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PREPARATION AND STRUCTURAL INVESTIGATIONS OF  
FLUORINATED TUNGSTEN(VI) ALKOXIDES

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Dedicated to Professor K. Weissermel on the occasion of  
his 65th birthday.

SUMMARY

The preparation and characterization of compounds of composition  $\text{Cl}_{6-x}\text{W}(\text{OCH}_2\text{CF}_3)_x$  ( $x = 1-6$ ) and  $\text{X}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$  ( $\text{X} = \text{Cl}, \text{F}$ ) together with  $^{19}\text{F}$  NMR spectra are reported. An X-ray structure analysis of  $\text{Cl}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$  shows a W-O-C angle of  $173.6^\circ$ , which is unusually large for metal alkoxides, and a short W-O distance of 181.9 pm. A discussion on structural aspects and a comparison with related tungsten-nitrogen compounds are presented.  $\text{Cl}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$  is monoclinic, space group  $\text{C2/m}$ , with  $a = 820.3(2)$ ,  $b = 1059.2(2)$ ,  $c = 1071.6(2)$  pm,  $\beta = 99.72(2)^\circ$ ,  $Z = 2$  and was refined to  $R = 0.031$  for 848 observed reflections.

## INTRODUCTION

The present interest in transition metal aryloxy and alkoxide chemistry [1] especially that of tungsten and molybdenum, is documented in several recent publications by Chisholm [2] and others [3]

Metal oxides provide the most versatile class of heterogeneous catalysts. Studies of the hydrocarbon soluble metal alkoxides, which can serve as model compounds, might lead to a new class of homogeneous catalysts [4]. The reactions of  $W_2(O^tBu)_6$  with alkynes provide a versatile route to Schrock-type tungsten alkylidyne complexes [5,6]. Furthermore, variation of the alkoxide moieties in compounds of the type  $(RO)_3W=CR$  allows fine tuning of the electronic properties of the metal atom [7]. The generation of a reasonably electrophilic metal center together with sufficient steric crowding proves essential for metathesis activity [8]. The favorable effect of the  $\pi$ -donating ability of oxygen for metathesis reactions was also shown theoretically [9].

$\pi$ -donation is associated with a change in the oxygen atom hybridization, which leads to large M-O-C angles. In the extreme case oxygen could even act as a four-electron donor with an angle of  $180^\circ$ . However, such a situation is rare as suitable orbitals at the metal are normally lacking. Angles very close to linearity have been reported for oxygen bridging two metal centers as in  $Cl_5TaOTaCl_5$  [2-10]. The structural consequences of  $\pi$ -donation with regard to aryloxy and alkoxide ligands were discussed by Rothwell and Huffmann [11].

Although a large number of dinuclear tungsten alkoxides have been synthesized, information concerning the W(VI) alkoxides of the general type  $\text{Cl}_x\text{W}(\text{OR})_{6-x}$  is scarce. To our knowledge only the series  $\text{Cl}_x\text{W}(\text{OCH}_3)_{6-x}$  was fully characterized [12]; this is probably due to the ease of reduction of  $\text{WCl}_6$  [13].

In our recent publications we have described new synthetic routes to metallacyclic compounds by reaction of suitable precursors with  $\text{WCl}_6$  [14,15]. In order to extend the spectrum of reactivity we are interested in substituting two or three chlorine atoms by reasonably electronegative substituents, which through their  $\pi$ -donating ability also stabilize the highest oxidation state of tungsten. This should make possible reactions with hard nucleophiles. For this purpose we investigated the reactions of  $\text{WCl}_6$  with two easily available fluorinated alcohols.

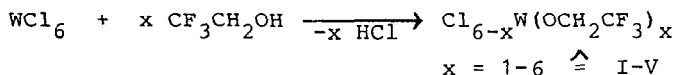
A discussion of the crystal structure of a tungsten(VI) alkoxide featuring a M-O-C angle close to linearity is included.

#### SYNTHESES AND PROPERTIES

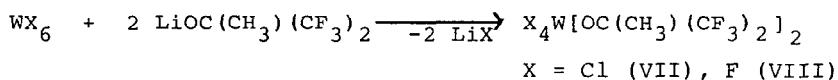
Contrary to the preparation of W(VI) aryloxides, which can be made easily from the corresponding phenols and  $\text{WCl}_6$ , analogous reactions of aliphatic alcohols (like ethanol) with  $\text{WCl}_6$  lead to reduced tungsten species [13]. This reduction can be avoided by using the silylether instead.

