Preparation and crystal structures of oxoosmium(VI) diolato complexes

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Reaction of OsO$_4$ with one equivalent of PPh$_3$ in the presence of the tertiary diols, 2,3-dimethyl-2,3-butanediol (H$_2$pin) and 1,1′-bicyclohexane-1,1′-diol (H$_2$bicy), afforded the new oxoosmium(VI) complexes [OsO(diol)$_2$]. The molecular structures of [OsO(pin)$_2$], [OsO(bicy)$_2$] and its adduct [OsO(bicy)$_2$]·H$_2$bicy·PPh$_3$O were determined by X-ray crystallography.

Introduction

Metal oxo compounds are well known to play an important role in organic oxidations due to their ability selectively to attach oxygen atoms to carbon–carbon double bonds. Osmium tetraoxide is one of the most effective reagents for the stoichiometric and catalytic dihydroxylation of alkenes to give the corresponding vicinal *cis*-diols.[1] Some oxoosmium(VI) diolates *e.g.* the oxo-bridged complex [Os$_2$O$_4$(pin)$_2$] (pin = 2,3-dimethylbutane-2,3-diolate, pinacolate) and dinuclear pyridine complex [Os$_2$O$_4$(cot)(py)$_4$] (cot = cyclooctane-1,2,5,6-tetrolate) have been isolated from reaction mixtures, and are suggested to be major intermediates in these reactions.[2,3] Oxoosmium(VI) diolato complexes are usually prepared by osmylation of the corresponding alkene in non-aqueous solvents or by adding the diol to a basic aqueous solution of K$_2$OsO$_4$·2H$_2$O.[4] The reaction of osmium tetraoxide with an excess of diol has been also used in the preparation of [OsO(eg)$_2$] (eg = 1,2-ethanediolate, ethylene glycolate).[2]

Diolato complexes of osmium(VI) may also be of interest as starting materials for new organometallic compounds. For instance, [OsO(eg)$_2$] and [OsO(pin)$_2$] **1** react with dimethylzinc forming [OsOMe$_4$] and [OsO(pin)Me$_2$], respectively. In these examples, the constitution of the diolato ligand has been used to control the selectivity of alkylation.[5,6]

Although simple oxoosmium(VI) diolates are generally well characterised by chemical and spectroscopic methods,[2,7,8] only few crystal structures have been reported to date. The dimeric complex [Os$_2$O$_4$(pin)$_2$][9] and monomeric complex [OsO(eg)$_2$][10] have been structurally fully confirmed. Lattice parameters of **1** are also known, but a full determination of the structure has proved difficult due to molecular disorder.[11]

We have previously reported the preparation and crystal structures of several diolato complexes of hexavalent metals including [W(diol)$_3$], [W(diol)$_2$Cl$_2$] and [ReO(diol)$_2$].[12,13] In this paper we report reactions of OsO$_4$ with PPh$_3$ and diols as a new method of preparation of osmium(VI) oxodiolato complexes. The diols used were the ditertiary alcohols H$_2$pin and H$_2$bicy = 1,1′-bicyclohexane-1,1′-diol. Complexes **1**, [OsO(bicy)$_2$]·H$_2$bicy·Ph$_3$PO **2** and [OsO(bicy)$_2$] **3** were isolated. Crystal structures of all three compounds are reported and discussed.

Discussion

Preparation of complexes

One of the common procedures to prepare metal alkoxides and oxoalkoxides is by the reaction between appropriate alcohols and metal oxides.[14] Polymeric molybdenum and tungsten oxides react with a large excess of 1,2-ethanediol at high temperature.[15] Soluble molecular oxides, such as Re$_2$O$_7$, react readily with an excess of ditertiary diol in an inert solvent.[13] Several compounds Re^V and Re^{VI}, *e.g.* [ReCp*O(diol)][16] (Cp* = pentamethylcyclopentadienyl) and [ReO(diol)$_2$][13] have been prepared by condensation of a suitable rhenium oxo precursor compound with the diol followed by reduction with a tertiary phosphine in the latter case. We have now employed the same procedure in the preparation of analogous osmium oxodiolato complexes. Thus, addition of two equivalents of a ditertiary diol and one equivalent of PPh$_3$ to a solution of OsO$_4$ in dichloromethane leads to the reduction of Os^{VIII} to Os^{VI} and formation of the corresponding [OsO(diol)$_2$] complexes (Scheme 1). Comparable reductions of osmium tetraoxide with
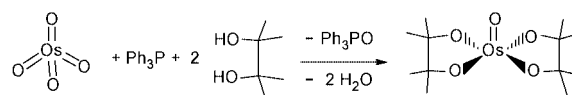
Scheme 1

