The Crystal Structure of Oxotetrachloro-*o*-phenylenebis(dimethylarsine)tungsten(VI): a Pentagonal Bipyramidal Tungsten Complex

By M. G. B. DREW* and R. MANDYCZEWSKY

(*Department of Chemistry, The University, Whiteknights Park, Reading* RG6 2AD)

Summary The crystal structure of oxotetrachloro-*o*-phenylenebis(dimethylarsine)tungsten(IV) shows the metal atom to exist in a seven-co-ordinate distorted pentagonal bipyramidal environment.

o-PHENYLENEBIS(DIMETHYLARSINE) (diarsine) has been used extensively as a bidentate ligand to stabilize high co-ordination numbers and unusual oxidation states.[1-3] Complexes of tungsten oxotetrachloride of the type $WOCl_4 \cdot L$ (L = MeCN, pyridine, diethyl ether, *etc.*) have been postulated as six-co-ordinate.[4] By using diarsine as a ligand, the complex $WOCl_4$·diarsine has been prepared[5] and a single crystal *X*-ray study shows the tungsten atoms to be seven-co-ordinate (pentagonal bipyramidal).

Yellow green plates of $C_{10}H_{16}As_2Cl_4OW$ (M 627·7) are orthorhombic, space group *Pbca*, with $a = 13{\cdot}690(9)$, $b = 15{\cdot}986(12)$, $c = 15{\cdot}904(12)$ Å, $U = 3480{\cdot}56$ Å^3, $D_m = 2{\cdot}40(2)$, $D_c = 2{\cdot}400$ g cm^{-3}, $Z = 8$. The intensities of 696 independent reflections ($2\theta < 30°$) 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 (W, As, Cl anisotropic, O, C isotropic) using all reflections has reached a conventional R factor of 0·10.

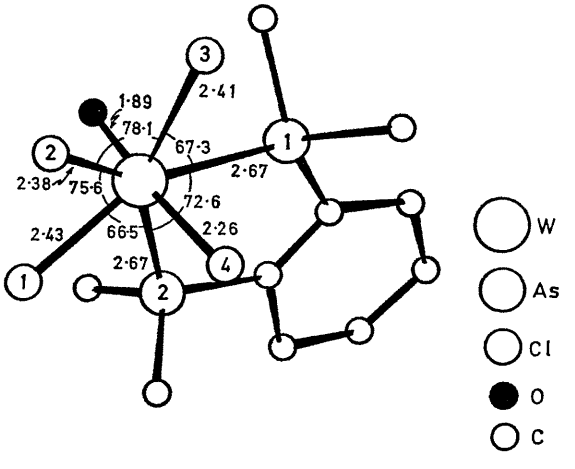

FIGURE. *One molecule of* $C_{10}H_{16}As_2Cl_4OW$ *as projected along the* a *axis of the crystal.*

The configuration around the tungsten atom is approximately pentagonal bipyramidal (see Figure). Standard deviations for bond distances were 0·01 for W–As, 0·02 for W–Cl, and 0·04 Å for W–O. The parameters of the carbon atoms have refined to acceptable values. Axial positions around the tungsten are filled by the oxygen atom and one chlorine atom. The remaining three chlorine atoms and the two arsenic atoms from the diarsine ligand take up the five equatorial positions.

The three W–Cl (equatorial) distances are equidistant within experimental error (average 2·40 Å) and rather longer than has been observed in an octahedral environment: *viz.* 2·29 and 2·26 Å respectively for the W–Cl bonds in $WOCl_4$[6] and WCl_6.[7] The W–Cl(axial) distance of 2·26(2) Å is significantly shorter than the equatorial distances. The W–As distances are 2·67(1) Å. The W–O distance [1·89(4) Å] is shorter than that found in $WOCl_4$ (2·20 Å),[6] where the oxygen atoms act as bridges between tungsten atoms, but longer than is observed (1·79 Å) in K_2WO_4.[8]

Angles between the axial and equatorial positions

O–W–Cl(1)	92·9(14)°	Cl(4)–W–Cl(1)	92·1(7)°
O–W–Cl(2)	105·2(13)	Cl(4)–W–Cl(2)	91·9(7)
O–W–Cl(3)	90·6(14)	Cl(4)–W–Cl(3)	92·4(8)
O–W–As(1)	84·0(12)	Cl(4)–W–As(1)	81·4(7)
O–W–As(2)	86·0(11)	Cl(4)–W–As(2)	80·8(6)

The maximum distance of any atom from the least-squares plane containing the tungsten and the five equatorial atoms is 0·15 Å, with the angles between adjacent atoms in the plane in the range 66·5—78·1°. Bond angles between axial and equatorial positions (see Table) show that the

two axial bonds are bent away from the three equivalent chlorine atoms towards the two arsenic atoms.

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