Diglyme ($C_6H_{14}O_3$) Complexes of Molybdenum and Tungsten: Crystal Structures of $[MO_2Cl_2(C_6H_{14}O_3)]$ (M = Mo or W) *

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The diglyme complexes $[MO_2Cl_2(C_6H_{14}O_3)]$ (M = Mo or W) have been prepared by reaction of MoO_2Cl_2 or $WOCl_4$–$Me_3SiOSiMe_3$ with diglyme. X-Ray diffraction studies have shown that in these complexes the metals exhibit distorted-octahedral geometry, with *cis*-dioxo and *trans*-chloro ligands. Two ether oxygen atoms are co-ordinated *trans* to the oxo ligands leaving one terminal oxygen atom of the ligand uncomplexed. Assignments of metal–ligand stretching vibrations as observed by IR and Raman spectroscopy are presented. Variable temperature $^{13}C-\{^1H\}$ NMR spectra in CD_2Cl_2 solution indicate rapid intramolecular exchange between free and bound terminal oxygen atoms.

Oxo complexes of molybdenum and tungsten are important as catalysts for the olefin metathesis reaction.[1] Molybdenum oxo complexes are also active catalysts for the oxidation of organic substances.[2] In such catalysts the metal oxide is deposited on an oxidic carrier, *e.g.*, Al_2O_3, SiO_2 or Bi_2O_3, the metal thus being surrounded by a co-ordination sphere of oxygen atoms. Although such catalysts are frequently applied in industrial processes, fundamental knowledge on the exact nature of these systems is scarce and relevant homogeneous models are still lacking. Pinacols have been used[3] as models for the surface silanol groups in the study of homogeneous tungsten imido complexes, of relevance as catalysts in the ammoxidation reaction. Molecular complexes, MO_3L_3, with L_3 = tridentate nitrogen donors such as diethylenetriamine,[4-6] 1,4,7-triazacyclononane or 1,4,7-trimethyl-1,4,7-triazacyclononane,[7] have facial arrangement of the oxo ligands and can therefore be regarded as models for surface MO_3 species. More relevant models for MO_3 adsorbed on an oxidic surface could be envisaged with tridentate neutral oxygen-donor ligands in place of nitrogen donors. The facile halogen–oxygen exchange in the reaction of Me_3Si–O–$SiMe_3$[8] or Bu^t–O–$SiMe_3$[9] with high-valent metal halides is a possible entry into ligated trioxo complexes. In the presence of tridentate ethers this reaction could give the desired type of complex. Reasoning along these lines provided the impetus for the present study in which two precursors to such complexes, *viz.* $[MoO_2Cl_2(C_6H_{14}O_3)]$ and $[WO_2Cl_2(C_6H_{14}O_3)]$ [$C_6H_{14}O_3$ = 2,5,8 trioxanonane-(diglyme)] are presented.

A further motive for our interest in diglyme complexes of molybdenum and tungsten stems from the exchange kinetics of dme (dme = 1,2-dimethoxyethane) in $[MO_2Cl_2(dme)]$ (M = Mo or W) which we have investigated by NMR line-broadening methods.[10] These studies revealed an exchange process not straightforwardly interpretable in terms of a pure associative or dissociative mechanism. It was therefore felt that an intramolecular process using diglyme instead of dme might be helpful in understanding the exchange process. The diglyme complexes presented here were therefore characterized by crystal structure determinations and by NMR, IR and Raman spectra.

Results and Discussion

The Structure of the Complexes.—The complexes $[MO_2Cl_2(C_6H_{14}O_3)]$ (M = Mo **1** or W **2**) are discrete chiral molecules in which the metals exhibit distorted-octahedral geometry. Views of **1** and **2** with the crystallographic numbering are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are given in Table 1 together with the corresponding data for the complexes $[MO_2Cl_2(dme)]$ (M = Mo **3**[12] or W **4**[13]) for comparison. The compounds **1** and **2** are not isostructural and their unit cells contain one and two pairs of enantiomeric molecules respectively. The diglyme ligand is bound to the metal *via* one terminal and the central oxygen atom giving a five-membered metallacycle as in the dme complexes **3** and **4**. Few diglyme complexes with this co-ordination mode have been characterized structurally, *viz.* $Ca(BH_4)_2{\cdot}2C_6H_{14}O_3$[14] and a titanium complex with a $Ti(\eta\text{-}C_5H_5)_2(C_6H_{14}O_3)$ moiety;[15] in other known structures diglyme is bound as a tridentate ligand to the metal atoms K,[16-18] Mg,[19] Ca,[14] Ti[20] and Cd.[21]