tertiary phosphines in the presence of proton donors are known, *e.g.* in the OsO$_4$–PR$_3$–HCl system [OsO$_2$Cl$_2$(PR$_3$)$_2$] is produced.[17] Following removal of the volatile materials *in vacuo*, the pinacolato complex **1** was readily recrystallised from hexane as long black needles. Attempts to purify complex **3**, similarly by recrystallisation, led to precipitation of the adduct **2** as black, shiny prisms. Treatment of **2** with NaH allowed the isolation of monomeric complex **3** as black needles.

The ^{1}H NMR spectrum of complex **1** shows two singlets at δ 1.33 and 1.43 which are assigned to the axial and equatorial methyl group hydrogens of the pinacolato ligand respectively. The magnetic inequivalence of these methyl groups indicates the chelate ring to be non-labile on the NMR timescale since exchange of these sites would require dissociation followed by reco-ordination of the diolato group. The ^{13}C NMR spectrum of **1** consists of singlets at δ 24.18 and 24.89 assigned to the magnetically inequivalent methyl carbons and a singlet at δ 93.80 for the ring carbons of the pinacolato chelate. For compound **3** the ^{1}H NMR spectrum shows several multiplets due to the cyclohexyl rings between δ 1.10 and 1.90. The ^{13}C NMR spectrum shows five singlets between δ 21.77 and 32.73 for the cyclohexyl ring carbons and a singlet at δ 94.29 assigned to the oxygen-bonded carbon atoms.
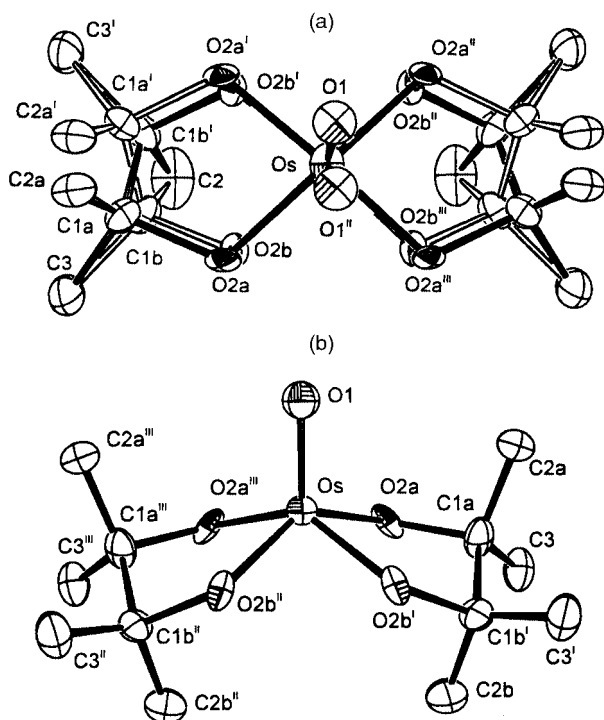
Fig. 1 (a) An ORTEP[18] view of complex **1** in the disordered position with 30% thermal ellipsoids showing the atom labelling scheme. Hydrogen atoms are not included and one half of all atoms and symmetry-related oxygens are labelled. Symmetry operations: I $1 - y$, $1 - x$, z; II $1 - x$, $1 - y$, z; III y, x, z. (b) An ORTEP view with 30% thermal ellipsoids showing the atom labelling system. Hydrogen atoms are not shown.
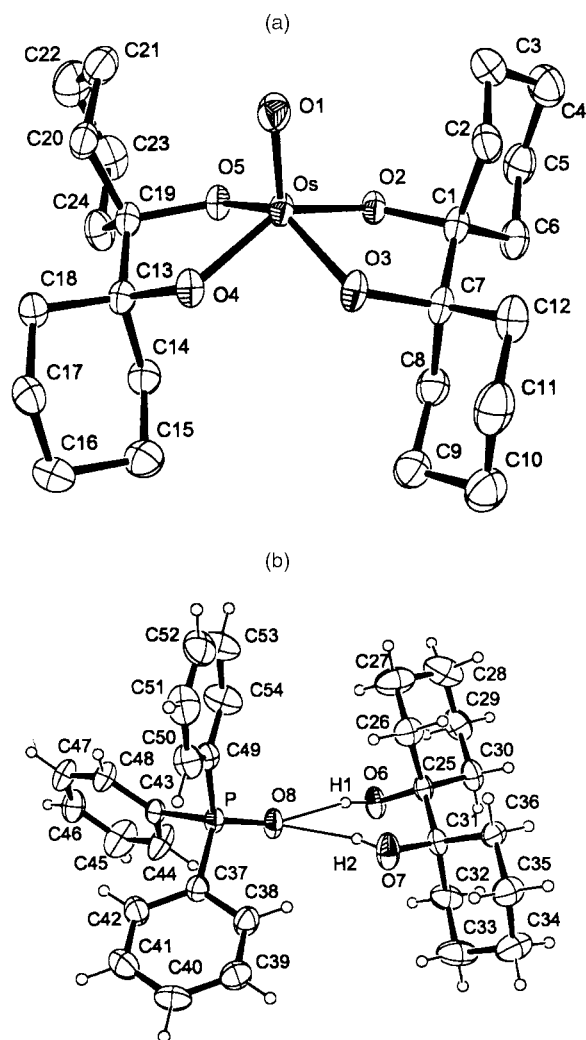
Fig. 2 (a) An ORTEP view of the osmium(VI) unit in complex **2** with 30% thermal ellipsoids showing the atom labelling system of the heavy atoms. (b) An ORTEP view of the triphenylphosphine oxide–diol unit with 30% thermal ellipsoids showing the atom labelling system of the heavy atoms and HO hydrogens.

