus allowing them to be handled in air for a brief period of time. A needle-shaped crystal of dimensions 0·15 × 0·10 × 0·40 mm was mounted in paraffin wax in a thin-walled capillary tube for X-ray measurements. Preliminary photographs established a C-centered monoclinic cell with no systematic absences other than those due to the centering condition (hkl, $h + k \neq 2n$).

Table 1. *Positional parameters for* WCl_5

All values ×10^4. Standard deviations are in parentheses; entries with no e.s.d.'s are fixed by the symmetry of the space group.

	x	y	z
W(1)	0·0	1077·5 (5)	0·0
W(2)	3331·3 (4)	1076·9 (4)	4332 (1)
Cl(1)	764 (3)	0·0	8607 (9)
Cl(2)	774 (3)	1923 (3)	8576 (8)
Cl(3)	769 (3)	944 (3)	3182 (7)
Cl(4)	2601 (3)	0·0	2395 (9)
Cl(5)	2582 (3)	1919 (3)	2363 (8)
Cl(6)	2509 (3)	948 (3)	6967 (7)
Cl(7)	4060 (3)	0·0	6251 (10)
Cl(8)	4070 (3)	1929 (3)	6300 (8)
Cl(9)	4156 (3)	945 (3)	1713 (8)

Intensity data were collected using a Syntex $P\bar{1}$ automated diffractometer, employing graphite-monochromated Mo $K\alpha$ radiation. The method of data collection has been described elsewhere (Cotton, Frenz, Deganello & Shaver, 1973).

1757 unique reflections were collected with $0 < 2\theta \leq 50°$, of which 1295 had intensities with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects.* The crystal was measured with a micrometer eyepiece before mounting, then the positions of the faces of the mounted crystal were ascertained using an optical goniometer. A numerical absorption correction (μ = 216·3 cm^{-1}) based on a Gaussian integration formula was applied to the data.* Transmission coefficients ranged from 4·5 to 23·3%, with an average value of 16·6%.

The structure was refined in the space group $C2/m$, in common with the isomorphous compounds $NbCl_5$ (Zalkin & Sands, 1958) and $MoCl_5$ (Sands & Zalkin, 1959). The metal and chlorine atomic positions reported for $MoCl_5$ by Sands & Zalkin (1959) were used as starting positions in the present structure. Full-matrix least-squares refinement with anisotropic temperature factors gave conventional discrepancy indices $R_1 = \sum ||F_o| - |F_c|| / |F_o|$ of 0·060 and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0·069. Refinement of an isotropic extinction parameter was attempted; however, no improvement in the agreement between observed and calculated structure factors resulted, so no extinction correction was included in the final refinement. The quantity minimized in all refinements was $\sum w(\Delta F)^2$. The standard deviation of an observation of unit weight was 1·72 with weights taken as $w = 1/\sigma^2 = 4F_o^2/\sigma^2(F_o^2)$.

Positional parameters are shown in Table 1; interatomic distances and angles are listed in Table 2.†

* Computer programs used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, were those of the Enraf–Nonius structure determination package.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33558 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°) *in* WCl_5

W(1)–Cl(1) (×2)	2·519 (3)	Cl(1)–W(1)–Cl(1′)	81·5 (1)
W(1)–Cl(2) (×2)	2·243 (3)	Cl(1)–W(1)–Cl(2)	91·1 (1)
W(1)–Cl(3) (×2)	2·254 (4)	Cl(1)–W(1)–Cl(2′)	172·6 (1)
		Cl(1)–W(1)–Cl(3)	85·3 (1)
W(2)–Cl(4)	2·520 (3)	Cl(1)–W(1)–Cl(3′)	85·7 (2)
W(2)–Cl(5)	2·249 (4)	Cl(2)–W(1)–Cl(2′)	96·3 (2)
W(2)–Cl(6)	2·259 (3)	Cl(2)–W(1)–Cl(3)	93·9 (2)
W(2)–Cl(7)	2·514 (3)	Cl(2)–W(1)–Cl(3′)	94·1 (1)
W(2)–Cl(8)	2·251 (4)	Cl(3)–W(1)–Cl(3′)	168·0 (2)
W(2)–Cl(9)	2·254 (3)	Cl(4)–W(2)–Cl(5)	90·7 (1)
W(1)–W(1′)	3·816 (2)	Cl(4)–W(2)–Cl(6)	85·8 (2)
W(2)–W(2′)	3·813 (1)	Cl(4)–W(2)–Cl(7)	81·5 (1)
		Cl(4)–W(2)–Cl(8)	173·0 (1)
		Cl(4)–W(2)–Cl(9)	85·5 (2)
		Cl(5)–W(2)–Cl(6)	93·8 (1)
		Cl(5)–W(2)–Cl(7)	172·2 (1)
		Cl(5)–W(2)–Cl(8)	96·3 (2)
		Cl(5)–W(2)–Cl(9)	94·1 (1)
		Cl(6)–W(2)–Cl(7)	85·6 (2)
		Cl(6)–W(2)–Cl(8)	93·6 (1)
		Cl(6)–W(2)–Cl(9)	168·2 (1)
		Cl(7)–W(2)–Cl(8)	91·5 (1)
		Cl(7)–W(2)–Cl(9)	85·4 (2)
		Cl(8)–W(2)–Cl(9)	94·1 (2)

