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cis-Dichlorotetramethoxytungsten(VI)

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Abstract. $C_4H_{12}O_4Cl_2W$, triclinic, $P\bar{1}$, $a=7.243(4)$, $b=11.620(6)$, $c=6.680(4)$ Å, $\alpha=91.14(1)$, $\beta=110.83(1)$, $\gamma=84.70(1)^\circ$ measured at 250(3) K; $Z=2$, $D_c=2.387$, $D_m=2.3(1)$ g cm $^{-3}$ (suspension, with decomposition). Crystals were prepared from a 4:1 stoichiometric mixture of $CH_3OSi(CH_3)_3$ and WCl_6 . The average W–O distance is 1.84(4) Å, and the W–Cl distances are 2.43(1) Å and 2.41(2) Å.

Introduction. A prismatic crystal of dimensions 0.09 × 0.09 × 0.31 mm was sealed in a nitrogen-filled capillary. 955 reflections with $2\theta < 40^\circ$ were examined on a manually operated G. E. XRD-5 quarter-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and a scintillation detection system. Rapid scans showed 560 of these to have intensity observable above background. Data collection for these 560 reflections involved θ – 2θ scans of 3° at 2° min $^{-1}$ and 20 s stationary background counts at each end of the scan range. 538 reflections were independent with $I > 2\sigma(I)$ where $\sigma(I) = (S + 5.06B + 0.0016I^2)^{1/2}$ (S = scan counts, B = sum of background counts, and $I = S - 2.25B$) or $\sigma(I)$ = deviation of background readings from mean background if the backgrounds differed by more than twice $\sigma(I)$ as calculated by the first equation. Crystal decay, Lorentz-polarization, and absorption corrections were applied [$\mu(\text{Mo } K\alpha) = 121$ cm $^{-1}$]. Neutral-atom scattering fac-

tors (International Tables for X-ray Crystallography, 1974) were used for all atoms. Anomalous dispersion corrections (Cromer, 1965) were employed for chlorine and tungsten. Full-matrix least-squares refinement resulted in a conventional residual of 0.070 and a weighted residual of 0.087 for the 538 reflections employed in the structure determination. Final atomic parameters are given in Table 1. Selected bond lengths and angles are collected in Table 2. The standard deviation of an observation of unit weight was 1.53, and the final difference Fourier map showed only one peak greater than 15% of a carbon peak. This was 50% of a carbon but was less than 1 Å from the tungsten and was not chemically interpretable.*

Table 2. Bond lengths and angles, with e.s.d.'s in parentheses

W—Cl(1)	2.43 (1) Å	Cl(1)–W–Cl(2)	85.9 (6)°
W—Cl(2)	2.41 (2)	Cl(1)–W–O(1)	175 (1)
W—O(1)	1.84 (4)	Cl(1)–W–O(2)	89 (1)
W—O(2)	1.87 (4)	Cl(1)–W–O(3)	85 (1)
W—O(3)	1.84 (3)	Cl(1)–W–O(4)	86 (1)
W—O(4)	1.82 (3)	Cl(2)–W–O(1)	89 (1)
O(1)–C(1)	1.47 (6)	Cl(2)–W–O(2)	174 (1)
O(2)–C(2)	1.32 (6)	Cl(2)–W–O(3)	87 (1)
O(3)–C(3)	1.47 (6)	Cl(2)–W–O(4)	83 (1)
O(4)–C(4)	1.49 (6)	O(1)–W–O(2)	96 (2)
		O(1)–W–O(3)	96 (1)
		O(1)–W–O(4)	92 (1)
W—O(1)–C(1)	140 (3)°	O(2)–W–O(3)	95 (2)
W—O(2)–C(2)	131 (3)	O(2)–W–O(4)	94 (2)
W—O(3)–C(3)	143 (3)	O(3)–W–O(4)	167 (1)
W—O(4)–C(4)	137 (3)		

Table 1. Positional ($\times 10^4$) and thermal parameters, e.s.d.'s in parentheses

	x	y	z	$B(\text{Å}^2)$
W	–1114 (4)	2292 (2)	2452 (4)	
Cl(1)	–3792 (22)	1746 (14)	–720 (23)	
Cl(2)	–3642 (25)	3442 (14)	3358 (25)	
O(1)	778 (52)	2803 (32)	4880 (56)	4.2 (8)
O(2)	674 (55)	1410 (33)	1477 (61)	4.9 (9)
O(3)	–1707 (48)	1069 (29)	3748 (53)	3.8 (8)
O(4)	–1149 (43)	3580 (26)	919 (47)	2.6 (7)
C(1)	2156 (93)	3704 (54)	5565 (97)	5.6 (15)
C(2)	1131 (66)	1526 (39)	–242 (77)	2.3 (10)
C(3)	–3338 (78)	560 (47)	4121 (88)	4.1 (12)
C(4)	–2660 (76)	4373 (46)	–706 (85)	3.7 (12)

Discussion. N.m.r. studies of alkoxytungsten(VI) halides have suggested substantial W–O π bonding (McFarlane, Noble & Winfield, 1971; Brinckman, Johannesen & Handy, 1972) similar to that postulated for the W–N framework of $[(CH_3)_2N]_6W$ (Bradley,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30653 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (cont.)

