Synthesis and Crystal Structures of Dinuclear Oxotungsten(VI) Diolato Complexes†

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Dinuclear complexes $[W_2O_3L_2(HL)_2]$ [H_2L = 2,3-dimethylbutane-2,3-diol (H_2pin), *trans*-cycloheptane-1,2-diol (H_2chpd) or *trans*-cyclooctane-1,2-diol (H_2cocd)] were prepared in high yield by hydrolysis of [W(eg)(pin)$_2$] (H_2eg = ethane-1,2-diolate), [W(chpd)$_3$] and [W(cocd)$_3$] in alcoholic solution. X-Ray diffraction studies showed that each tungsten(VI) ion is bonded to one diolate, one hydrogendiolate, one terminal and one bridging oxide ligand. Two tungsten-centred units are also linked together by intramolecular O $\cdots$ H–O hydrogen bonds between the diolate and hydrogendiolate ligands. The geometry of the dinuclear unit is dependent on the nature of the diolate ligands.

Oxo complexes of tungsten(VI) have been shown to be very useful catalysts in olefin metathesis.[1] Terminal oxo groups may play an important role as spectators in active metathesis catalysts.[2] In heterogeneous catalysis the active metal compound is usually deposited on an oxide support, typically SiO_2 or Al_2O_3. The co-ordination sphere of the metal atom is generally formed of oxygen atoms. It is thought that in heterogeneous supported tungsten catalysts the tungsten and oxygen atoms are bonded in several different ways, including short terminal W=O, long M–O–W (M = Si or Al) and bridging W–O–W bonds.[3,4]

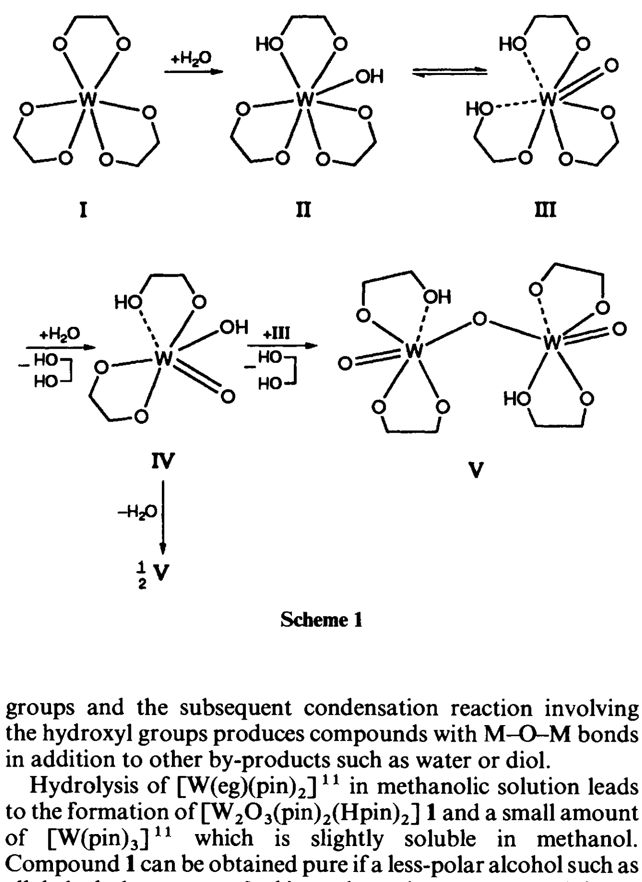
A number of molecular analogues of supported complexes have been prepared: [WO_3L] (L = 1,4,7-triazacyclononane or 1,4,7-trimethyl-1,4,7-triazacyclononane)[5] and [WO_2Cl_2L][6] [L = 2,5,8-trioxanonane (diglyme)] have been proposed as models for surface WO_3 groups. Binuclear oxoalcoholato and oxoalkyl complexes such as $[W_2O_5(OMe)_4]^{2-}$[7] and $[W_2O_3(CH_2CCH_3)_6]$[8] are other possible model compounds, as the co-ordination sphere around the tungsten(VI) ion is similar to that believed to be important in heterogeneous catalysts.

Metal alcoholato complexes are known for their ability to undergo hydrolysis to form the metal oxide. Controlled partial hydrolysis leads instead to the formation of oxometal alcoholato complexes, which can be regarded as intermediates between mono- or oligo-meric alcoholato complexes and polymeric oxides.[9] Hydrolysis reactions are used in the preparation of oxide thin films and uniform bulk oxide materials.[10]

In the present paper we report the synthesis and crystal structures of three dimeric oxotungsten(VI) diolato complexes $[W_2O_3L_2(HL)_2]$ [H_2L = 2,3-dimethylbutane-2,3-diol (pinacol, H_2pin), *trans*-cycloheptane-1,2-diol (H_2chpd) or *trans*-cyclooctane-1,2-diol (H_2cocd)].

Discussion

The monomeric tungsten(VI) complexes [W(eg)(pin)$_2$] [H_2eg = ethane-1,2-diol (ethylene glycol)], [W(chpd)$_3$] and [W(cocd)$_3$] are soluble in alcohols. If such solutions are allowed to stand in the presence of moisture, crystals of $[W_2O_3L_2(HL)_2]$ are obtained. A possible mechanism for the formation of these dinuclear complexes includes hydrolysis and condensation reactions, as shown in Scheme 1. In the hydrolysis reaction the alcoholate ligands are replaced with oxo or hydroxyl groups and the subsequent condensation reaction involving the hydroxyl groups produces compounds with M–O–M bonds in addition to other by-products such as water or diol.



