

The Molecular Structure of Tungsten Hexamethoxide, $W(OCH_3)_6$, by Gas Electron Diffraction

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In this note we report the molecular structure of $W(OMe)_6$, determined by gas electron diffraction (GED), as part of what we hope will be a series of studies of metal alkoxides.¹

$W(OMe)_6$ was synthesized by low temperature cocondensation of WF_6 and $Si(OMe)_4$ as described elsewhere.² The GED data were recorded on Balzers Eldigraph KDG-2 with a nozzle temperature of $105 \pm 10^\circ C$. Structure refinements were based on data from six plates obtained with a nozzle-to-plate distance of 50 cm (s from 13.75 to 130.000 nm^{-1} with increment $\Delta s = 1.25\text{ nm}^{-1}$) and seven plates obtained with a nozzle-to-plate distance of 25 cm (s from 25.00 to 250.00 nm^{-1} with $\Delta s = 2.50\text{ nm}^{-1}$). Optical densities were recorded on a Joyce–Loebl densiometer and processed by standard procedures.³ Atomic scattering factors were taken from Ref. 4.⁴ Calculated intensities included three-atom scattering. Backgrounds were drawn as eighth degree polynomials to the difference between total and calculated molecular intensities.

The infrared and Raman spectra (including polarization measurements) of $W(OMe)_6$ in the solid and liquid phase and in solution have been recorded and assigned.⁵ The spectra are compatible with a WO_6 core of octahedral

symmetry, but show that WOC angles are non-linear. Since no $W-O$ torsional modes were assigned, the spectra offer little information on the overall symmetry of the molecule.

The highest possible molecular symmetry is D_{3d} . One such model is shown in Fig. 1(A). (Another D_{3d} model, obtained from that in the figure by rotating each OMe group 180° about the $W-O$ bond, may be discarded out of hand since this would lead to prohibitively short $C \cdots C$ contacts.) In a D_{3d} model the *trans* MeOWOME fragments are in a planar *anti* conformation and are constrained to lie in symmetry planes. Rotation of each OMe group about the $W-O$ bonds by the same angle in such a way that the centre of symmetry (and the *anti* conformation of the *trans* MeOWOME fragments) is retained, yields the S_6 model shown in Fig. 1(B), while rotation under retention of the twofold symmetry axes yields the D_3 model shown in Fig. 1(C).

All our refinements were based on the assumption that the WO_6 core has octahedral and the methyl groups C_{3v} symmetry. Since torsional modes in the vibrational spectrum are unknown, shrinkage corrections were neglected.

The D_{3d} model is described by six independent para-

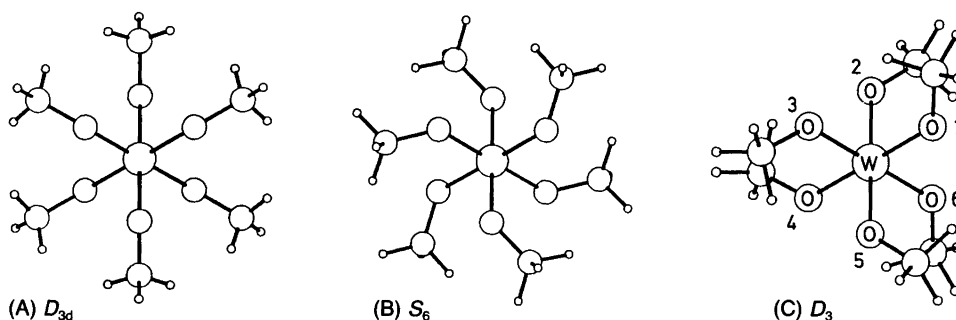


Fig. 1. Molecular models of $W(OMe)_6$ viewed down a C_3 symmetry axis; (A) D_{3d} model; (B) S_6 model; and (C) D_3 (best model). In all models $\angle WOC = 132^\circ$. Carbon atoms (Table 1) are numbered as the oxygen atom to which they are bonded.

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Table 1. Internuclear distances, vibrational amplitudes (l) and valence angles of $W(OMe)_6$. Molecular symmetry D_3 . Estimated standard deviations in parentheses in units of the last figure.

	r_a /pm	l /pm
Bond distances		
W–O	190.2(3)	4.8(3)
O–C	140.1(3)	5.3(3)
C–H	109.5(5)	5.8(7)
Non-bonded distances		
W...C	302.9(4)	8.1(8)
W...H	313(3)	38(10)
W...H	356(5)	14(7)
W...H	390(2)	11(5)
O...O	269.0(3)	12.5(4)
O...O	380.4(4)	[8.5] ^a
O(3)...C(1)	306(2)	17(3) ^b
O(2)...C(1)	330(2)	17(3) ^b
O(5)...C(1)	383(2)	17(3) ^b
O(6)...C(1)	403(2)	17(3) ^b
O(4)...C(1)	486(1)	12(1)
C(1)...C(2)	378(5)	44(7) ^c
C(1)...C(3)	412(3)	44(7) ^c
C(1)...C(6)	540(2)	44(7) ^c
C(1)...C(4)	572(1)	34(10)
Valence angles/°		
∠WOC	132.4(4)	
∠HCH	107(1)	
Dihedral angles/°		
φ[O(2)WO(1)C(1)]	61(2)	
φ(WOCH)	92(5)	
R^d %	3.70	

^aNot refined. ^{b,c}Groups of amplitudes assumed equal. ^d $R = [\sum w(l_{obs} - l_{calc})^2 / \sum w l_{obs}^2]^{1/2}$.

meters, for instance the W–O, O–C and C–H bond distances, the ∠WOC and ∠HCH valence angles and a methyl group tilt angle. Attempts to redefine the tilt angle did not succeed, and it was subsequently fixed at 3° (in such a way that W...H distances increased), which was the value that yielded the best fit.