Structural studies

The molecular structures of the bis-diolato-(O,O')oxo-osmium(VI) compounds **1**, **2** and **3** are presented in Fig. 1, 2 and 3; relevant bond distances and angles are collected in Table 1. Compound **1**, [OsO(pin)₂], is isostructural with [ReO(pin)₂] and exhibits similar disorder. In **1** the osmium(VI) cation is bonded to one oxo ligand and to two deprotonated pinacolato ligands forming a distorted square pyramid, the oxo ligand being in the axial site.

The disordered [OsO(pin)₂] molecule can reside on its position in the crystal either having the orientation **A** or **B** (Fig. 1) in a ratio 50 : 50. These orientations are related by rotation of 180° around the average Os=O axis. The overall results of this disorder are shown in Fig. 1(a) where the molecule having orientation **A** is described by those atoms connected by solid bond symbols and those atoms connected by unfilled bonds describe orientation **B**. The carbon atoms C2b and C3 are at the same position in both orientations. The actual molecule with C_s symmetry is shown in Fig. 1(b).

In both orientations the opposing diolato chelates are manifested by adopting λδ conformations simultaneously; the terminal oxygen O(1) also resides in two positions. The overall effect is that the sum of these two superimposed orientations results in two mutually perpendicular mirror planes. The atom labelling in Fig. 1(a) reflects this disorder. The λ conformation of the chelate ring is displayed by atoms O2a, C1a, C1b^I and O2b^I [torsion angle = −43(2)°], and the δ conformation by the atoms O2b, C1b, C1a^I and O2a^I [torsion angle = 43(2)°]. The atoms of the transoid diolato ligand connected by the solid (filled in) bonds (Fig. 1a) also define a δ conformation. One of two [OsO(pin)₂] molecules with a λδ conformation pair is shown in Fig. 1(b).

The square pyramidal co-ordination sphere of the osmium-(VI) atom in complex **1** is comparable to those of the related oxodiolates [OsO(eg)₂][10] and [Os₂O₄(pin)₂].[9] In [OsO(eg)₂],

however, the molecule has C_2 symmetry indicating that the ligand conformations around Os^{VI} are either λλ or δδ.

