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Synthesis and characterisation of the platinum group mixed metal clusters $[Os_3M(\mu\text{-}H)_3(CO)_{12}]$ (M = Rh, Ir); the X-ray crystal structure of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$

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Abstract

The mixed-metal cluster $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**) has been prepared in 60% yield by the reaction of the co-ordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{12}]$ with the dimer $[(Rh(CO)_2Cl)_2]$. The analogous iridium complex $[Os_3Ir(\mu\text{-}H)_3(CO)_{12}]$ (**2**) is best prepared by the reaction of the anion $[Os_3H(CO)_{11}]^-$ with the labile cyclooctadiene complex $[(Ir(cod)Cl)_2]$, and is obtained in 40% yield. Both complexes **1** and **2** have been characterised by IR, ^1H NMR, and ESCA (Electron Spectroscopy for Chemical Analysis) spectroscopic techniques, and the structure of **1** has been confirmed by a single crystal X-ray analysis, which shows it to be isostructural with the known cobalt analogue $[Os_3Co(\mu\text{-}H)_3(CO)_{12}]$. Complex **1** crystallises in the triclinic space group $P\bar{1}$, with a 8.288(2), b 9.185(2), c 13.655(2) Å, α 82.26(2), β 80.10(1), γ 68.91(1)°, $Z = 2$; 2897 observed data with $F > 5\sigma(F)$ were refined by blocked-cascade least squares to $R = 0.055$ and $R_w = 0.058$.

Introduction

The chemistry of the platinum-group mixed metal clusters has been extensively developed over the past five years. However, the greater proportion of the studies have involved the lighter elements of the group [1], and clusters containing the heavier elements have been less extensively investigated. One route into the area of the mixed-metal clusters is via the co-ordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which can behave either as a Lewis acid [2] or as a Lewis base [3], and add a variety of mono- and dinuclear metal species to give tetra- and pentanuclear clusters, respectively, which contain a triosmium unit [4–11]. An alternative route into these systems, which has been less widely exploited, is the use of the anion $[Os_3H(CO)_{11}]^-$, which has previously been shown to add $[AuPR_3]^+$ fragment to give tetra- and pentanuclear mixed OsAu clusters [12]. We now report that either the unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ or the anion $[Os_3H(CO)_{11}]^-$ may be employed to synthesise the mixed clusters $[Os_3M(\mu\text{-}H)_3(CO)_{12}]$ (M = Rh (**1**), Ir (**2**)).

Structural studies on the mixed systems $[Os_3M(\mu\text{-}H)_3(CO)_{12}]$ (M = Co, Rh, Ir) make an interesting comparison with those on the related homometal systems $[M_4(\mu\text{-}H)_4(CO)_{12}]$ (M = Ru [13], Os [14]) and $[M_4(CO)_{12}]$ (M = Co [15], Rh [16], Ir [17]). The difference in the number and location of the hydrides between the homo- and heterometal systems (a requirement of an even electron count) may be reflected in the reactivity of these molecules. Also, the change from icosahedral to cubeoctahedral ligand polyhedral arrangements in going from Co to Ir in the $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) series has been attributed to both steric [18] and electronic [19] factors, and the comparison with the mixed systems may suggest which of these factors predominates.

Results and discussion

The reaction of the co-ordinatively unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with the dimer $[(Rh(CO)_2Cl)_2]$, in toluene, under a hydrogen atmosphere, affords a yellow precipitate, which was separated and washed with dichloromethane. An Electron Spectroscopy for Chemical Analysis (ESCA) study on the product showed that the elements Os, Rh, C, and O were present, and that the Os/Rh ratio was approximately 3/1. The IR spectrum of this yellow product in the ν(CO) region showed only the presence of terminal carbonyls, and the ^{1}H NMR spectrum showed only a singlet in the bridging hydride region (Table 1). On the basis of this data the complex was characterised as $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**).

With $[(Ir(COD)Cl)_2]$ (COD = cyclooctadiene), the reaction of $[(Ph_3P)_2N][Os_3H(CO)_{11}]$, in the presence of $Tl[PF_6]$, in dichloromethane under a hydrogen atmosphere, affords a red-orange product, which was treated in situ with carbon monoxide to give a microcrystalline product, which was recrystallised from a hexane/dichloromethane mixture. The IR and ^{1}H NMR spectra (Table 1) closely resembled that of **1**, and the ESCA spectrum showed an Os/Ir ratio of 3/1. This product was thus characterised as $[Os_3Ir(\mu\text{-}H)_3(CO)_{12}]$ (**2**).