The preparation of  $\text{W}(\text{OMe})_6$  [12] and of the much more easily reducible U(VI) and Mo(VI) hexamethoxides is possible by reacting the corresponding hexafluorides with  $\text{CH}_3\text{OSiMe}_3$  [16].

This technique was also applied for the preparation of  $U(OCH_2CF_3)_6$  [17,18]. We report here the synthesis of the whole series of compounds of composition  $Cl_{6-x}W(OCH_2CF_3)_x$ .



These compounds can be prepared easily by reacting trifluoroethanol with  $WCl_6$ , although in case of V forcing conditions are required. VI can only be prepared by reacting IV or V with  $NaOCH_2CF_3$ . I to V are hydrolytically very unstable liquids. The colors change from red to yellow with increasing alkoxide substitution. Only the mono- and disubstituted alkoxides are unstable and could not be isolated in pure state. Contrary to the behaviour of ethanol no reduction occurs with trifluoroethanol. This can be explained by two arguments: 1)  $CF_3CH_2OH$  is less susceptible to chlorination. 2) The high acidity of  $CF_3CH_2OH$  ( $pK_A=12.4$ ;  $CH_3CH_2OH$ :  $pK_A=15.9$ ) [19] increases the stability of the conjugate acid. Reactions of  $WCl_6$  or  $WF_6$  with  $LiOC(CH_3)(CF_3)_2$  yield exclusively the disubstituted products



The colorless liquid VIII is very sensitive to moisture, contrary to red VII, which is remarkably stable. Crystals of VII can be stored in air for days without noticeable change.

<sup>19</sup>F NMR spectra

All <sup>19</sup>F NMR spectra recorded, except that of VIII, were of first order with high multiplicities due to 'through-space' fluorine coupling. Because of small differences in shifts (relative to CFCl<sub>3</sub>) the shift data given were determined from mixtures of the compounds I to VI and are also listed relative to VI.

TABLE I

	$\delta$ (CFCl <sub>3</sub> )	$\delta$ (VI)
I	-71.0 (s)	5.0
II	-73.4 (s)	2.6
	-73.4 (s)	2.6
III	-73.0 (m); -73.5 (q)	3.0; 2.5
IV	-74.4 (s)	1.6
	-74.2 (m); -74.5 (m)	1.8; 1.5
V	-74.8 (m); -75.3 (q)	1.2; 0.7
VI	-76.0 (s)	0

multiplicities given, derived from proton decoupled spectra; m refers to only partially resolved first order signals.

In the series of compounds I to VI there is a general trend leading to a high field shift of the -CF<sub>3</sub>-signals with higher substitution. In the case of compound II cis and trans isomers can be observed in a ratio of 3:1. We cannot make a definite assignment, but we think that the trans isomer is preferentially formed. For III only the mer-isomer exists, which was also observed for the methoxy analogue[12]. Compound IV consists of both trans (Cl<sub>2</sub>) and cis (Cl<sub>2</sub>) isomers in a ratio of 15:85.

The coupling constants do not vary much within the series:

$^3J(^1\text{H}-^{19}\text{F})$ : 8 Hz;  $^4J(^{183}\text{W}-^{19}\text{F})$ : 1-1.2 Hz;  $J(^{19}\text{F}-^{19}\text{F})$ : 0.7 Hz;

$^3J(^{183}\text{W}-^1\text{H})$ : 3.2 Hz.

No isomers could be detected in the  $^{19}\text{F}$  NMR spectrum of VII; therefore, the trans isomer (see below) is formed exclusively. In the case of VIII the structure can be assigned by  $^{19}\text{F}$  NMR and the sole existence of the cis-isomer was detected. This tendency of fluorine to form cis-isomers was noted before, when fluorine was found to exert a considerable trans-effect [12,20,21].

#### Crystal structure of $\text{Cl}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$ (VII)

In the crystal VII shows exact  $\text{C}_{2h}$ -symmetry. In addition, the six ligand atoms around tungsten are arranged at  $90^\circ$  with respect to each other forming a somewhat compressed octahedron (Fig. 1). Relevant bond lengths and angles are : W-Cl(1) 229.5(2), W-Cl(2) 229.9(3), W-O 181.9(6) pm, W-O-C(1)  $173.6(7)^\circ$ .