The arrangement of the six ligating atoms around the metal centre is the same for both compounds, *i.e.* the octahedron is composed of a *cis*-dioxo O(1)=M=O(2) group, *trans*-dichloro ligands and two neutral donor atoms, one terminal oxygen atom, O(3), and the central oxygen atom, O(4), of the diglyme ligand, *trans* to the *cis*-dioxo group. The oxygen atoms O(1), O(2), O(3) and O(4) are approximately coplanar with deviations of the metal atom from the best plane of 0.026 and 0.016 Å for molybdenum and tungsten, respectively. The deviations from regular octahedral geometry as observed in the molecular structures of **1** and **2** are characteristic of *cis*-dioxo complexes $MO_2Cl_2L_2$ (L = neutral donor), *i.e.* the axial chloro ligands are bent away from the *cis*-dioxo moiety, the angle O–M–O of the *cis*-dioxo group is significantly larger and L–M–L substantially smaller than 90°.[12,13,22-29] Calculations on the model complex $MoO_2H_4^{2-}$ indicate that such distortions maximize the two metal oxo π-bond interactions.[30] The six metal–ligand distances and the angles O(1)–M–O(2), O(3)–M–O(4) and Cl(1)–M–Cl(2) are very close to the corresponding parameters found in molecules **3** and **4**.

As in molecules **3** and **4** there are no noteworthy deviations in **1** and **2** from other observed distances and angles in complexes $MO_2Cl_2L_2$.[12,13,22-29] The main difference between **1** and **2** lies in the conformations around the bonds a–f of the diglyme ligand as defined in Table 2. Only the torsion angles of one chiral molecule of **1** and **2** are listed; the torsion angles of the

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

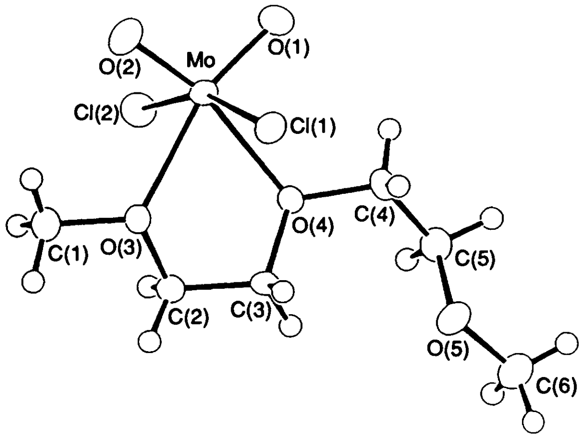

Fig. 1 The $[MoO_2Cl_2(C_6H_{14}O_3)]$ **1** molecule showing the crystallographic numbering. The thermal ellipsoids enclose 50% probability[11]

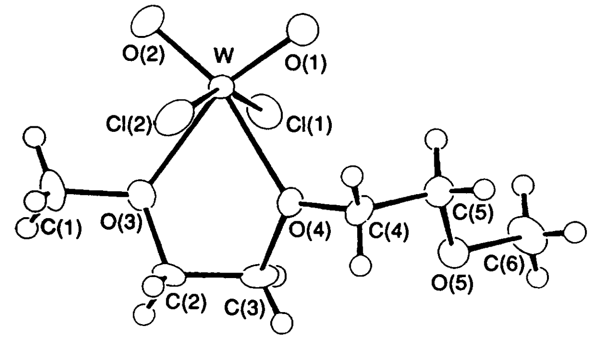

Fig. 2 The $[WO_2Cl_2(C_6H_{14}O_3)]$ **2** molecule showing the crystallographic numbering. The thermal ellipsoids enclose 50% probability[11]