Scheme 1

Hydrolysis of [W(eg)(pin)$_2$][11] in methanolic solution leads to the formation of $[W_2O_3(pin)_2(Hpin)_2]$ **1** and a small amount of [W(pin)$_3$][11] which is slightly soluble in methanol. Compound **1** can be obtained pure if a less-polar alcohol such as allyl alcohol or propan-2-ol is used as solvent. However it is not found if [W(pin)$_3$] is used as starting material under these conditions. The compounds $[W_2O_3(chpd)_2(Hchpd)_2]$ **2** and $[W_2O_3(cocd)_2(Hcocd)_2]$ **3** can be prepared pure in methanol in good yields. All three compounds are stable in the presence of oxygen and moisture and can be recrystallised from the parent alcohols without further hydrolysis.

The molecular structures of compounds **1**–**3** are shown in Figs. 1, 2 and 3, respectively, with the relevant bond distances and angles collected in Table 1. The structures of all three compounds reveal that each tungsten(VI) ion is bonded to one diolate ligand, one hydrogendiolate ligand, one terminal oxide ligand and one oxygen atom, with the latter forming a bridge to another tungsten(VI) ion. The hydroxyl proton of **1** was found

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

from a Fourier-difference map, and its position indicates the possibility of hydrogen bonds across the dimer, so that the two tungsten-centred units are also linked together by two intramolecular O···H–O hydrogen bonds between diolate and hydrogendiolate ligands attached to the two different tungsten(VI) ions. When the diol used is H_2pin the two tungsten(VI) units are identical as the bridging oxygen lies on a two-fold axis. When it is H_2chpd or H_2cocd the other half of the dimer is similar but not crystallographically identical.

In compound **1** the hydrogen-bond parameters are as follows: O(5)–H(25) 0.867 Å, O(5)···O(3^I) (I 1 − $x, y, z - \frac{1}{2}$) 2.63(1) Å and O(5)–H(25)···O(3^I) 173.7°. The OH-hydrogen atoms were not found from the Fourier maps of **2** and **3**. However the O(3)···O(10) and O(5)···O(8) distances were 2.58(3) and 2.57(3) in **2**. The relevant distances in **3** were 2.59(3) and 2.56(3) Å.

On the whole the structure of compound **1** is very similar to that of the molybdenum(VI) complex [Mo_2O_3(pin)$_2$(Hpin)$_2$],[13] which means that the structures of these dimers are not very metal sensitive. The bond distances and angles in **1** are also closely similar to the corresponding values found in the phenylimidotungsten complex [W_2O(NPh)$_2$(pin)$_2$(Hpin)$_2$],[14] so the steric demand of the monodentate terminal ligand has

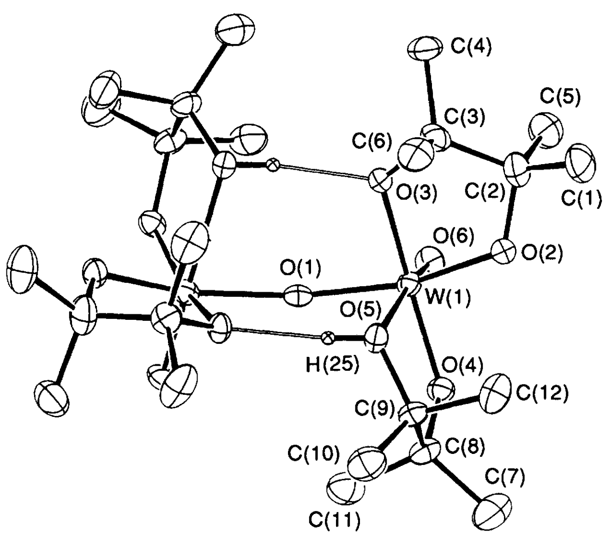


Fig. 1 An ORTEP[12] drawing of compound **1**. Thermal ellipsoids are drawn at 30% probability

no significant effect on the W–O bond lengths or the O–W–O angles.

To retain the +VI oxidation state for tungsten, one diolato oxygen in each tungsten-centred unit remains protonated. These hydroxyl groups lie *trans* to the terminal oxide ligands where the considerably longer W–O bond distances are observed. The strong *trans*-influencing ability of the multiply bonded oxygen ligand can explain the disposition of the diolate ligands, which are arranged with the weakest π-bonding donor atom *trans* to the oxide group. A good example of a similar arrangement with neutral and anionic alcoholate ligands is the monomeric complex [WO_2(5-Bu^t-sap)(MeOH)] [5-Bu^{t}sap = 5-*tert*-butyl-2-(salicylideneamino)-phenolate(2−)], where the W–O_{MeOH} and W=O bond lengths in *trans* positions are 2.392 and 1.642 Å, respectively.[15]