The most interesting structural feature in early transition metal alkyl- and aryl oxides is the large angle at oxygen indicating extensive M-O multiple bond character. As a consequence of the efficient delocalization of electron density into empty metal d-orbitals, angles approach  $180^\circ$  in the case of oxygen bridging two metal centers [10]. In dimolybdenum (III) metal centers, metal-oxygen distances of about 190 pm have been said to incorporate multiple character [22]. In accord with this the tungsten-oxygen distance of 181.9 pm observed for VII must involve strong multiple bond character. This distance is certainly amongst the shortest

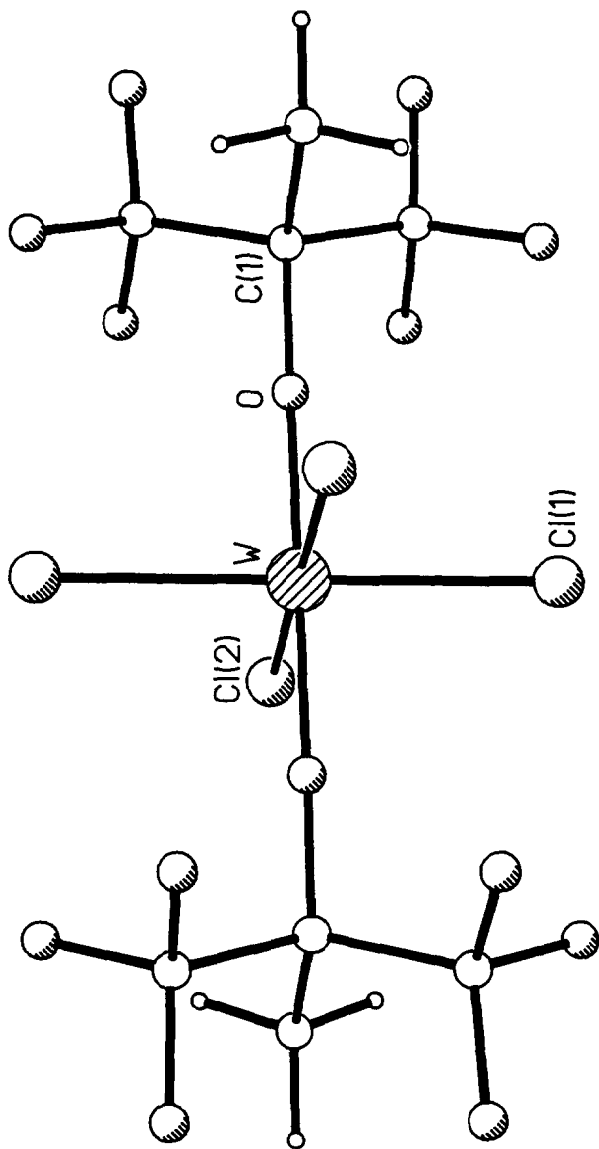


Fig. 1. Structural representation of VII.

W-O 'single' bonds yet reported [22b] and is accompanied by a large W-O-C angle. However caution is advisable in comparing the highly electron-deficient tungsten atom in compound VII with a dinuclear triple bonded species in a different hybridization state; recent theoretical calculations have indicated that the hybridization state of transition metals influences their bond lengths [23]. As very few structural data on comparable tungsten alkoxides are available [24], we offer a comparison with related nitrogen bonded species. In the case of nitrogen a formal single bond also gains considerable multiple bond character when an electron-deficient transition metal is involved.

The relative length of the bonds from a given element to oxygen and nitrogen can be considered in terms of the covalent radii of N and O [25]. A good correlation with the difference in covalent radii was also observed for transition metal oxo and organoimido bonds, where the latter were found to be approximately 5 pm longer (but with variation from 2 to 9 pm) [26]. For an assessment of the tungsten-oxygen bond order representative tungsten-nitrogen distances are listed [27].

$W \equiv N-R$	169-175 pm	$W=N=R$	182 pm	$W=NR_2$	192-203 pm
	[28a]		[28]		[28]

It has been stated that even though alkoxide ligands seem to be better  $\pi$ -donors than aryloxy ligands, the M-O-C angle widening effect is usually more pronounced in the case of the latter [24]. This is attributed to the fact that the phenyl substituents in a coplanar arrangement can take part in delocalization [29]. Similarly



comparison with the W-N-P angle in related amido species might prove useful :

$\text{cis}(\text{Me}_3\text{PN})_2\text{WF}_4$	$139.1^\circ$	[28b]
$\text{cis}(\text{O}_3\text{PN})_2\text{WF}_4$	$157.2^\circ$	[28b]
$(\text{O}_3\text{PNTaCl}_4)_2$	$176.8^\circ$	[30]

The larger angle in  $(\text{O}_3\text{PN})_2\text{WF}_4$  than in  $(\text{Me}_3\text{PN})_2\text{WF}_4$  can be rationalized in the same way as for the aryloxy derivatives.