The IR spectra of the two complexes **1** and **2** closely resemble each other, but differ from that observed for the cobalt analogue $[Os_3Co(\mu\text{-}H)_3(CO)_{12}]$ [9] which shows additional bands. However, the ^{1}H NMR spectra, in the hydride region, for all three complexes are essentially the same, and no fluxionality in the temperature

Table 1

Spectroscopic data for complexes **1** and **2**

	1	**2**
IR ν(CO)(cm^{-1})	2080s, 2050s, 2022m	2080s, 2050s, 2022m
in CH_2Cl_2	2000m	2000m
^{1}H NMR δ (ppm) in $CDCl_3$	−19.7(s)	−20.6(s)
ESCA	Os, Rh, C, O	Os, Ir, C, O
Metal ratio	Os/Rh 3/0.9	Os/Ir 3/0.9

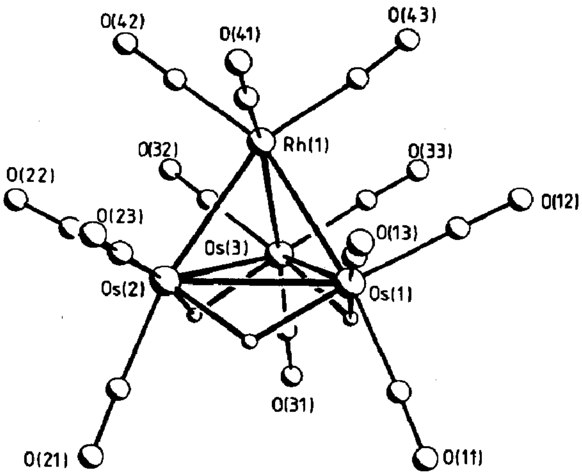

Fig. 1. The molecular structure of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (1) showing the atom numbering scheme.

range −85 to 30 °C is observed. It was not possible to obtain good quality ^{13}C NMR spectra for **1** and **2** because of solubility problems, and the fluxionality of the carbonyl groups in these complexes could not be investigated. The difference in the IR of the spectra between the complexes, however, may reflect the existence of a fast isomerisation process in the cobalt complex in which the exchange occurs too rapidly to be observed in the NMR spectrum.

In order to elucidate the molecular structure of **1**, and to establish whether it was similar to that of $[Os_3Co(\mu\text{-}H)_3(CO)_{12}]$ [9], a single-crystal X-ray analysis was undertaken. The structure of **1** is shown in Fig. 1 while bond parameters are listed in Table 2. The hydride ligands were not located directly, but their positions were assigned from potential energy calculations [20], and it is these positions that are shown in Fig. 1. Complex **1** is isostructural with that of the cobalt containing cluster [9]. The four metal atoms define a distorted tetrahedron, and the three hydrides bridge the three Os–Os edges. All twelve carbonyl ligands are terminally bound, three to each metal, and the average M–C–O angle of 177(3)° does not deviate significantly from linearity. The Os–Os distances in **1** (average 2.916(5) Å) are marginally longer than those in $[Os_3Co(\mu\text{-}H)_3(CO)_{12}]$ [9] (average 2.901(3) Å), and are somewhat shorter than the average of 2.964(3) Å for the hydride-bridged Os–Os edges in the parent cluster $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ [14]. However, all these distances are significantly longer than the Os–Os bond lengths (average 2.877(3) Å) in $[Os_3(CO)_{12}]$ [21], and this is consistent with the edge lengthening influence of the bridging hydrides. The carbonyl ligands also bend away from these bridged Os–Os edges, with an average *cis* Os–Os–C angle of 115(2)°, in keeping with the steric demands of the hydrides. The average Os–Rh distance in **1** of 2.763(2) Å is longer than the equivalent Os–Co distance of 2.694(3) Å in $[Os_3Co(\mu\text{-}H)_3(CO)_{12}]$ [9], and is also longer than the Os–Rh distances of 2.703(1) Å in the related complex $[Os_3Rh(\mu\text{-}H)_3(CO)_9(\eta^6\text{-}C_6H_5Me)]$ [22]. The Os–C(carbonyl) and Rh–C(carbonyl) bond lengths do not show any significant variation from each other, and have an average value of 1.92(3) Å. The high estimated standard deviations on these parameters precludes an accurate assessment of the bonding within these carbonyl units.

