Tungsten Hexadimethylamide

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Summary In the structure of tungsten hexadimethylamide W(NMe$_2$)$_6$, determined by *X*-ray diffraction, the WN$_6$ group is octahedral but the planar WNC$_2$ groups give a configuration having the rare symmetry point group T_h.

THE well-known binary compounds of tungsten(VI), WF$_6$, WCl$_6$, and W(OPh)$_6$ and the recently prepared WF$_5$Cl[1] and WF$_5$(OR)[2] all involve co-ordination with the electronegative donor atoms F, O, or Cl. Fowles[3] found that WCl$_6$ was reduced by amines forming tungsten(IV) chloride dialkylamide complexes and thus we expected the reaction involving WCl$_6$ and LiNR$_2$ to produce tungsten tetradialkylamides. Although reduction occurred with predominant formation of polymeric tungsten tris-dimethylamide (from WCl$_6$ and LiNMe$_2$, 0°, petrol–benzene) we have also isolated significant amounts of W(NMe$_2$)$_6$. The orange crystals gave satisfactory elemental analyses and were volatile (sublimes *ca.* 90°/10^{-3} mm. Hg); mass spectrum, M^+, m/e = 448 for ^{184}W (NMe$_2$)$_6^{+\cdot}$. This compound is perceptibly less readily hydrolysed than other typical transition metal dimethylamides [*e.g.* Zr(NMe$_2$)$_4$ or Ta(NMe$_2$)$_5$]. It is monomeric in benzene, is diamagnetic and has i.r. and Raman spectra consistent with an octahedral WN$_6$ unit [*e.g.* $\nu_1(a_{1g})$, 555 cm.$^{-1}$; ν_3 (f_{1u}), 545 cm.$^{-1}$]. The single-line n.m.r. spectrum (τ = 6·56 in toluene) showed no change with temperature (+100 to −90°) and the orange colour is due to tailing into the visible region of an intense electronic absorption (max. *ca.* 30,000—33,000 cm.$^{-1}$).

In view of its interest as the first metal hexadimethylamide and speculation on the degree of nitrogen → metal π-bonding in metal dialkylamides,[4] a single-crystal *X*-ray structural determination was carried out. Crystal data: W[N(CH$_3$)$_2$]$_6$; M = 448·18; cubic, a = 9·80 Å, D_m = 1·57, Z = 2, D_c = 1·577; space group *Im*3 or *Im*3*m*. Intensity data were recorded on a Siemens Automatic Diffractometer using Cu-K_α radiation. Structure analysis and refinement has proceeded straightforwardly on the assumption that the space group was *Im*3*m*: R is currently 0·03 for 116 reflections, as yet uncorrected for absorption (μCu-K_α = 114 cm.$^{-1}$).

The structure has an octahedral WN$_6$ configuration with planar WNMe$_2$ groups disordered equally about two positions. Examination of molecular models suggests that in fact the crystal must contain molecules having the symmetry point group T_h (see Fig.), disordered either randomly or in domains. Subsequent refinement will attempt to distinguish between these possibilities.

The planarity of C$_2$NWNC$_2$ groups suggests delocalised nitrogen → tungsten ($p_\pi \rightarrow d_\pi$) π-bonding since the nitrogen p-atomic orbitals transform as $T_{2g} + T_1u$ (in localised O_h symmetry of WN$_6$ group) and the T_{2g} set can interact with the vacant tungsten t_{2g}-orbitals. Thus the tungsten shares in an 18-electron valency group and the W–N bond order may approach 1·5. The observed W–N distance (2·032 ± 0·025 Å) suggests that some π-bonding occurs although the estimated single bond (2·04—2·07 Å) and double bond (1·92—1·95 Å) distances are subject to considerable uncertainty. The small CNC angle (104·92°) of the dimethylamide groups suggests that the W–N σ-bond has more s-character than the C–N bonds.

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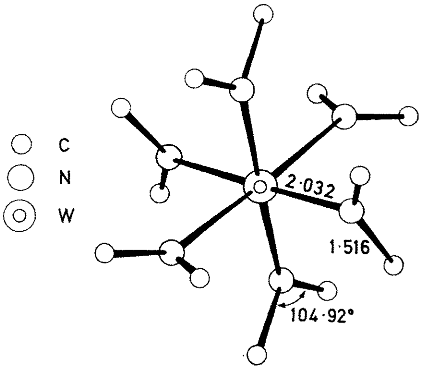

FIGURE

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[1] G. W. Fraser, M. Mercer, and R. D. Peacock, *J. Chem. Soc.* (*A*), **1967**, 1091.
[2] A. M. Noble and J. M. Winfield, *Chem. Comm.*, 1969, 5151.
[3] G. W. A. Fowles, in *Progr. Inorg. Chem.*, 1964, **6**, 1.
[4] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1969, 980.