The S_6 and D_3 models require two more parameters, viz. the dihedral angles $\varphi(W-O) = \varphi[O(2)WO(1)C(1)]$ and $\varphi(O-C) = \varphi(WOCH)$.

The best fit between observed and calculated intensities was obtained with the D_3 model: least-squares refinement of seven structure parameters and twelve r.m.s. vibrational amplitudes yielded the best values listed in Table 1. (The estimated standard deviations have been multiplied by a factor of 2.5 to compensate for data correlation and expanded to include an estimated scale uncertainty of 0.1%). Experimental and calculated radial distribution curves for the best model are shown in Fig. 2.

Refinements of the S_6 model yielded R -factors of ca. 6%, about 1.5 times higher than for the D_3 model, and failed to converge properly. Inspection of calculated radial distribution curves showed that the S_6 model fails to reproduce the very broad and low peak at $r = 570$ pm, which in the D_3 model is assigned to the largest C...C distance,

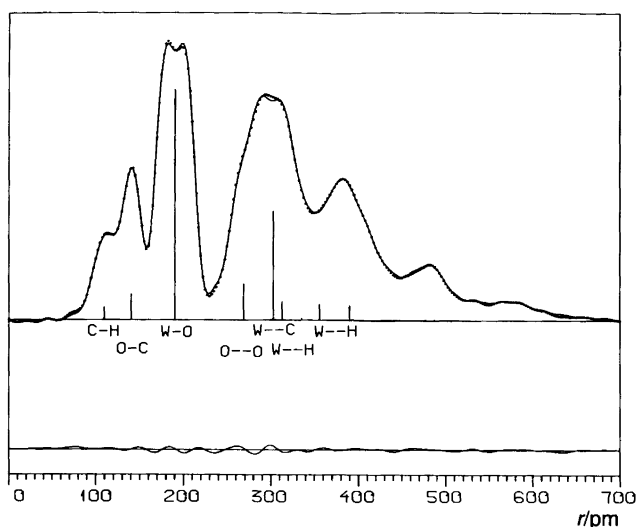


Fig. 2. Experimental (•) and calculated (—) radial distribution curves for $W(OMe)_6$. Below: Difference curve. Artificial damping constant $k = 20$ pm².

C(1)...C(5): in the S_6 model this distance is found at about 605 pm. The D_{3d} model could not be brought into satisfactory agreement with experimental data, and can be ruled out with confidence.

Discussion

Of the three models in Fig. 1 only the D_3 model is in satisfactory agreement with the data. The gas may have consisted exclusively of this conformer (and its enantiomer), but the presence of the S_6 or other less symmetric conformers has not been ruled out. It is not clear why the D_3 conformer should be particularly stable.

The dihedral angle $\varphi[O(2)WO(1)C(1)] = 61(2)^\circ$ is reasonably close to the value corresponding to perfect staggering of O–C bonds with respect to W–O bonds, $\varphi = 45^\circ$.

The wide angle, $\angle WOC = 132.5(5)^\circ$, may be due to tungsten–methyl and oxygen–methyl repulsions: $W...C = 304$ pm and $O(2/3)...C(1) = 330/307$ pm, or to W–O π -bonding.

As expected, the W–O bond distance falls between the W–F bond distance in WF_6 , 183.2(3) pm by GED,⁶ and the W–N bond distance in $W(NMe_2)_6$, 201.6(6) pm by XRD⁷ and 203.5(5) pm by GED.⁸

$W(NMe_2)_6$ has T_d symmetry in both the crystal⁷ and gas⁸ phase, with each N–C bond eclipsing a W–N bond. Since the O–C bonds in $W(OMe)_6$ are staggered with respect to the W–O bonds, we suggest that the conformation of the amide is determined by inter-ligand Me...Me repulsions.

Finally, we note that the W–O bond distance in $W(OMe)_6$ is 5–7 pm greater than found in two homoleptic $W(IV)$ aryloxides.⁹

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References

1. Thaler, E. G., Rypdal, K., Haaland, A. and Caulton, K. G. *Inorg. Chem.* 28 (1988) 2431.
2. Jacob, E. *Angew. Chem. Suppl.* (1982) 317.
3. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
4. Schäfer, L., Yates, A. C. and Bonham, R. A. *J. Chem. Phys.* 55 (1971) 3055.
5. Tatzel, G., Greune, M., Weidlein, J. and Jacob, E. *Z. Anorg. Allg. Chem.* 83 (1986) 533.
6. Seip, H. M. and Seip, R. *Acta Chem. Scand.* 20 (1966) 2698.
7. Galyer, A. and Wilkinson, G. *J. Chem. Soc., Dalton Trans.* (1976) 2235.
8. Hagen, K., Holwill, C. J., Rice, D. A. and Runnacles, J. D. *Acta Chem. Scand., Ser. A* 42 (1988) 578.
9. Listemann, M. L., Schrock, R. R., Dewan, J. C. and Kolodziej, R. *Inorg. Chem.* 27 (1988) 264.

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