corresponding enantiomers have opposite signs. The existence of two crystallographically independent molecules in $Ca(BH_4)_2 \cdot 2C_6H_{14}O_3$,[14] in which the only distinguishing feature is the difference between the conformations of the unco-ordinated parts of the bidentate diglyme ligands, has been ascribed to intermolecular interaction. In the molybdenum compound the shortest intermolecular contacts involving the C(4), C(5), O(5), C(6) side chain are $O(1)\cdots C(4^{I})$ 3.247(5) and $O(1)\cdots C(5^{I})$ 3.140(4) Å (symmetry code: I $1-x, 1-y, -z$). Corresponding contacts in the tungsten compound are appreciably longer, *viz.* $O(1)\cdots C(5^{II})$ 3.42(1), $O(1)\cdots C(6^{II})$ 3.51(1), $O(5)\cdots C(5^{III})$ 3.49(1) and $O(5)\cdots C(6^{IV})$ 3.45(2) Å (symmetry codes: II $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; III $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; IV $1-x, -y-1, 1-z$). Thus, in comparison with the sum of the van der Waals radii of oxygen and carbon, 3.25 Å,[31] close intermolecular contacts exist in the molybdenum structure **1**, but not in the tungsten structure **2**. This could explain the different conformations of diglyme in molecules **1** and **2**.

Table 1 Interatomic distances (Å) and angles (°) involving the non-hydrogen atoms within the $[MoO_2Cl_2(C_6H_{14}O_3)]$ **1** and $[WO_2Cl_2(C_6H_{14}O_3)]$ **2** molecules and selected distances and angles within $[MoO_2Cl_2(dme)]$ **3** and $[WO_2Cl_2(dme)]$ **4**

	1	**3**	**2**	**4**
M–Cl(1)	2.363(1)	2.340(4)	2.350(3)	2.344(4)
M–Cl(2)	2.368(1)	2.347(4)	2.357(3)	2.344(3)
M–O(1)	1.688(2)	1.667(11)	1.697(8)	1.69(1)
M–O(2)	1.695(2)	1.673(11)	1.696(8)	1.69(1)
M–O(3)	2.268(2)	2.289(7)	2.263(8)	2.292(8)
M–O(4)	2.327(2)	2.281(7)	2.247(8)	2.253(7)
C(1)–O(3)	1.454(4)		1.45(1)	
O(3)–C(2)	1.447(4)		1.45(1)	
C(2)–C(3)	1.495(5)		1.49(2)	
C(3)–O(4)	1.446(4)		1.47(1)	
O(4)–C(4)	1.462(4)		1.44(1)	
C(4)–C(5)	1.496(5)		1.50(2)	
C(5)–O(5)	1.425(4)		1.41(1)	
O(5)–C(6)	1.421(5)		1.44(1)	
Cl(1)–M–Cl(2)	159.75(3)		157.8(1)	157.6(2)
Cl(1)–M–O(1)	96.71(9)		97.4(3)	
Cl(1)–M–O(2)	95.15(9)		96.8(3)	
Cl(1)–M–O(3)	81.81(6)		80.1(2)	
Cl(1)–M–O(4)	80.84(6)		82.2(2)	
Cl(2)–M–O(1)	95.91(9)		96.6(3)	
Cl(2)–M–O(2)	96.89(9)		96.1(3)	
Cl(2)–M–O(3)	81.12(6)		81.4(2)	
Cl(2)–M–O(4)	83.34(6)		80.2(2)	
O(1)–M–O(2)	104.7(1)	104.5(1)	105.3(4)	105.1(5)
O(1)–M–O(3)	161.1(1)		162.5(4)	
O(1)–M–O(4)	90.2(1)		91.9(3)	
O(2)–M–O(3)	94.2(1)		92.2(3)	
O(2)–M–O(4)	165.0(1)		162.7(4)	
O(3)–M–O(4)	70.96(8)	71.4(1)	70.6(3)	70.5(3)
M–O(3)–C(1)	120.9(2)		120.9(8)	
M–O(3)–C(2)	115.2(2)		118.0(6)	
C(1)–O(3)–C(2)	112.1(3)		110.7(9)	
O(3)–C(2)–C(3)	106.9(3)		108.3(9)	
C(2)–C(3)–O(4)	107.1(3)		106.1(9)	
M–O(4)–C(3)	114.1(2)		117.2(6)	
M–O(4)–C(4)	116.6(2)		125.9(7)	
C(3)–O(4)–C(4)	113.5(2)		116.8(9)	
O(4)–C(4)–C(5)	114.1(3)		112.5(9)	
C(4)–C(5)–O(5)	110.0(3)		108.2(10)	
C(5)–O(5)–C(6)	110.8(3)		110.6(9)	