The cis-configuration certainly leads to an angle decrease at nitrogen, possibly due to steric interaction; the monosubstituted tantalum compound has a much larger angle. Seen exclusively from a steric point of view, the  $\text{O}_3\text{PN}$  and the  $\text{Me}_3\text{PN}$ -group should be comparable in size to the tert. hexafluorobutoxylate residue. Therefore we think that steric effects play a minor role in the formation of the cis-configuration in  $(\text{O}_3\text{PN})_2\text{WF}_4$ ,  $(\text{Me}_3\text{PN})_2\text{WF}_4$  and VIII, but not in VII.

In the cis-configuration, three tungsten d-orbitals ( $d_{xz}$ ,  $d_{yz}$  and  $d_{xy}$ ) are available for  $\pi$ -bonding, in the trans-configuration only two ( $d_{xz}$  and  $d_{yz}$ ). Thus stronger  $\pi$ -back-donation (e.g. when the other ligands are more electron-withdrawing, i.e. F rather than Cl) will favor cis, whereas steric factors favor trans. Ligands of the type  $\text{R}_3\text{PN}$ - should be good  $\pi$ -donors (because of the important resonance extreme  $\text{R}_3\text{P}^+-\text{N}^-$ ) and so particularly favor cis. Because the  $\pi$ -bonding situation is unsymmetrical for cis ligands (it is weaker in the xy plane because the  $d_{xy}$  orbital is shared) the angle at N or O may deviate more from  $180^\circ$  for cis complexes, as

expected also from steric considerations. These considerations account for the cis tendencies of N-ligands [31] and compounds where the other substituents are F (e.g. VIII), the rough balance between cis and trans observed here for II-IV, and the trans structure of VII, in which the ligand subtends the largest solid angle.

### Concluding remarks

The short W-O bond length and wide oxygen valence angle in  $\text{Cl}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$  are consistent with strong  $\pi$ -back-bonding from oxygen to tungsten. In an attempt to gain further insight into the combined electronic and steric effects of the alkoxy substituent around the transition metal atom, we are currently investigating the reactions of further transition metal halides with sterically and electronically interesting alkoxy nucleophiles. However the n.m.r. data for  $\text{Cl}_{6-x}\text{W}(\text{OCH}_2\text{CF}_3)_x$  and literature data for tungsten complexes with nitrogen ligands indicate that the relative stabilities of cis and trans isomers are determined by a nice balance of  $\pi$ -bonding and steric effects.

### EXPERIMENTAL

All experiments were conducted in carefully dried solvents under an atmosphere of dry nitrogen.

$\text{LiOC}(\text{CH}_3)(\text{CF}_3)_2$  was prepared by condensing hexafluoroacetone onto methylolithium in ether at  $-78^\circ\text{C}$ .

$^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectra were recorded on a Bruker WP 80 SY relative to TMS or  $\text{CFCl}_3$  ( $^{19}\text{F}$  multiplicities given were derived from proton

decoupled spectra). Mass spectra : Varian MAT CH5 (70 eV); Infra-red spectra : Perkin Elmer 180, Nujol mulls between KBr plates.

$\text{Cl}_5\text{W}(\text{OCH}_2\text{CF}_3)_1$  (I) and  $\text{Cl}_4\text{W}(\text{OCH}_2\text{CF}_3)_2$  (II) : To a stirred slurry of  $\text{WCl}_6$  (5.45 g, 13.7 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_3\text{CH}_2\text{OH}$  (1.37 g, 13.7 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$  was added dropwise over a period of 2 h. Stirring was continued for 24 h. The solvent was stripped off in vacuo and the oily residue distilled (0.01 Torr/ 50 °C) to give an unseparable red mixture of I and II.  $^{19}\text{F}$ -NMR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ ) : I  $\delta$  -71.0 (s); II  $\delta$  -73.4 (s).