The conformation of the five-membered chelate rings is an envelope or a half-chair, or something between, as seen from the values of the ring torsion angles (Table 2). The absolute values of the ring torsion angles range from 3 to 56°, those of the O–C–C–O torsion angles from 13 to 56°. A negative value of the O–C–C–O torsion angle indicates the δ conformation for the chelate ring and a positive value the λ conformation. The diols H_2chpd and H_2cocd were racemic mixtures of (−)-(*R,R*) and (+)-(*S,S*) diols. The (−)-(*R,R*)-diol forms a δ conformation with the metal ion, the (+)-(*S,S*)-diol a λ conformation. From the O–C–C–O torsion angles one can deduce that the diolate and hydrogendiolate ligands in the asymmetric unit of compound **1** have different conformations (δ and λ) around the W^{VI}, and the C_2 symmetry generates the corresponding conformation around the other W atom. The O–C–C–O torsion angles of **2**, in turn, indicate that the asymmetric unit contains two (−)-chpd and two (+)-Hchpd ions. In the asymmetric unit of **3** there are one (−)-cocd, one (+)-cocd and two (+)-Hcocd ions.

The O–W–O bite angles and relevant O···O distances in compounds **1**–**3** vary significantly. The bite angles are smaller when the ligand is a monoanionic hydrogendiolate, and the O···O distances are smaller in the dianionic diolate ligands. For instance, in **1** the O(2)–W(1)–O(3) angle is 76.7(3)° (dianionic) and O(4)–W(1)–O(5) is 72.9(3)° (monoanionic ligand). The O(2)···O(3) and O(4)···O(5) distances are 2.41(1) and 2.54(1) Å, respectively. The difference is due to the fact that the W(1)–O(2) and W(1)–O(3) bond lengths are 1.900(8) and 1.974(7) Å while W(1)–O(4) and W(1)–O(5) are 1.871(8) and 2.351(7) Å. Differences between corresponding ligands in different complexes also are noticeable.

Few dinuclear tungsten(VI) complexes containing bridging

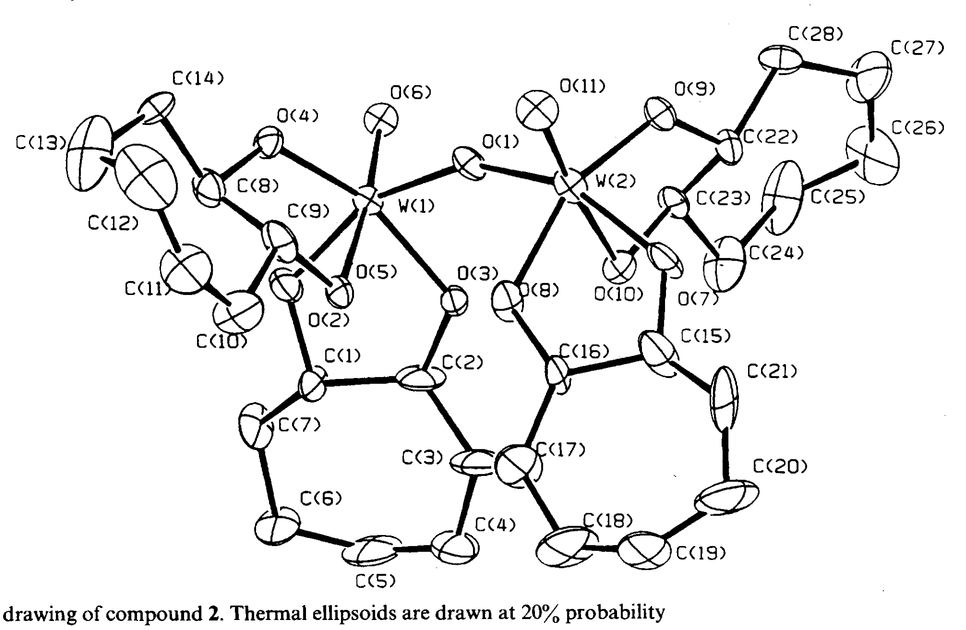


Fig. 2 An ORTEP drawing of compound **2**. Thermal ellipsoids are drawn at 20% probability

