Hexadecamethoxy- and Hexadecaethoxy-tetratungsten: Preparation and *X*-Ray Crystal and Molecular Structure of $W_4(OEt)_{16}$

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Summary In hydrocarbon solvents, $W_2(NMe_2)_6$ and the alcohols MeOH and EtOH react to give $W_4(OR)_{16}$ compounds; the ethoxide adopts a structure akin to that of $[Ti(OEt)_4]_4$, but with distortions due to M–M bonds which arise from the presence of the four tungsten d^2 ions.

$W_2(NMe_2)_6$[1] reacts with each of MeOH and EtOH (>> 6 equiv.) in hydrocarbon solvents at ambient temperatures to give dark solutions from which dark green or brown crystals of empirical formula $W(OR)_4$ are obtained (R = Me or Et) by concentrating the solution and by cooling to *ca.* −10 °C.† The compounds are diamagnetic, air-sensitive, and hydrocarbon-soluble. The ^1H n.m.r. spectrum of the methoxide recorded in $C_6D_5CD_3$ at 220 MHz showed eight lines of equal integral intensity in the temperature range −45 to +65 °C. The ^1H n.m.r. spectrum of the ethoxide under similar conditions showed too many overlapping signals to allow any informative interpretation.

Crystal data: $W_4(OEt)_{16}$ (at −164 °C)triclinic, space group $P\bar{1}$, $a = 12{\cdot}129(6)$, $b = 10{\cdot}985(6)$, $c = 9{\cdot}692(5)$ Å, $\alpha = 93{\cdot}28(3)$, $\beta = 108{\cdot}64(2)$, $\gamma = 105{\cdot}71(2)°$, $D_c = 2{\cdot}079$ g cm^{-3} ($Z = 1$). The structure was solved by Patterson and Fourier techniques using 5365 unique intensities collected on an automated diffractometer using Mo-K_α radiation for $6 \leqslant 2\theta \leqslant 55°$. Experimental procedures and data reduction formula have been previously described.[2] Full-matrix isotropic refinement has converged to $R(F) = 0{\cdot}060$. The molecule possesses a crystallographic centre of symmetry and no disorder is apparent.

The structure of the ethoxide is tetranuclear (Figure) and bears a striking resemblance to that found for the $[Ti(OR)_4]_4$ compounds where R = Et[3] and Me.[4] In this regard, the structure is that predicted by Bradley's[5] original structural theory for metal alkoxides; the tungsten(4+) ions achieve an octahedral co-ordination environment by the minimum degree of oligomerization which, for any compound of empirical formula $M(OR)_4$, is four.

The presence of the four third-row transition metal d^2 ions produces significant changes in the central M_4O_{16} unit; the tungsten atoms are all closer to each other than are the titanium (see Figure caption).

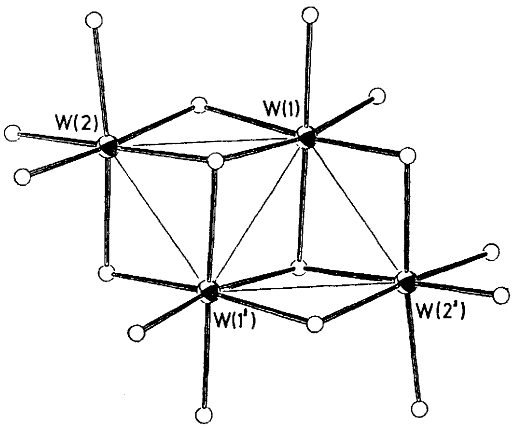

Figure. ORTEP view of the central W_4O_{16} unit of the $W_4(OEt)_{16}$ molecule emphasizing the WO_6 octahedra. The *trans* O–W–O angles all fall within the range 169—180°. Pertinent bond distances (with those for the analogous titanium complex in square brackets) are W(1)–W(2) = 2·645(2) [3·34], W(1)–W(1′) = 2·763(2) [3·42], W(1)–W(2′) = 2·936(2) [3·50], W–O(terminal) = 1·96 (average), W–O(μ_2) = 2·02 (average), and W–O(μ_3) = 2·18 (average) Å.

A consideration of the spacial properties of the four sets of t_{2g}-type d-orbitals available for M–M bonding in the $W_4(OEt)_{16}$ molecule suggests that delocalized rather than localized M–M bonding should occur. The W–W distances also indicate the existence of delocalized M–M bonds in the $W_4(OEt)_{16}$ molecule.

Two further points are worthy of comment. (1) The formation of these alkoxides involves oxidation of tungsten from the 3+ to the 4+ oxidation state. Intermediates analogous to $W_4(\mu\text{-}H)_2(OPr^i)_{14}$, previously found in the reaction between $W_2(NMe_2)_6$ and Pr^iOH (excess),[6,7] may be involved in the reactions involving MeOH and EtOH (but this remains to be established). (2) The ^1H n.m.r. spectra of $W_4(OMe)_{16}$ imply that the tetrameric structure is maintained in solution and, furthermore, that the presence of the W_4-cluster bonding electrons makes this unit rigid on the n.m.r. time-scale. This contrasts with the properties of $[Ti(OR)_4]_4$ compounds, which in solution dissociate to form trimers and are fluxional.[8]

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† Inert atmospheres and dry and oxygen-free solvents were used.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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