NMR and Vibrational Spectroscopy.—The $^{13}C-\{^1H\}$ NMR spectra of complexes **1** and **2** show three resonances each, one for the methyl and two for the methylene nuclei. One singlet for the protons of the two methyl groups and two sets of unresolved multiplets for the four methylene protons appear in the ^1H NMR spectra. These multiplets are not triplets implying a higher than first-order spectrum. All co-ordination shifts, δ(complex) – δ(free ligand), of complexes **1** and **2** are positive. Based on the molecular structure in the solid state two separate methyl resonances are expected. The observation of only one methyl resonance at 25 °C can be explained by two non-fluxional molecular structures different from the one found in the solid state: one in which diglyme is co-ordinated to the metal *via* the two terminal oxygen atoms to form a six-co-ordinated species with an eight-membered chelate ring and another in which all three oxygen atoms are co-ordinated to the metal giving a seven-co-ordinated species. Fluxionality of the diglyme ligand can, however, also explain the observed spectra; on fast exchange between free and metal-bound terminal oxygen atoms the resonances of the methoxy-groups average to one signal. Temperature-dependent spectral changes, *i.e.* line broadening and coalescence, are indicators of fluxionality thus giving a possibility to differentiate between rigid and fluxional binding of the diglyme ligand. The changes in the ^1H NMR spectra observed down to –70 °C indicate fluxionality. All three proton signals broaden uniformly, half-widths at –70 °C being 19 and 12 Hz for the methylene and 7 and 24 Hz for the methyl groups in complexes **1** and **2** respectively. Since viscosity changes can cause line broadenings of that order the interpretation is, however, not unambiguous. The low-temperature $^{13}C-\{^1H\}$ NMR spectra of complexes **1** and **2** shown in Fig. 3(*a*) and 3(*b*) are more conclusive. In the case of $[WO_2Cl_2(C_6H_{14}O_3)]$ **2** the resonances of carbon atoms C_a and C_b broaden progressively down to –69 °C. The half-width of the signal of the carbon atoms attached to the central oxygen atom of diglyme [C_c in Fig. 3(*b*)] is not affected over the measured temperature range. Thus, complex **2** undergoes an intramolecular dynamic process

Table 2 Conformation of diglyme C(1)–O(3)^{a}C(2)^{b}C(3)^{c}O(4)^{d}C(4)^{e}C(5)^{f}O(5)–C(6) in molecules **1** and **2**. Torsion angles (°) around bonds a–f. The sign of the dihedral angle in an arrangement of atoms 1–2–3–4 is positive when looking from atom 2 to 3; a clockwise motion of atom 1 would superimpose it on 4

Complex	a	b	c	d	e	f
1	170.9(3)	55.1(3)	−178.0(3)	−58.3(4)	86.6(4)	170.8(3)
2	179.9(9)	47(1)	135.1(9)	96(1)	−68(1)	176.2(9)