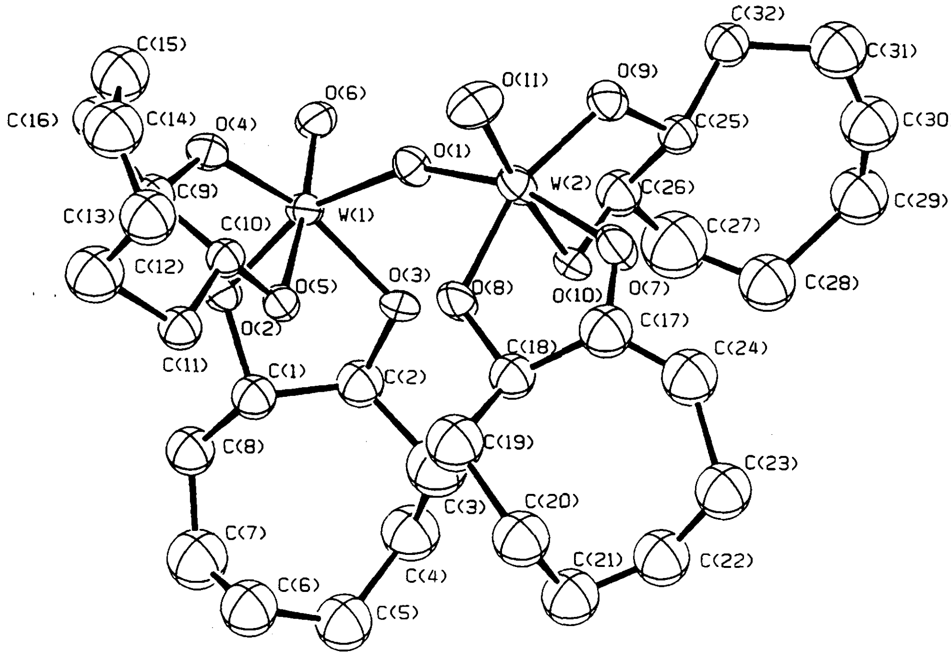


Fig. 3 An ORTEP drawing of compound **3**. Thermal ellipsoids as in Fig. 2

Table 1 Geometric parameters (bond lengths in Å, angles in °) for the $[W_2O_3L_2(HL)_2]$ complexes **1**–**3**

	1	2	3		1	2	3
W(1)–O(1)	1.900(2)	1.92(2)	2.00(2)	W(2)–O(8)		1.96(2)	1.88(2)
W(1)–O(2)	1.900(8)	1.90(2)	1.82(2)	W(2)–O(9)		1.85(2)	1.88(2)
W(1)–O(3)	1.974(7)	1.97(2)	1.91(2)	W(2)–O(10)		2.34(2)	2.25(2)
W(1)–O(4)	1.871(8)	1.89(2)	1.90(2)	W(2)–O(11)		1.71(2)	1.81(2)
W(1)–O(5)	2.351(7)	2.33(2)	2.37(2)	O(2)···O(3)	2.41(1)	2.45(3)	2.47(3)
W(1)–O(6)	1.689(7)	1.68(2)	1.66(2)	O(4)···O(5)	2.54(1)	2.56(2)	2.49(2)
W(2)–O(1)		1.89(2)	1.81(2)	O(7)···O(8)		2.39(3)	2.36(3)
W(2)–O(7)		1.93(2)	1.88(2)	O(9)···O(10)		2.55(3)	2.55(3)
O(1)–W(1)–O(2)	155.2(4)	155.9(7)	157.0(7)	O(7)–W(2)–O(8)		75.7(8)	77.4(9)
O(1)–W(1)–O(3)	83.8(3)	82.6(7)	80.6(7)	O(7)–W(2)–O(9)		90.5(9)	90.8(9)
O(1)–W(1)–O(4)	100.3(3)	99.1(8)	92.8(7)	O(7)–W(2)–O(10)		81.8(9)	87(1)
O(1)–W(1)–O(5)	79.0(2)	79.9(7)	76.6(6)	O(7)–W(2)–O(11)		104(1)	99(1)
O(1)–W(1)–O(6)	97.8(3)	97.8(8)	95.3(7)	O(8)–W(2)–O(9)		155.4(8)	159.8(9)
O(2)–W(1)–O(3)	76.7(3)	78.5(8)	83.0(7)	O(8)–W(2)–O(10)		83.8(8)	87.2(8)
O(2)–W(1)–O(4)	92.7(3)	92.5(8)	95.0(8)	O(8)–W(2)–O(11)		104.6(9)	101(1)
O(2)–W(1)–O(5)	84.9(3)	83.2(7)	85.7(7)	O(9)–W(2)–O(10)		73.9(7)	75.7(7)
O(2)–W(1)–O(6)	101.2(3)	101.6(8)	105.1(8)	O(9)–W(2)–O(11)		98.5(9)	96(1)
O(3)–W(1)–O(4)	158.6(3)	156.6(7)	154.0(7)	O(10)–W(2)–O(11)		170.7(9)	170.6(9)
O(3)–W(1)–O(5)	87.4(3)	83.5(6)	83.5(7)	W(1)–O(1)–W(2)	161.4(5)	154.3(9)	154.6(9)
O(3)–W(1)–O(6)	102.5(3)	105.7(8)	108.4(8)	W(1)–O(2)–C(02)	120.3(7)	121(2)	118(2)
O(4)–W(1)–O(5)	72.9(3)	74.0(7)	70.5(7)	W(1)–O(3)–C(03)	120.0(7)	120(2)	113(2)
O(4)–W(1)–O(6)	97.8(4)	97.2(8)	97.1(8)	W(1)–O(4)–C(04)	128.9(7)	125(2)	128(2)
O(5)–W(1)–O(6)	169.3(3)	170.2(7)	164.5(7)	W(1)–O(5)–C(05)	112.0(7)	111(1)	113(1)
O(1)–W(2)–O(7)		154.6(9)	160.4(9)	W(2)–O(7)–C(07)		125(2)	125(2)
O(1)–W(2)–O(8)		85.7(7)	86.4(7)	W(2)–O(8)–C(08)		120(2)	121(2)
O(1)–W(2)–O(9)		100.0(8)	101.3(7)	W(2)–O(9)–C(09)		124(1)	121(2)
O(1)–W(2)–O(10)		79.0(7)	81.5(7)	W(2)–O(10)–C(010)		107(2)	108(2)
O(1)–W(2)–O(11)		97.4(9)	95.3(9)				