The ligand arrangement in the cluster $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**) is of interest. The $M(CO)_3$ units adopt an eclipsed conformation as observed in $[Os_3Co(\mu\text{-}$

Table 2

Bond lengths (Å) and bond angles (°) for **1**

Os(1)–Os(2)	2.923(1)	Os(1)–Os(3)	2.918(1)
Os(1)–Rh(1)	2.761(1)	Os(1)–C(11)	1.895(14)
Os(1)–C(11)	1.941(18)	Os(1)–C(13)	1.877(18)
Os(2)–Os(3)	2.908(1)	Os(2)–Rh(1)	2.761(1)
Os(2)–C(21)	1.907(20)	Os(2)–C(22)	1.929(15)
Os(2)–C(23)	1.920(21)	Os(3)–Rh(1)	2.766(1)
Os(3)–C(31)	1.932(16)	Os(3)–C(32)	1.900(15)
Os(3)–C(33)	1.919(21)	Rh(1)–C(41)	1.924(20)
Rh(1)–C(42)	1.922(15)	Rh(1)–C(43)	1.943(19)
C(11)–O(11)	1.139(19)	C(12)–O(12)	1.121(23)
C(13)–O(13)	1.190(25)	C(21)–O(21)	1.170(25)
C(22)–O(22)	1.138(19)	C(23)–O(23)	1.133(27)
C(31)–O(31)	1.129(21)	C(32)–O(32)	1.119(21)
C(33)–O(33)	1.143(26)	C(41)–O(41)	1.142(26)
C(42)–O(42)	1.143(21)	C(43)–O(43)	1.115(27)
Os(2)–Os(1)–Os(3)	59.7(1)	Os(2)–Os(1)–Rh(1)	58.0(1)
Os(2)–Os(1)–C(11)	114.6(5)	Os(2)–Os(1)–C(12)	147.1(5)
Os(2)–Os(1)–C(13)	98.2(5)	Os(3)–Os(1)–Rh(1)	58.2(1)
Os(3)–Os(1)–C(11)	115.4(5)	Os(3)–Os(1)–C(12)	96.4(6)
Os(3)–Os(1)–C(13)	148.7(4)	Rh(1)–Os(1)–C(11)	171.6(4)
Rh(1)–Os(1)–C(12)	90.8(5)	Rh(1)–Os(1)–C(13)	91.8(4)
C(11)–Os(1)–C(12)	95.6(7)	C(11)–Os(1)–C(13)	93.3(7)
C(12)–Os(1)–C(13)	92.6(8)	Os(1)–Os(2)–Os(3)	60.1(1)
Os(1)–Os(2)–Rh(1)	58.0(1)	Os(1)–Os(2)–C(21)	111.3(5)
Os(1)–Os(2)–C(22)	149.1(6)	Os(1)–Os(2)–C(23)	98.5(4)
Os(3)–Os(2)–Rh(1)	58.3(1)	Os(3)–Os(2)–C(21)	114.3(7)
Os(3)–Os(2)–C(22)	98.2(6)	Os(3)–Os(2)–C(23)	148.8(5)
Rh(1)–Os(2)–C(21)	168.7(6)	Rh(1)–Os(2)–C(22)	92.5(5)
Rh(1)–Os(2)–C(23)	91.6(5)	C(21)–Os(2)–C(22)	97.3(7)
C(21)–Os(2)–C(23)	93.9(9)	C(22)–Os(2)–C(23)	90.7(8)
Os(1)–Os(3)–Os(2)	60.2(1)	Os(1)–Os(3)–Rh(1)	58.0(1)
Os(1)–Os(3)–C(31)	117.3(5)	Os(1)–Os(3)–C(32)	145.4(6)
Os(1)–Os(3)–C(33)	95.8(5)	Os(2)–Os(3)–Rh(1)	58.2(1)
Os(2)–Os(3)–C(31)	115.9(6)	Os(2)–Os(3)–C(32)	95.2(7)
Os(2)–Os(3)–C(33)	146.3(5)	Rh(1)–Os(3)–C(31)	173.4(7)
Rh(1)–Os(3)–C(32)	89.0(6)	Rh(1)–Os(3)–C(33)	89.6(5)
C(31)–Os(3)–C(32)	94.5(8)	C(31)–Os(3)–C(33)	95.7(8)
C(32)–Os(3)–C(33)	93.7(8)	Os(1)–Rh(1)–Os(2)	63.9(1)
Os(1)–Rh(1)–Os(3)	63.7(1)	Os(1)–Rh(1)–C(41)	94.6(5)
Os(1)–Rh(1)–C(42)	157.6(5)	Os(1)–Rh(1)–C(43)	97.0(5)
Os(2)–Rh(1)–Os(3)	63.5(1)	Os(2)–Rh(1)–C(41)	96.4(6)
Os(2)–Rh(1)–C(42)	95.4(6)	Os(2)–Rh(1)–C(43)	156.9(5)
Os(3)–Rh(1)–C(41)	154.9(5)	Os(3)–Rh(1)–C(42)	100.2(5)
Os(3)–Rh(1)–C(43)	97.1(5)	C(41)–Rh(1)–C(42)	96.5(7)
C(41)–Rh(1)–C(43)	98.2(8)	C(42)–Rh(1)–C(43)	100.7(8)
Os(1)–C(11)–O(11)	177.0(17)	Os(1)–C(12)–O(12)	177.3(16)
Os(1)–C(13)–O(13)	176.1(13)	Os(2)–C(21)–O(21)	177.8(14)
Os(2)–C(22)–O(22)	178.0(16)	Os(2)–C(23)–O(23)	178.1(13)
Os(3)–C(31)–O(31)	178.6(21)	Os(3)–C(32)–O(32)	177.0(21)
Os(3)–C(33)–O(33)	178.9(16)	Rh(1)–C(41)–O(41)	174.2(18)
Rh(1)–C(42)–O(42)	178.7(18)	Rh(1)–C(43)–O(43)	174.5(15)