The co-ordination spheres of the isostructural d² [OsO(pin)₂] and d¹ [ReO(pin)₂] complexes are similar, although small structural differences are observed. In the osmium compound the O1–Os–O2 (a and b) angles are 111.6(7) and 109.5(9)° whereas the relevant O1–Re–O2 angles are 114.6(8) and 100.7(1)°.[13]

The asymmetric unit of complex **2** contains an [OsO(bicy)₂], a H₂bicy diol and a triphenylphosphine oxide molecule. The square pyramidal co-ordination sphere of the osmium(VI) atom (Fig. 2(a)) is similar to that of **1** and to that in the related [ReO(bicy)₂] complex and of the d² complex anion [TcO(cat)₂]⁻ (cat = catecolate).[19] The diolato ligands around the Os^{VI} adopt λδ conformations with a pseudo mirror plane in a molecule. The remaining part of the structure of **2** consists of a H₂bicy–triphenylphosphine oxide adduct associated by two hydrogen bonds as shown in Fig. 2(b). It is of interest that triphenylphosphine oxide has been shown to be a good crystallisation aid for many organic compounds;[20] the behaviour observed in compound **2** may be related to this property. The strength of the two hydrogen bonds appears to be moderate as the contacts between the hydrogen bonded oxygens are 2.802(5) and 2.886(6) Å respectively.

The structure of complex **3** is composed of three distorted square pyramidal osmium(VI) units similar to that in **2**. Fig. 3(a) shows the labelling system for the second molecule and the

Table 1 Selected bond lengths [Å] and angles [°] in complexes **1**, **2**, **3** and [ReO(bicy)₂]

	1[a]	**2**	**3**[b]	**3**[c]	[ReO(bicy)₂][d]
Os–O(1)	1.692(10)	1.672(3)	1.667(6)	1.672(6)	1.690(4)
Os–O(2)	1.891(10)	1.882(3)	1.889(5)	1.893(5)	1.900(3)
Os–O(3)	1.891(10)	1.899(3)	1.903(5)	1.909(5)	1.892(3)
Os–O(4)		1.902(3)	1.897(6)	1.898(5)	1.907(3)
Os–O(5)		1.892(3)	1.882(6)	1.904(5)	1.886(3)
O(1)–Os–O(2)	111.6(7)	109.39(15)	111.5(3)	109.2(3)	107.4(2)
O(1)–Os–O(3)	109.5(9)	110.56(16)	108.0(3)	111.4(3)	111.7(2)
O(1)–Os–O(4)		111.86(15)	114.8(3)	111.5(3)	105.3(2)
O(1)–Os–O(5)		108.51(17)	106.4(3)	108.4(3)	112.5(2)
O(2)–Os–O(3)	79.2(6)	82.14(14)	82.8(2)	82.2(2)	80.9(1)
O(2)–Os–O(4)	138.3(8)	138.75(14)	133.7(2)	139.3(2)	147.1(1)
O(2)–Os–O(5)	92.7(17)	85.56(13)	85.6(2)	85.0(2)	84.7(1)
O(3)–Os–O(4)	80.4(16)	82.95(14)	83.3(2)	83.5(2)	98.2(1)
O(3)–Os–O(5)		140.93(14)	145.6(3)	140.2(2)	135.8(1)
O(4)–Os–O(5)		82.32(13)	81.6(2)	82.2(2)	80.8(1)