Anisotropic thermal parameters ($\times 10^4$) in the form: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	163 (6)	71 (2)	188 (9)	–21 (2)	55 (5)	11 (3)
Cl(1)	251 (44)	117 (19)	236 (57)	–90 (23)	–110 (39)	–2 (25)
Cl(2)	376 (53)	110 (19)	355 (63)	41 (24)	235 (48)	–13 (26)

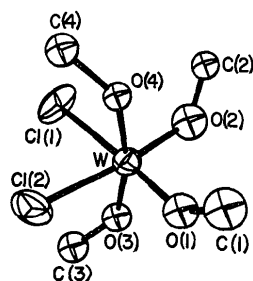


Fig. 1. Molecular structure and atom labeling for *cis*-dichlorotetramethoxytungsten(VI).

Chisholm, Heath & Hursthouse, 1969). The present work was undertaken to determine if structural features consistent with *d-p* π bonding are present in the alkoxides. Further, it was of interest to determine if these tungsten alkoxides would remain monomeric in the solid state, or expand the coordination number of tungsten and thus form polymeric species as are commonly found for titanium alkoxides (Bradley & Holloway, 1969). The structure of $(\text{CH}_3\text{O})_4\text{WCl}_2$ is shown in Fig. 1, and is monomeric with the same *cis* configuration as in solution (Handy, Sharp & Brinckman, 1972). The molecule has an approximate mirror plane containing W, O(3), O(4), C(3), and C(4), but this near mirror symmetry is not maintained in the crystal lattice. The molecular packing exhibits no unusual features. The lack of experimental values for hydrogen positions prevents a complete analysis, but within this restriction all intermolecular non-bonding contacts are normal van der Waals distances.

The standard deviations of carbon and oxygen parameters are quite large, reflecting the dominance of tungsten in the scattering. Consequently, the bond lengths and angles associated with these atoms also are rather imprecise. If one looks at methoxy groups 1, 3, and 4, the crystallographic standard deviations of the distances and angles in Table 2 might appear to be overestimates of the actual uncertainties. Methoxy 2, however, is clearly distinct from the others, with a carbon-oxygen distance which is unreasonably short and the smallest W-O-C angle. C(2) is responsible for these anomalous values. Its positional parameters and temperature factor are assumed to be artifacts of the data set. Indeed, from the structural data alone, methoxy group 2 might as easily be described as a very unusual carbonyl group. The crystal taken for study, however, was selected from a sample whose preparation and properties, including ^1H n.m.r. spectrum, were identical with material prepared and fully characterized earlier as $(\text{CH}_3\text{O})_4\text{WCl}_2$ (Handy, Sharp & Brinckman, 1972).

While it is not possible to determine the relative influences of electronic, intramolecular steric, and packing forces, especially without hydrogen positions,

the large angles at oxygen are consistent with substantial π -bonding by oxygen. That these angles are not entirely dominated by steric considerations is suggested by the fact that the shortest inter- or intramolecular non-bonding contacts of C(3) and C(4) are with the chlorines. If a smaller angle at oxygen were strongly favored, it could be attained by opening the O(3)-W-O(4) angle from the observed 167° toward 180° while maintaining the C...Cl contacts. The average W-O distance is $1.84(4)$ Å, which is only slightly longer than the value of 1.79 Å in WO_4^{2-} (Zachariassen & Plettinger, 1961) and substantially shorter than the 2.20 Å W-O distance for the bridging oxygen in WOCl_4 (Hess & Hartung, 1966). If this short W-O distance is taken to be evidence of W-O π -bonding, then the W-Cl bonds should be lengthened since oxygen is a better π -donor than chlorine. The W-Cl bond lengths of $2.43(2)$ and $2.41(2)$ Å are much longer than the 2.26 Å distance in WCl_6 (Ewems & Lister, 1938), and are more nearly comparable with the average equatorial W-Cl distance of 2.40 Å in the heptacoordinate diarsine adduct $\text{C}_{10}\text{H}_{16}\text{As}_2\text{WOCl}_4$ (Drew & Mandyczewsky, 1970), in which the coordination geometry would be expected to reduce W-Cl π -bonding, or to the bridging W-Cl distance of 2.44 Å in $[\text{WCl}_4\text{CCl}_3\text{Cl}_2\text{N}]_2$ (Drew, Fowles, Rice & Rolfe, 1971).

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