oxygen atoms have been structurally characterised. In the single oxo-bridged complexes the W–O–W angle ranges from linear 180° in $Na_6[\{WO_2(cit)\}_2O]\cdot 10H_2O$ [16] [cit = citrate(4–)] and $[W_2O_3(CH_2CCH_3)_6]$ [8] to 152.2(2)° in $[(LWO_2)(\mu\text{-}O)WO(O_2)(H_2O)]$ [5] (L = 1,4,7-triazacyclononane) and 157(2)° in $[W_2O(NPh)_2(pin)_2(Hpin)_2]$. In complexes **1**–**3** the W–O–W angles are 161.4(5), 154.3(9) and 154.6(9)°, respectively. Clearly these values are dependent on the diolate ligands. The angles between the two O_t–W–O_b planes (O_t is the terminal and O_b the bridging oxide ligand) inside the dinuclear unit are 109.40, 95.38 and 97.75° in compounds **1**, **2** and **3**, respectively. These values show that also the twisting of the planes is dependent on the ligands. The bridging W–O bond distances are *ca.* 1.90 Å, of the same magnitude as for other single-oxygen-bridged tungsten(VI) compounds.

The IR spectra of compounds **1**–**3** show strong absorption bands at 959, 964 and 959 cm^{-1}, respectively. These are due to the W=O asymmetric stretch. The W=O stretchings in spectra of $[WO_2Cl_2L]$ (L = 1,2-dimethoxyethane or diglyme) have been found at 976 and 974 cm^{-1}, respectively.[6] Oxygen-bridged complexes of Mo and W which contain a non-linear OMOMO core such as $[Mo_2O_3(pin)_2(Hpin)_2]$ [17] and Na$_2$-

Table 2 Selected torsion angles (°) for $[W_2O_3L_2(HL)_2]$

Complex **1**			
O(2)–C(2)–C(3)–O(3)	−36(1)	O(4)–C(8)–C(9)–O(5)	34(1)
C(2)–C(3)–O(3)–W(1)	25(1)	C(8)–C(9)–O(5)–W(1)	−29(1)
C(3)–O(3)–W(1)–O(2)	−3.7(8)	C(9)–O(5)–W(1)–O(4)	13.0(7)
O(3)–W(1)–O(2)–C(2)	−22.2(9)	O(5)–W(1)–O(4)–C(8)	9.4(9)
W(1)–O(2)–C(2)–C(3)	−40(1)	W(1)–O(4)–C(8)–C(9)	−29(1)
Complex **2**			
O(2)–C(1)–C(2)–O(3)	32(3)	O(4)–C(8)–C(9)–O(5)	−48(3)
C(1)–C(2)–O(3)–W(1)	−23(3)	C(8)–C(9)–O(5)–W(1)	39(2)
C(2)–O(3)–W(1)–O(2)	4(2)	C(9)–O(5)–W(1)–O(4)	−15(2)
O(3)–W(1)–O(2)–C(1)	19(2)	O(5)–W(1)–O(4)–C(8)	−16(2)
W(1)–O(2)–C(1)–C(2)	−34(3)	W(1)–O(4)–C(8)–C(9)	43(3)
O(7)–C(15)–C(16)–O(8)	13(5)	O(9)–C(22)–C(23)–O(10)	−53(3)
C(15)–C(16)–O(8)–W(2)	−5(5)	C(22)–C(23)–O(10)–W(2)	39(2)
C(16)–O(8)–W(2)–O(7)	−3(3)	C(23)–O(10)–W(2)–O(9)	−13(2)
O(8)–W(2)–O(7)–C(15)	13(3)	O(10)–W(2)–O(9)–C(22)	−21(2)
W(2)–O(7)–C(15)–C(16)	−18(5)	W(2)–O(9)–C(22)–C(23)	50(3)
Complex **3**			
O(2)–C(1)–C(2)–O(3)	46(3)	O(4)–C(9)–C(10)–O(5)	−43(3)
C(1)–C(2)–O(3)–W(1)	−37(3)	C(9)–C(10)–O(5)–W(1)	33(2)
C(2)–O(3)–W(1)–O(2)	10(2)	C(10)–O(5)–W(1)–O(4)	−12(2)
O(3)–W(1)–O(2)–C(1)	21(2)	O(5)–W(1)–O(4)–C(9)	−18(2)
W(1)–O(2)–C(1)–C(2)	−44(3)	W(1)–O(4)–C(9)–C(10)	41(3)
O(7)–C(17)–C(18)–O(8)	−21(4)	O(9)–C(25)–C(26)–O(10)	−56(3)
C(17)–C(18)–O(8)–W(2)	22(3)	C(25)–C(26)–O(10)–W(2)	44(2)
C(18)–O(8)–W(2)–O(7)	−12(2)	C(26)–O(10)–W(2)–O(9)	−17(2)
O(8)–W(2)–O(7)–C(17)	−3(3)	O(10)–W(2)–O(9)–C(25)	−18(2)
W(2)–O(7)–C(17)–C(18)	15(4)	W(2)–O(9)–C(25)–C(26)	48(3)