[a] O2a = O2, O2b[I] = O3, O2b[II] = O4 and O2a[II] = O5. [b] For the first [OsO(bicy)] unit. [c] For the second [OsO(bicy)] unit, in which O(7) corresponds to O(1), O(8) to O(2), and so on. [d] See ref. 13.
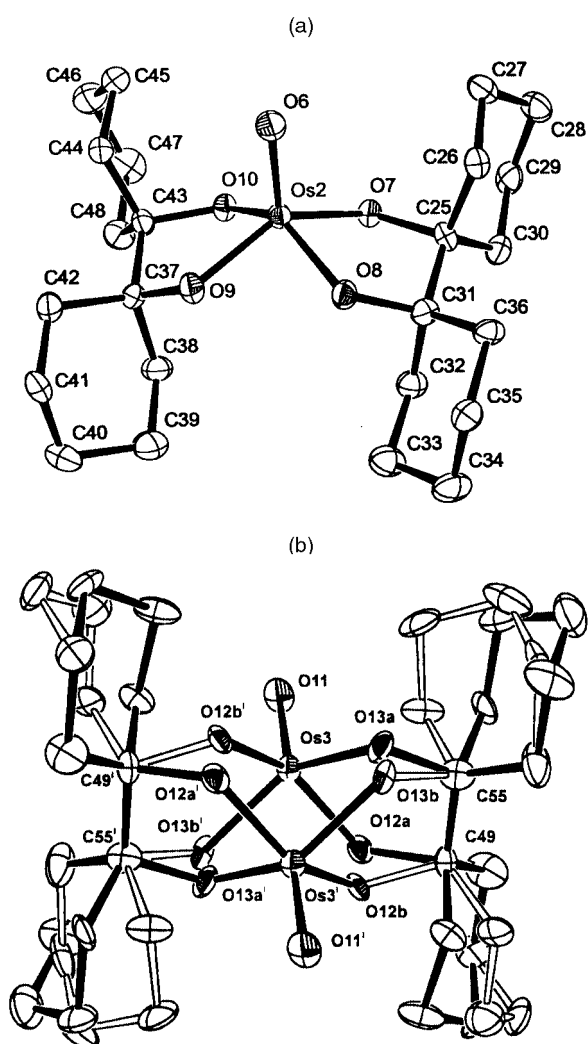

Fig. 3 (a) An ORTEP view of the second osmium(VI) unit in complex **3** with 30% thermal ellipsoids showing the heavy atom labelling system. (b) An ORTEP view of the disordered third unit 30% thermal ellipsoids showing partly the heavy atom labelling system. Symmetry operation: I = −x, 1 − y, 2 − z.

labelling system for the first molecule is the same as for **2** in Fig. 2(a). The third molecule is disordered and appears inverted around the centre of symmetry, the osmium atoms being split between two symmetry related sites of equal occupancy. The centrosymmetrically disordered structure is represented in Fig. 3(b). The orientations of the osmium centres are related by inverting Os3 and O11 over the centre of symmetry. This means that the diol must be rotated around the C49–C55 bond to get two different orientations for the diol. The diolato ligands related to one osmium orientation are described by those atoms connected by unfilled and solid bond symbols and the diol conformations are λ and δ. The reason for this disorder might be that the space for this molecule is large enough to allow two orientations.

In complex **3**, as well as in **1** and **2**, the diolato ligands around all osmium(VI) atoms adopt λδ conformations. The bond parameters of the co-ordination spheres of the three [OsO-(bicy)₂] units, one from **2** and the two from **3**, are compared in Table 1. This comparison shows that all units have similar, but not identical, bond parameters indicating some flexibility in the square pyramidal co-ordination sphere of the Os[VI]. The bond lengths in [ReO(bicy)₂] (Table 1) are also quite similar to the corresponding distances in **3** with the exception of the M–O bonds where Re–O1 is clearly longer than Os–O1.

Conclusion

Oxoosmium(VI) bis(diolato) complexes can be prepared from OsO₄ and tertiary diol in the presence of PPh₃. They form distorted square pyramidal structures with the oxo ligand at the top of the pyramid, and at least a pseudo mirror plane meaning that the ligand conformations are λδ or δλ.

Experimental

Preparations

[OsO(pin)₂] 1. The compounds OsO₄ (150 mg, 0.60 mmol) and H₂pin (150 mg, 1.30 mmol) were dissolved in 20 ml of dichloromethane. Triphenylphosphine (160 mg, 0.60 mmol) was added whereupon the solution turned black and the reaction mixture was stirred for two hours. Solvent was then evaporated and black residue extracted with hot hexane (20 ml).