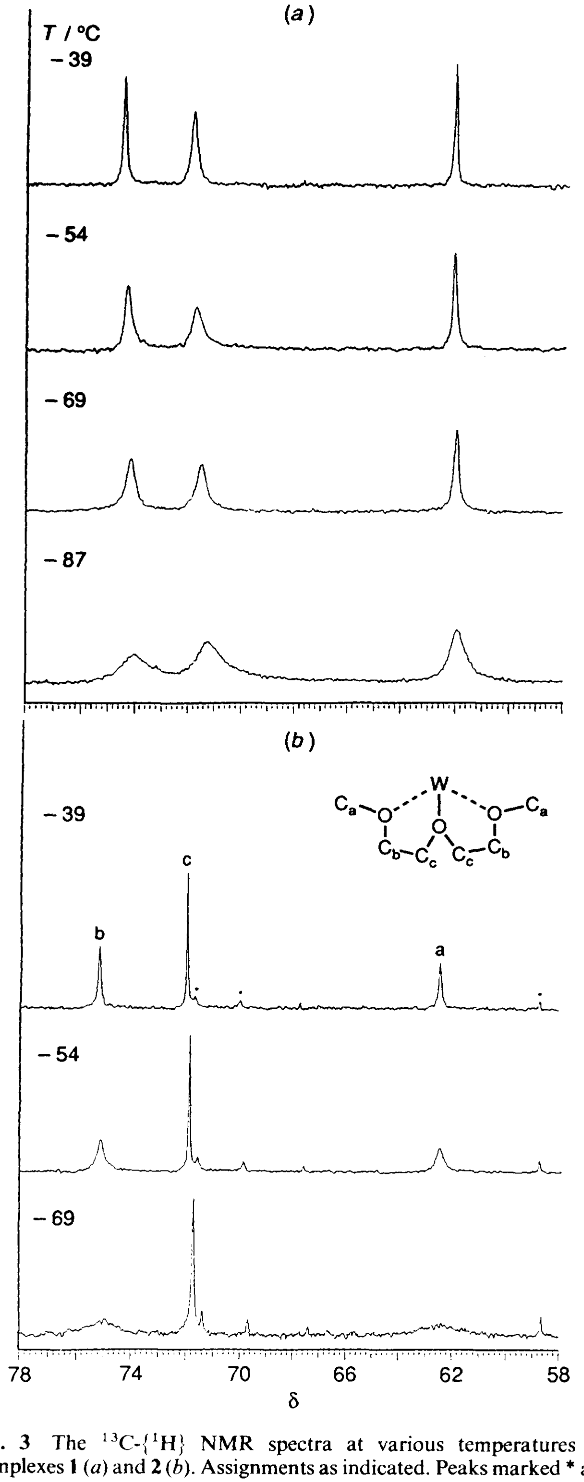

Fig. 3 The ^{13}C-{^1H} NMR spectra at various temperatures of complexes **1** (*a*) and **2** (*b*). Assignments as indicated. Peaks marked * are due to traces of free diglyme formed by hydrolysis

involving an exchange of the terminal methoxy groups with the central oxygen atom bound to the tungsten atom. This exchange can proceed dissociatively *via* a five-co-ordinated transition state or intermediate or associatively *via* a seven-co-ordinated transition state or intermediate, as depicted schematically in Fig. 3(*b*). The experimental results do not, however, allow a distinction between mechanisms, but the high *trans* influence of the oxo-ligands ought to favour a dissociative pathway. The complex [$MoO_2Cl_2(C_6H_{14}O_3)$] **1** behaves differently from **2**; on lowering the temperature all three carbon resonances broaden uniformly. Consequently a dynamic process different from that for **2** should operate. Though the limiting spectrum, where co-ordinated and unco-ordinated methoxy-groups are resolved, cannot be obtained for either compound it is evident that the activation energy of the dynamic process in complex **1** must be lower than that of **2**.