Table 3 Crystal data and experimental details

Compound	1	2	3
Formula	$C_{24}H_{50}O_{11}W_2$	$C_{28}H_{50}O_{11}W_2$	$C_{32}H_{58}O_{11}W_2$
M_r	882.36	930.42	986.50
Crystal dimensions/mm	0.20 × 0.15 × 0.15	0.10 × 0.10 × 0.20	0.25 × 0.20 × 0.20
Crystal appearance	Bright, prism	Bright, prism	Bright, prism
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*Cc*	*Cc*
a/Å	16.885(7)	17.068(2)	17.753(3)
b/Å	13.353(4)	16.738(3)	17.602(4)
c/Å	13.465(6)	11.862(2)	12.049(2)
β/°	93.14(4)	94.81(1)	99.66(2)
U/Å^3	3031(2)	3376.7(8)	3712(1)
Z	8	4	4
D_c/g cm^{-3}	1.933	1.838	1.765
μ/cm^{-1}	77.97	70.05	63.77
F(000)	1720	1832	1944
h, k, l ranges	0–20, 0–16, −16 to 16	0–20, 0–20, −14 to 14	0–21, 0–21, −14 to 14
R_{int}	0.040	0.056	0.060
Measured reflections	2015	3203	3507
Unique reflections	1929	3093	3387
Obs. reflections [$I > 3\sigma(I)$]	1257	1791	2262
Minimum, maximum transmission coefficients	0.86, 1.15	0.94, 1.00	0.88, 1.00
No. of parameters	168	367	226
R^a	0.028	0.038	0.053
R'^b	0.031	0.043	0.055
Goodness of fit	1.11	1.37	1.72
Maximum Δ/σ	0.01	0.34	0.27
Maximum, minimum $\Delta\rho$/e Å^{-3}	−0.46, 0.49	−0.59, 0.62	0.78, −0.67

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

$[W_2O_5(cat)_2]\cdot 2H_2O$[18] [cat = catecholate(2−)] have asymmetric M=O stretches at 950 and 915 cm^{-1}. The asymmetric M–O–M stretches occur at 762 and 770 cm^{-1}, respectively. For compounds **1**–**3** the corresponding bands are at 787, 787 and 791 cm^{-1}.

Conclusion

Dimeric tungsten(VI) diolato complexes containing non-linear OWOWO cores were prepared by hydrolysis of tris(diolato)-tungsten(VI) complexes. Hydrolysis in alcohol solutions led to the formation of pure products in good yield. The co-ordination