$\text{Cl}_3\text{W}(\text{OCH}_2\text{CF}_3)_3$  (III) : To a stirred slurry of  $\text{WCl}_6$  (8.3 g, 20.9 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$ ,  $\text{CF}_3\text{CH}_2\text{OH}$  (20.9 g, 209 mmol) in 20 ml  $\text{CH}_2\text{Cl}_2$  was added dropwise over a period of 2 h. Stirring was continued for 20 h. The solvent and excess  $\text{CF}_3\text{CH}_2\text{OH}$  were removed in vacuo and the oily residue was purified by distillation (0.01 Torr/ 56-58 °C) to yield 10.2 g (83 %) of red-orange liquid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) :  $\delta$  5.58 (q, cis), 5.78 (q, trans);  $^{19}\text{F}$ -NMR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ ) :  $\delta$  -73.0 (m, trans to Cl), -73.5 (q, trans to OR). EI-MS (m/z) : 550 (M-Cl). IR : 2960 s, 2900 s, 1435 m, 1395 m, 1280 sst, 1170 sst, 1100 sst, 945 st, 830 st, 715 st, 620 m, 525 m, 320 st  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_6\text{H}_6\text{Cl}_3\text{F}_9\text{O}_3\text{W}$  : C, 12.27; H, 1.03; Cl, 18.11. Found : C, 12.9; H, 1.2; Cl, 17.9.

$\text{Cl}_2\text{W}(\text{OCH}_2\text{CF}_3)_4$  (IV) : general procedures as described above.  $\text{WCl}_6$  (5.0 g, 12.6 mmol),  $\text{CF}_3\text{CH}_2\text{OH}$  (12.6 g, 126 mmol) refluxed in  $\text{CH}_2\text{Cl}_2$  for 48 h. distillation (0.01 Torr/45-48 °C) yielded 5.3 g (64 %) of an orange liquid.  $^{19}\text{F}$ -NMR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ ) :  $\delta$  -74.4

(s, trans isomer); -74.5 (m, cis isomer), -74.2 (m, cis isomer).  
 EI-MS (m/z) : 615 (M-Cl). IR : similar to III. Anal. Calcd. for  $C_8H_8Cl_2F_{12}O_4W$  : Cl, 10.89. Found : Cl, 10.7.

$ClW(OCH_2CF_3)_5$  (V) : general procedures as described above.

$WCl_6$  (7.2 g, 18.1 mmol),  $CF_3CH_2OH$  (18.1 g, 181 mmol) refluxed in toluene for 48 h, distillation (0.01 Torr/48-52 °C) yielded 9.7 g (75 %) of a dark yellow oily liquid.  $^{19}F$ -NMR ( $CH_2Cl_2$ ,  $CDCl_3$ ) :  $\delta$  -74.8 (m, trans), -75.3 (q, cis). EI-MS (m/z) : 679 (M-Cl). IR : similar to III. Anal. Calcd. for  $C_{10}H_{10}ClF_{15}O_5W$  : Cl, 4.96. Found : Cl, 4.2.

$W(OCH_2CF_3)_6$  (VI) : To  $NaOCH_2CF_3$  (0.9 g, 7.4 mmol) in 50 ml toluene  $Cl_2W(OCH_2CF_3)_4$  (IV) (2.4 g, 3.7 mmol) was added. The solvent was removed in vacuo and the residue sublimed (0.01 Torr/50 °C) to give 1.7 g (60 %) of a yellow solid with m.p. 82 °C.  $^{19}F$ -NMR ( $CH_2Cl_2$ ,  $CDCl_3$ ) :  $\delta$  -76.0 (s). EI-MS (m/z) : 679 (M- $OCH_2CF_3$ ). IR : similar to III, but without  $\nu$ -W-Cl (320  $cm^{-1}$ ). Anal. Calcd. for  $C_{12}H_{12}F_{18}O_6W$  : C, 18.52; H, 1.55. Found : C, 17.6; H, 2.1.

$Cl_4W[OC(CH_3)(CF_3)_2]_2$  (VII) : A mixture of  $LiOC(CH_3)(CF_3)_2$  (0.92 g, 5 mmol) and  $WCl_6$  (0.99 g, 2.5 mmol) in 20 ml toluene was stirred at room temperature for 2 h. The solvent was removed in vacuo. To the remaining solid 15 ml hexane was added and the suspension filtered off. Evaporation of the solvent, sublimation (0.01 Torr/70 °C) and recrystallisation from hexane gave 1.0 g (59 %) of red crystals m.p. 121 °C. Single crystals suitable for X-ray analysis were obtained by slow cooling of a saturated solution in hexane.