Infrared and Raman data for the diglyme complexes **1** and **2** and the dimethoxyethane complexes **3** and **4** are given in Table 3. The assignments of the metal–oxygen donor stretching and the symmetric in-plane deformation vibrations of the dioxo-metal moiety have been made in accordance with assignments in $MoO_2Cl_2(O_l)_2$ complexes where O_l is a neutral monodentate oxygen donor.[32] The similarity of the molecular structural data of the molybdenum compounds **1**, **3** and the tungsten compounds **2**, **4** is clearly reflected in the metal–ligand vibrations, especially in the symmetric and antisymmetric metal–oxo stretching vibrations. For free diglyme a strong IR absorption at 1105 cm^{-1} has been assigned to C–O stretching vibrations;[33] bands of medium intensity at 1098 and 1104 cm^{-1} for **1** and **2**, respectively, might therefore be attributed to the C–O vibrations of the uncomplexed part of diglyme. The strong and broad absorptions around 1020 cm^{-1} in the IR spectra of the dme complexes **3** and **4** are C–O interligand stretching vibrations of the co-ordinated oxygen atoms, permitting assignment of the corresponding vibrations in the diglyme compounds **1** and **2**. The C–O stretching vibrations are shifted towards the red on co-ordination of oxygen to the metal. In complex **1** this is matched by longer C–O bonds associated with the oxygen atoms, O(3) and O(4), bound to molybdenum than the C–O bonds involving the free methoxy group, *i.e.* O(5)–C(5) and O(5)–C(6). The lower precision of the structural data for complex **2** precludes a similar observation in this case.

Experimental

General Procedures and Syntheses.—All manipulations were performed on a vacuum line using standard Schlenk techniques and argon as inert gas. Infrared spectra (Nujol between CsI plates) were recorded with a Nicolet 20SXC spectrometer, Raman spectra with a Bruker FRA instrument (excitation radiation 1064 nm, resolution 4 cm^{-1}, 3000 scans, laser power 10 mW) and NMR spectra in CD_2Cl_2 with a Varian XL 300 spectrometer (300 MHz). Elemental analyses were performed by Analytische Laboratorien Malissa und Reuter, Germany and Mikro Kemi, Sweden.

2,5,8-Dioxanonane was distilled under argon over CaH_2. The starting compounds $WOCl_4$ and MoO_2Cl_2 were prepared according to the literature.[8] The compounds [$MoO_2Cl_2(C_6H_{14}O_3)$] **1** and [$WO_2Cl_2(C_6H_{14}O_3)$] **2** were prepared from MoO_2Cl_2 and $WOCl_4$ according to the published method for the synthesis of [MoO_2Cl_2(dme)] **3**[12,13] and [WO_2Cl_2(dme)] **4**[13] with diglyme instead of dme.

[$MoO_2Cl_2(C_6H_{14}O_3)$] **1**: yield 74% (Found: C, 21.5; H, 4.3; Cl, 20.4. $C_6H_{14}ClMoO_5$ requires C, 21.6; H, 4.2; Cl, 21.3%).

Table 3 IR (Nujol, CsI) and Raman (in italics) bands (cm^{-1}) of [$MoO_2Cl_2(C_6H_{14}O_3)$] **1**, [$WO_2Cl_2(C_6H_{14}O_3)$] **2**, [MoO_2Cl_2(dme)] **3** and [WO_2Cl_2(dme)] **4**; O_t = oxo, O_l = neutral oxygen donor, v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad

	Complex			
	3	**1**	**4**	**2**
$\nu(C-O_l)$	1026vs (br), *1031vw*	1035s (br)	1019vs (br), *1015vw*	1025s (br)
$\nu_{sym}[M(O_t)_2]$	960s, *960vs*	960s, *963vs*	976s, *976vs*	974s
$\nu_{asym}[M(O_t)_2]$	923vs, *934s*	922vs, *930s*	933vs, *942s*	932vs (br)
$\nu_{sym}[M(O_l)_2]$	419m, *423s*	431m, *437m*	415m, *420m*	439m
$\nu_{asym}[M(O_l)_2]$	396w	389m (sh), *394m*	402m (sh)	402m
$\delta_{sym}[M(O_t)_2]$	363s, *374m*	370m (sh), *374m*	367w, *368m*	370m
$\nu(MCl_2)$	347s, *345w* (sh)	344vs (br), *348w*	349s	332s (br)
	308 (sh), *312m*	319vs (br), *320s*	339s, *338m*	

Table 4 Fractional atomic coordinates for the non-hydrogen atoms in [$MoO_2Cl_2(C_6H_{14}O_3)$] **1**