Table 4 Positional parameters

Atom	x	y	z	Atom	x	y	z
$[W_2O_3(pin)_2(Hpin)_2]$							
W(1)	0.583 97(3)	0.309 80(4)	0.164 48(4)	C(4)	0.720(1)	0.093(1)	0.327(1)
O(1)	$\frac{1}{2}$	0.332 8(7)	$\frac{1}{4}$	C(5)	0.783 0(9)	0.237(1)	0.190(1)
O(2)	0.656 7(4)	0.230 2(6)	0.096 0(5)	C(6)	0.616(1)	0.037(1)	0.205(1)
O(3)	0.615 4(4)	0.205 2(6)	0.262 4(5)	C(7)	0.485(1)	0.371(1)	−0.120(1)
O(4)	0.540 5(4)	0.366 3(5)	0.046 6(6)	C(8)	0.472 2(8)	0.334(1)	−0.015(1)
O(5)	0.487 7(4)	0.197 3(6)	0.098 5(5)	C(9)	0.462 6(8)	0.222(1)	−0.003 5(9)
O(6)	0.642 1(4)	0.407 3(6)	0.201 7(6)	C(10)	0.380(1)	0.182(1)	−0.029(1)
C(1)	0.744(1)	0.090(1)	0.080(1)	C(11)	0.400 0(9)	0.388(1)	0.029(1)
C(2)	0.713 8(9)	0.169(1)	0.151(1)	C(12)	0.524(1)	0.167(1)	−0.067(1)
C(3)	0.667 6(8)	0.125(1)	0.235(1)				
$[W_2O_3(chpd)_2(Hchpd)_2]$							
W(1)	0.457 3	0.960 97(7)	0.653 0	C(9)	0.331(2)	0.903(2)	0.456(2)
W(2)	0.371 9(1)	0.778 10(7)	0.771 2(1)	C(10)	0.317(2)	0.866(2)	0.341(3)
O(1)	0.401(1)	0.883(1)	0.734(1)	C(11)	0.234(2)	0.878(3)	0.291(4)
O(2)	0.527(1)	0.997(1)	0.548(2)	C(12)	0.177(3)	0.938(5)	0.317(4)
O(3)	0.542(1)	0.881(1)	0.673(1)	C(13)	0.215(3)	1.019(4)	0.325(6)
O(4)	0.371(1)	1.015(1)	0.577(1)	C(14)	0.254(2)	1.037(2)	0.449(3)
O(5)	0.411(1)	0.878(1)	0.504(1)	C(15)	0.417(3)	0.618(3)	0.697(3)
O(6)	0.475(1)	1.027(1)	0.759(1)	C(16)	0.416(3)	0.668(2)	0.593(2)
O(7)	0.384(2)	0.664(1)	0.777(2)	C(17)	0.461(4)	0.654(2)	0.497(4)
O(8)	0.399(1)	0.749(1)	0.619(2)	C(18)	0.493(4)	0.579(3)	0.471(5)
O(9)	0.387(1)	0.784(1)	0.927(1)	C(19)	0.471(5)	0.509(3)	0.514(5)
O(10)	0.508(1)	0.773(1)	0.816(2)	C(20)	0.458(4)	0.485(3)	0.625(6)
O(11)	0.272(1)	0.792(1)	0.756(2)	C(21)	0.408(3)	0.530(2)	0.694(4)
C(1)	0.589(2)	0.943(2)	0.506(3)	C(22)	0.456(2)	0.758(2)	0.993(2)
C(2)	0.612(2)	0.890(2)	0.612(3)	C(23)	0.523(2)	0.796(2)	0.937(2)
C(3)	0.646(3)	0.809(3)	0.591(4)	C(24)	0.608(2)	0.772(3)	0.970(4)
C(4)	0.722(4)	0.808(3)	0.536(5)	C(25)	0.629(3)	0.798(3)	1.098(5)
C(5)	0.750(3)	0.880(4)	0.485(6)	C(26)	0.586(4)	0.742(4)	1.185(4)
C(6)	0.714(3)	0.940(3)	0.413(5)	C(27)	0.506(3)	0.753(3)	1.210(4)
C(7)	0.648(2)	0.988(2)	0.457(3)	C(28)	0.448(2)	0.786(2)	1.120(2)
C(8)	0.335(2)	0.995(2)	0.460(2)				
$[W_2O_3(cocd)_2(Hcocd)_2]$							
W(1)	0.999 6	0.965 39(6)	1.000 5	C(11)	1.141(2)	0.883(2)	1.325(3)
W(2)	1.094 44(9)	0.796 48(7)	0.899 2(1)	C(12)	1.220(3)	0.924(3)	1.398(4)
O(1)	1.063(1)	0.891(1)	0.932(1)	C(13)	1.289(3)	0.891(3)	1.360(4)
O(2)	0.934(1)	0.998(1)	1.091(2)	C(14)	1.311(3)	0.957(3)	1.313(4)
O(3)	0.927(1)	0.884(1)	0.969(1)	C(15)	1.265(3)	1.018(3)	1.214(4)
O(4)	1.087(1)	1.014(1)	1.084(1)	C(16)	1.198(2)	1.040(2)	1.221(3)
O(5)	1.052(1)	0.887 3(9)	1.154(1)	C(17)	1.094(2)	0.643(3)	0.981(4)
O(6)	0.987(1)	1.025(1)	0.892(2)	C(18)	1.059(2)	0.693(2)	1.066(3)
O(7)	1.101(2)	0.690(1)	0.895(2)	C(19)	1.080(3)	0.674(3)	1.189(4)
O(8)	1.074(1)	0.768(1)	1.042(2)	C(20)	1.060(3)	0.578(3)	1.221(4)
O(9)	1.086(1)	0.802(1)	0.742(2)	C(21)	0.980(3)	0.557(3)	1.181(4)
O(10)	0.968(1)	0.783(1)	0.836(1)	C(22)	0.985(3)	0.523(3)	1.078(4)
O(11)	1.196(1)	0.818(1)	0.931(2)	C(23)	1.037(3)	0.498(3)	1.008(4)
C(1)	0.880(2)	0.942(2)	1.128(3)	C(24)	1.069(3)	0.575(3)	0.944(4)
C(2)	0.853(2)	0.900(2)	1.015(3)	C(25)	1.018(2)	0.773(2)	0.669(2)
C(3)	0.823(3)	0.816(3)	1.017(4)	C(26)	0.952(2)	0.808(2)	0.719(3)
C(4)	0.724(3)	0.844(2)	1.025(4)	C(27)	0.874(3)	0.781(3)	0.659(5)
C(5)	0.729(3)	0.823(2)	1.166(4)	C(28)	0.859(3)	0.706(3)	0.616(4)
C(6)	0.780(3)	0.863(3)	1.263(4)	C(29)	0.876(3)	0.705(3)	0.475(4)
C(7)	0.760(3)	0.939(3)	1.233(4)	C(30)	0.945(3)	0.703(3)	0.459(4)
C(8)	0.819(2)	0.981(2)	1.179(3)	C(31)	0.999(3)	0.743(3)	0.451(4)
C(9)	1.124(2)	0.997(2)	1.199(3)	C(32)	1.029(2)	0.796(2)	0.551(3)
C(10)	1.124(2)	0.911(2)	1.207(2)				

in these dimeric complexes is not very sensitive to the metal or to the terminal ligand, but is more dependent on the diolate ligands. The values of the W–O–W angles and O_b–W–O_t planes, in particular, are likely to vary with the diolate ligand. These differences may perhaps lead to different reactivities of the complexes in further reactions.

Experimental

The compound H_2chpd (Aldrich) was purified by sublimation; H_2cocd (Aldrich, 85%) was used without further purification. Solvents were purified by standard methods and stored over 4 Å molecular sieves. The complex [W(eg)(pin)$_2$] was prepared as described earlier;[11] [W(chpd)$_3$] and [W(cocd)$_3$] were prepared similarly with the corresponding diols instead of H_2pin. The IR spectra were measured on a Mattson Galaxy FTIR spectrometer as Nujol mulls, ^{1}H and ^{13}C NMR spectra on a JEOL GSX-400 spectrometer in $CDCl_3$. Tungsten was determined by gravimetric methods.