Discussion. Gaseous WCl_5 is known from electron diffraction measurements (Spiridonov & Romanov, 1968) to consist of mononuclear, trigonal-bipyramidal molecules, but the structure of the crystalline material has remained unknown, beyond the fact that it is certainly isomorphous and probably isostructural with $MoCl_5$ (Boorman, Greenwood, Hildon & Whitfield, 1967).

Solid WCl_5 is now shown conclusively to be isomorphous with $NbCl_5$ (Zalkin & Sands, 1958) and $MoCl_5$ (Sands & Zalkin, 1959), consisting of dimeric W_2Cl_{10} molecules made up of two WCl_6 octahedra sharing an edge. There are two crystallographically independent molecules in the monoclinic unit cell, one with $2/m$ crystallographic symmetry, the other containing only a mirror plane. However, the two types of molecule are for all practical purposes identical. The molecular structure for the averaged W_2Cl_{10} molecule, bearing the atomic labels for both molecules, is shown in Fig. 1. The average W–terminal Cl distance is 2·251 ± 0·005 Å, while the average W–bridging Cl distance is 2·518 ± 0·003 Å; in the gas phase the W–Cl distance is 2·26 ± 0·02 Å (Spiridonov & Romanov, 1968).

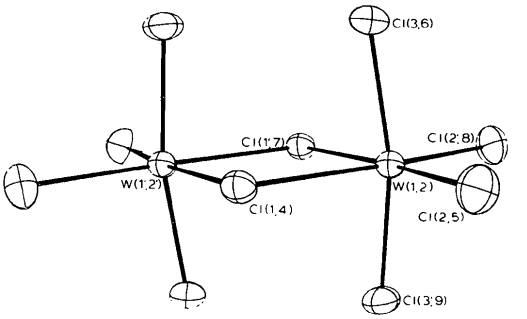

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the averaged W_2Cl_{10} molecule. Thermal ellipsoids enclose 50% of the electron density. In the atom labels the first number in parentheses refers to molecule (1) [W(1), Cl(1–3)]; the second number to molecule (2) [W(2), Cl(4–9)].

In the W_2Cl_{10} dimer the W atoms are displaced from ideal octahedral geometry away from each other. This evidence of repulsion and the long W–W separation of 3·814 (2) Å indicates that there is no bonding between the metal atoms, despite the fact that the W^{5+} d^1 configuration would allow the formation of a single W–W bond. Molecular-orbital calculations for the W_2Cl_{10} molecule are in agreement with the observed lack of metal–metal bonding (Pak, Korol'kov & Voronovich, 1973; Pak & Korol'kov, 1970).

References

Boorman, P. M., Greenwood, N. N., Hildon, M. A. & Whitfield, H. J. (1967). *J. Chem. Soc. A*, pp. 2017–2018.

Cotton, F. A., Frenz, B. A., Deganello, G. & Shaver, A. (1973). *J. Organomet. Chem.* **50**, 227–240.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Pak, V. N. & Korol'kov, D. V. (1970). *Teor. Eksp. Khim.* **6**, 387–390.

Pak, V. N., Korol'kov, D. V. & Voronovich, N. S. (1973). *Teor. Eksp. Khim.* **9**, 116–119.

Sands, D. E. & Zalkin, A. (1959). *Acta Cryst.* **12**, 723–726.

Spiridonov, V. P. & Romanov, G. V. (1968). *Vestn. Mosk. Univ. Khim.* **23**, 10–14.

Zalkin, A. & Sands, D. E. (1958). *Acta Cryst.* **11**, 615–619.