Atom	*x*	*y*	*z*	B_{eq}
Mo	0.634 57(3)	0.719 09(3)	0.216 70(4)	1.50(2)
Cl(1)	0.891 6(1)	0.648 8(1)	0.154 5(1)	1.82(4)
Cl(2)	0.418 2(1)	0.734 7(1)	0.366 4(1)	2.24(4)
O(1)	0.567 7(3)	0.673 6(3)	−0.008 4(3)	2.3(1)
O(2)	0.601 0(3)	0.903 9(3)	0.228 0(4)	2.5(1)
C(1)	0.704 1(5)	0.827 3(4)	0.667 3(6)	2.5(2)
O(3)	0.740 3(3)	0.699 7(2)	0.524 3(3)	1.6(1)
C(2)	0.753 3(4)	0.564 7(4)	0.603 1(5)	1.8(2)
C(3)	0.815 0(4)	0.439 6(4)	0.453 6(5)	1.5(2)
O(4)	0.715 1(2)	0.471 9(2)	0.279 2(3)	1.5(1)
C(4)	0.764 3(4)	0.360 9(4)	0.116 7(5)	1.9(2)
C(5)	0.778 7(4)	0.207 3(4)	0.151 9(5)	2.1(2)
O(5)	0.925 7(3)	0.134 9(3)	0.242 3(4)	2.2(1)
C(6)	0.950 1(5)	−0.018 0(4)	0.249 4(7)	2.9(2)

Table 5 Fractional atomic coordinates for the non-hydrogen atoms in [$WO_2Cl_2(C_6H_{14}O_3)$] **2**

Atom	*x*	*y*	*z*	B_{eq}
W	0.788 56(3)	0.063 78(3)	0.345 41(4)	1.38(2)
Cl(1)	0.758 0(2)	−0.005 8(4)	0.541 2(2)	2.4(1)
Cl(2)	0.825 5(2)	0.012 3(4)	0.148 8(2)	2.5(1)
O(1)	0.689 1(6)	0.190 3(12)	0.313 4(7)	2.3(3)
O(2)	0.878 5(6)	0.212 6(11)	0.377 7(7)	2.3(4)
C(1)	0.990 2(8)	−0.157 1(19)	0.360 7(11)	2.9(6)
O(3)	0.888 5(5)	−0.173 1(11)	0.376 7(6)	2.1(3)
C(2)	0.853 5(9)	−0.348 8(15)	0.340 7(10)	2.0(5)
C(3)	0.748 5(9)	−0.357 4(16)	0.359 4(11)	2.4(5)
O(4)	0.706 4(5)	−0.191 8(11)	0.309 1(7)	2.0(3)
C(4)	0.618 0(8)	−0.209 1(16)	0.237 0(9)	1.8(5)
C(5)	0.531 3(8)	−0.175 6(16)	0.304 7(10)	2.1(5)
O(5)	0.523 6(5)	−0.317 3(11)	0.386 2(6)	2.1(3)
C(6)	0.444 9(9)	−0.286 2(18)	0.459 3(10)	2.9(6)

NMR (223 K, CD_2Cl_2, $SiMe_4$ as internal standard with δ 0): ^1H, δ 3.68 (s, 6 H, CH_3), 3.82–3.92 (m, 4 H, CH_2) and 4.24–4.36 (m, 4 H, CH_2); $^{13}C-\{^1H\}$, δ 61.8 (CH_3), 71.4 (CH_2) and 73.9 (CH_2).

[$WO_2Cl_2(C_6H_{14}O_3)$] **2**: yield 54% (Found: C, 16.8; H, 3.3; Cl, 16.4. $C_6H_{14}ClO_5W$ requires C, 17.1; H, 3.3; Cl, 16.8%). NMR (293 K, CD_2Cl_2): ^1H, δ 3.78 (s, 6 H, CH_3), 3.95–4.00 (m, 4 H, CH_2) and 4.40–4.45 (m, 4 H, CH_2); $^{13}C-\{^1H\}$, δ 62.2 (CH_3), 71.9 (CH_2) and 74.9 (CH_2).