$^1\text{H-NMR}$  ( $\text{C}_6\text{O}_6$ ) :  $\delta$  1.63 (m,  $^4J_{\text{HF}} = 1.1$  Hz);  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6$ ) :  
 $\delta$  -73.4 (q). EI-MS (m/z) : 653 (M-Cl). IR : 1390 st, 1300 st,  
 1230 sst, 1170 st, 1140 st, 1120 st, 1090 sst, 1020 st, 880 m,  
 795 m, 705 st, 620 w, 540 w, 510 w, 330 sst  $\text{cm}^{-1}$ . Anal. Calcd. for  
 $\text{C}_8\text{H}_6\text{Cl}_4\text{F}_{12}\text{O}_2\text{W}$  : C, 13.94; H, 0.87. Found : C, 13.5; H, 1.0.

$\text{F}_4\text{W}[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$  (VIII) : At  $-78^\circ\text{C}$   $\text{WF}_6$  (1.35 g, 4.5 mmol)  
 was condensed onto  $\text{LiOC}(\text{CH}_3)(\text{CF}_3)_2$  (1.7 g, 9.0 mmol) in 25 ml  
 ether. The solution was warmed to room temperature and stirred for  
 2 h. The solvent was removed in vacuo and the remaining oil  
 distilled (0.1 Torr/ $100^\circ\text{C}$ ) to give a colorless liquid 0.9 g  
 (32 %).  $^{19}\text{F-NMR}$  ( $\text{C}_6\text{D}_6$ ) :  $\delta$  116.1 (m), -76.4 (p;  $J_{\text{FF}} = 1.4$  Hz).  
 IR : 1455 w, 1395 w, 1305 m, 1230 st, 1170 m, 1120 m, 1095 st,  
 1015 m, 880 w, 800 w, 740 w, 710 m, 690 m, 660 m, 640 w, 515 w  
 $\text{cm}^{-1}$ .

### Crystal Structure Analysis of VII

Monoclinic, space group  $\text{C2/m}$ ,  $a = 820.3(2)$ ,  $b = 1059.2(2)$ ,  $c =$   
 $1071.6(2)$  pm,  $\beta = 99.72(2)^\circ$ ,  $V = 0.918 \text{ nm}^3$ ,  $Z = 2$ ,  $D_c = 2.489$   
 $\text{g}\cdot\text{cm}^{-3}$ ,  $F(000) = 640$ ,  $\mu$  (Mo- $\text{K}\alpha$ ) =  $7.13 \text{ mm}^{-1}$ ; Stoe-Siemens four-  
 circle diffractometer, crystal size  $0.5 \times 0.4 \times 0.2 \text{ mm}^3$ , 848 unique  
 reflections ( $2\theta_{\text{max}} = 50^\circ$ ), all with  $|F| > 4\sigma(F)$ , empirical absorp-  
 tion correction ( $R_{\text{int}} = 0.026$  for 400 azimuthal scans); structure  
 solved by Fourier techniques, H atoms located by difference  
 electron-density synthesis, full-matrix refinement (on F) of  
 73 parameters, all non-hydrogen atoms anisotropic, riding model  
 employed for H atoms with  $r(\text{C-H}) = 96$  pm and  $U(\text{H}) = 1.5 \cdot U_{\text{eq}}(\text{C})$ ,

weighting scheme  $w^{-1} = \sigma^2(F) + 0.0006 \cdot F^2$ , final  $R = 0.031$  ( $wR = 0.040$ ), all calculations performed with SHELXTL. Atomic parameters are given in Table II. Tables of bond lengths and angles, anisotropic thermal parameters, hydrogen coordinates and structure factors have been deposited with the Publishers as Supplementary Material.

TABLE II

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{pm}^2 \times 10^{-1}$ ) for VII\*

	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
W	0	0	5000	37(1)
Cl(1)	0	2167(2)	5000	71(1)
Cl(2)	-2371(3)	0	5878(3)	71(1)
O	1244(7)	0	6575(6)	46(2)
C(1)	2359(13)	0	7721(10)	58(3)
C(2)	4172(18)	0	7447(17)	149(12)
C(3)	2100(21)	1196(11)	8413(12)	118(6)
F(31)	2383(15)	2177(7)	7778(9)	170(5)
F(32)	478(13)	1251(11)	8586(9)	172(5)
F(33)	3061(16)	1250(8)	9525(8)	179(5)

\* Equivalent isotropic  $\underline{U}$  defined as one third of the trace of the orthogonalised  $\underline{U}_{ij}$  tensor.

## ACKNOWLEDGEMENT

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