Table 2 Crystal data and experimental details for complexes **1** to **3**

	1	**2**	**3**
Formula	$C_{12}H_{24}O_5Os$	$C_{54}H_{77}O_8OsP$	$C_{24}H_{40}O_5Os$
Formula weight	438.52	1075.33	598.76
Crystal system	Tetragonal	Triclinic	Triclinic
Space group (no.)	$P4_2nm$ (102)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a/Å	10.251(3)	15.055(5)	16.421(8)
b/Å	10.251(3)	15.899(8)	17.103(5)
c/Å	7.283(2)	12.677(5)	12.299(5)
α/°		107.08(4)	107.61(3)
β/°		96.18(3)	96.28(4)
γ/°		112.90(3)	67.01(3)
U/Å^3	765.3(3)	2585(2)	3031(2)
Z	2	2	5
μ(Mo-Kα)/cm^{-1}	83.40	25.48	52.90
T/K	294(2)	294(2)	294(2)
Measured reflections	446	9491	11092
Independent reflections	399	9113	10686
R(int)		2.34	3.57
$R1$ [$I > 2\sigma(I)$]	0.024	0.036	0.043
$wR2$ [$I > 2\sigma(I)$]	0.055	0.070	0.088

This solution was kept at $-20\,°C$ for four days until 150 mg (60%) of large black needles were separated (Found: C, 33.10; H, 5.50. $C_{12}H_{24}O_5Os$ requires C, 32.90; H, 5.50%). NMR (CDCl$_3$, standard SiMe$_4$): δ_H 1.33 (CH$_3$) and 1.43 (CH$_3$); δ_C 24.18 (CH$_3$), 24.89 (CH$_3$) and 93.80 (CO).

[OsO(bicy)$_2$]·H$_2$bicy·Ph$_3$PO 2. This complex was prepared similarly from 100 mg (0.40 mmol) of OsO$_4$, 180 mg (0.90 mmol) of H$_2$bicy and 110 mg of triphenylphosphine (0.40 mmol). From the hexane solution 260 mg of [OsO(bicy)$_2$]·H$_2$bicy·Ph$_3$PO (60% based on osmium) were precipitated as black, shiny prisms (Found: C, 60.80; H, 7.40. $C_{54}H_{77}O_8OsP$ requires C, 60.30; H, 7.20%).

[OsO(bicy)$_2$] 3. Sodium hydride (100 mg) was added to a black solution of complex **2** (200 mg in 10 ml of diethyl ether) and the mixture allowed to stand overnight. It was filtered, concentrated to 5 ml and kept at $-20\,°C$. After 2 d, 80 mg (72%) of black needles were separated (Found: C, 48.25; H, 6.70. $C_{24}H_{40}O_5Os$ requires C, 48.15; H, 6.75%). NMR (CDCl$_3$, standard SiMe$_4$): δ_H 1.10–1.90, several multiplets (CH$_2$); δ_C 21.77 (CH$_2$), 21.90 (CH$_2$), 25.73 (CH$_2$), 31.75 (CH$_2$), 32.73 (CH$_2$) and 94.29 (CO).

Crystallography

Crystal data for compounds **1**–**3** and other experimental details are summarised in Table 2. The unit cell parameters were determined by least-squares refinements from 20 carefully centred reflections measured at ambient temperature on a Rigaku AFC5S diffractometer using Mo-Kα radiation ($\lambda = 0.71069$ Å). The data obtained were corrected for Lorentz-polarisation effects. The intensity variations of three check reflections showed no decay for **1**, 1.8% decay for **2** and 2.2% decay for **3** during the data collections. These effects were corrected using linear correction factors. Absorption (ψ-scan)[22] corrections were also applied and a secondary extinction was taken into account for **1**. The coefficient was 0.0081(8).

The structures were solved by direct methods and subsequent Fourier syntheses. Data reduction and subsequent calculations were performed with TEXSAN for Windows.[23] The structures were refined on F^2 with SHELXL 97.[24] The heavy atoms refined anisotropically, and the hydrogen atoms included in calculated positions with fixed thermal parameters. In compound **1** O1 was refined isotropically and H atoms were not included. In the refinements of **3** the H atoms of the disordered part were not included. Compound **3** did not refine in a space group $P1$. Figures were drawn with ORTEP 3 for Windows.[18]

CCDC reference number 186/1551.

See http://www.rsc.org/suppdata/dt/1999/2785/ for crystallographic files in .cif format.

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