Suitable crystals for X-ray crystallography of complexes **1** and **2** were obtained by adding heptane to a CH_2Cl_2 solution and cooling at 0 °C for 1 week. The crystals are extremely unstable, decomposing immediately on exposure to the atmosphere at ambient temperature.

Crystallography.—Crystal data. $C_6H_{14}Cl_2MoO_5$, M = 333.0, triclinic, space group $P\bar{1}$, a = 9.437(2), b = 9.670(2), c = 7.046(2) Å, α = 97.80(2), β = 97.50(2), γ = 69.58(1)°, U = 594.6(2) Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections in the range 46.1 < 2θ < 49.9°, λ = 0.710 69 Å), Z = 2, D_c = 1.86 g cm^{-3}, $F(000)$ = 332, colourless, rod-shaped crystals, approximate dimensions 0.40 × 0.20 × 0.20 mm, μ(Mo-Kα) = 15.25 cm^{-1}.

$C_6H_{14}Cl_2O_5W$, M = 420.9, monoclinic, space group $P2_1/c$, a = 13.940(3), b = 7.457(3), c = 11.358(2) Å, β = 93.87(2)°, U = 1178(1) Å^3 (by least-squares refinement on diffractometer setting angles for 24 automatically centred reflections in the range 32.2 < 2θ < 40.9°, λ = 0.710 69 Å), Z = 4, D_c = 2.37 g cm^{-3}, $F(000)$ = 792, colourless plates, approximate dimensions 0.10 × 0.20 × 0.20 mm, μ(Mo-Kα) = 104.7 cm^{-1}.

Data collection and processing. Crystals were mounted in glass capillaries under an inert atmosphere at approximately −150 °C,[34] and transferred at the same temperature to a Rigaku AFC6R diffractometer.

For complex **1**, diffracted intensities were measured at −120 °C, ω–2θ scan mode with an ω-scan rate of 32° min^{-1} and a scan width of (1.21 + 0.30tanθ)°; graphite-monochromated Mo-Kα radiation from a RU200 rotating anode operated at 9 kW (50 kV, 180 mA); weak reflections [$I < 10\sigma(I)$] were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reaction; ratio of peak counting time *vs.* background counting time 2 : 1.2089 Unique reflections (3.5 < 2θ < 50.0°); no correction for absorption, 1781 reflections with $I > 3\sigma(I)$.

For complex **2**, diffracted intensities were measured at −120 °C as for **1**, ω–2θ scan mode with an ω-scan rate of 16° min^{-1} and a scan width of (0.79 + 0.30tanθ)°; graphite-monochromated Mo-Kα radiation. 2248 Unique reflections (3.5 < 2θ < 50.0°); empirical correction for absorption based on azimuthal scans for several reflections (maximum, minimum transmission factors = 0.75, 1.00), 1586 reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. For complex **1** the coordinates of the molybdenum and chlorine atoms were obtained by direct methods (MITHRIL)[35] and those of the remaining atoms from subsequent electron-density maps. Full-matrix least-squares refinement including anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms gave a final R = 0.024, R' = 0.030 for 183 parameters and 1781 reflections; maximum residual electron density = 0.42 e Å^{-3}. Weighting scheme: $w = [\sigma^2(F_o)]^{-1}$. For atomic scattering factors, anomalous dispersion corrections and computer programs used, see ref. 36.

For complex **2** the structure was solved as for **1**. Full-matrix least-squares refinement, including anisotropic thermal parameters for the non-hydrogen atoms and with the hydrogen atoms as a fixed contribution in calculated positions [C–H 1.0 Å; $B = 1.2B_{eq}$ of the carrying carbon atom $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$], gave a final R = 0.038, R' = 0.046 for 127 parameters and 1586 reflections; maximum residual electron density = 2.0 e Å^{-3} in the vicinity of, *i.e.* 1.0 Å from, the tungsten atom. Weighting scheme and other details as for **1**.

Final atomic positional parameters are given in Tables 4 (Mo) and 5 (W).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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