Preparations.—All reactions were carried out in Erlenmeyer flasks, which were connected to a water flask (1 cm^3 of water) by a U-shaped glass tube. The flasks were kept at room temperature and water vapour was allowed to diffuse into the alcohol solution.

[{WO(pin)(Hpin)}$_2$O]. The complex [W(eg)(pin)$_2$] (500 mg, 1.05 mmol) was dissolved in propan-2-ol (3.0 cm^3). Bright prismatic crystals formed during 2 d (yield 370 mg, 80%) at room temperature. They were decanted and washed with diethyl ether (5.0 cm^3). The product is soluble in alcohols and chloroform but insoluble in toluene or tetrahydrofuran (thf) (Found: C, 32.60; H, 5.80; W, 39.9. $C_{24}H_{50}O_{11}W_2$ requires C, 32.65; H, 5.70; W, 41.65%). IR: 1460s, 1366s, 1260w, 1221w, 1198m, 1142s (br), 1107m, 959s, 895s, 787s (br), 770s (br), 692s, 665m, 617s, 556m, 494m and 444w cm^{-1}. NMR ($CDCl_3$, $SiMe_4$ as internal standard); ^{1}H, δ 1.25–1.52 (m); ^{13}C, δ 23.0–26.5 (m, Me groups), 82.2 (COH) and 91.2–93.3 (3 peaks, COW).

[{WO(chpd)(Hchpd)}$_2$O]. The complex [W(chpd)$_3$] (300 mg, 0.32 mmol) was dissolved in methanol (2.0 cm^3). Bright prismatic crystals (190 mg, 77%) were separated by decantation after 2 d and washed with ether (5.0 cm^3). They are soluble in alcohols and $CHCl_3$ but insoluble in thf or toluene (Found: C, 36.35; H, 5.90; W, 38.9. $C_{28}H_{50}O_{11}W_2$ requires C, 36.15; H, 5.40; W, 39.50%). IR: 1346m, 1304w, 1244w, 1186w, 1078s (br), 1051s (br), 1042s (br), 964s, 937s, 897m, 847m, 787s (br), 752m, 679s (br), 644s, 575s, 501w and 473m cm^{-1}. NMR ($CDCl_3$, $SiMe_4$): ^{1}H, δ 1.53 (m), 1.97 (m), 3.60 (m) and 4.45–4.74 (m); ^{13}C, δ 24.0 (m, CH_2), 32.8 (m, CH_2), 79.2 (COH) and 89.5–93.8 (m, COW).

[{WO(cocd)(Hcocd)}$_2$O]. The complex [W(cocd)$_3$] (300 mg, 0.30 mmol) was dissolved in methanol (2.0 cm^3) and the solution kept for 3 d at room temperature. Bright prisms (195 mg, 80%) were separated and washed with ether (5.0 cm^3). They were soluble in alcohols and chloroform (Found: C, 39.65; H, 6.30; W, 36.9%. $C_{32}H_{58}O_{11}W_2$ requires C, 38.95; H, 5.95; W, 37.25%). IR: 1346m, 1269w, 1148w, 1109s, 1071s, 1020s (br), 986s (br), 959s (br), 907m, 791s (br), 729m, 669s (br), 631m and 571m cm^{-1}. NMR ($CDCl_3$, $SiMe_4$): ^{1}H, δ 1.52–1.63 (m), 2.50, 3.46, 3.58 and 4.75; ^{13}C, δ 22.6 (m, CH_2), 26.6 (m, CH_2), 32.0–37.0, 78.4 (COH) and 88.2–93.7 (m, COW).

Crystallography.—Crystal data for compounds **1**–**3**, along with other experimental details, are summarised in Table 3. The unit-cell parameters were determined by least-squares refinements from 25 carefully centred high-angle reflections measured at ambient temperature on a Rigaku AFC5S diffractometer using Mo-Kα radiation (λ = 0.710 69 Å). The data obtained were corrected for Lorentz and polarisation effects. Absorption corrections (DIFABS[19] for **1** and ψ scans for **2** and **3**) were also made. The intensity variations of three check reflections were negligible during the data collections.

The structure of complex **1** was solved by direct methods and subsequent Fourier syntheses. Least-squares refinements converged to an R value of 0.028 (R' = 0.031). Neutral atomic scattering and dispersion factors were taken from ref. 20. The heavy atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions with fixed thermal parameters, except OH hydrogen [H(25)] which was found from a Fourier map and was fixed to that position. The structure of **2** was solved by direct methods and refined in the same way to an R value of 0.038 (R' = 0.043). The heavy atoms were refined anisotropically. The hydrogen atoms were not included due to the high thermal parameters of the host atoms. The structure of **3** was solved by the Patterson method and refined to R = 0.053 (R' = 0.055). The tungsten and oxygen atoms were refined anisotropically and 15 carbon atoms isotropically. The rest of the carbon atoms had to be refined with fixed thermal parameters due to the disorder of the cyclooctane ring. The use of another enantiomer for **2** and **3** did not improve the R values. All calculations were performed using the TEXSAN[21] crystallographic software. Figures were drawn with ORTEP.[12] The final atomic positional coordinates are listed in Table 4.

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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