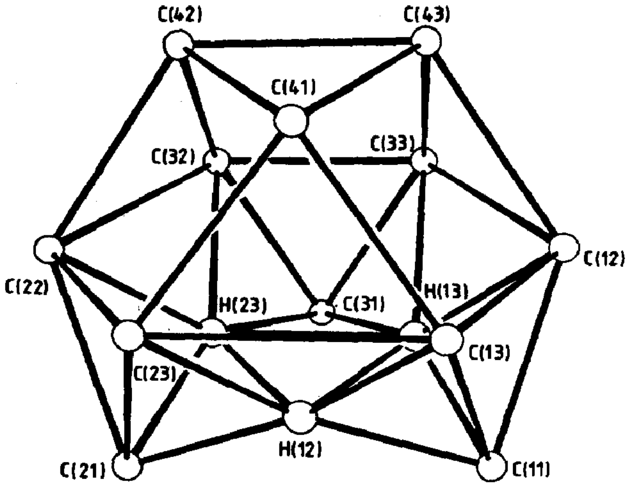

Fig. 2. The ligand packing arrangment in (**1**) drawn using the co-ordinates of the carbon and hydrogen atoms.

H)$_3$(CO)$_{12}$] [9] and [Ir$_4$(CO)$_{12}$] [17]. The inclusion of the three hydrides in the ligand polyhedron results in a 15-vertex polyhedron, the structure of which is shown in Fig. 2, a diagram drawn using the crystallographic co-ordinates of the carbon and hydrogen atoms. This arrangement does not correspond to the lowest energy arrangement for a 15-vertex polyhedron as predicted by Benfield and Johnson and observed is some hexanuclear rhodium clusters [23]. However, the introduction of the hydride ligands into the carbonyl packing may negate the simple packing arguments used to predict the ligand arrangements, although there is good evidence to suggest that a hydride has similar steric requirements to that of a carbonyl ligand [23]. Using the Föppl notation, the ligand arrangment in **1** may be described as a 3 : 6 : 3 : (3) polyhedron, which is generally reminiscent of the anticubeoctahedral packing arrangement in [Ir$_4$(CO)$_{12}$] [17] if the hydrides in **1** are ignored. From the electronic point of view, the fact that for **1** only one isomer is observed, and that isomer corresponds to the case where the hydrides bridge Os–Os edges only, may indicate that the increased Os–H bond strength over Rh–H bond strength may be an important factor in determining the ground state structure, and that packing forces involving the hydrides are of less significance.

The cluster [Os$_3$Rh(μ-H)$_3$(CO)$_{12}$] (**1**) readily undergoes substitution reactions with nucleophiles, in the presence of Me$_3$NO, which labilises a carbonyl ligand by oxidation. With excess cyclooctadiene (COD) (**1**) affords the product [Os$_3$RhH$_3$(COD)(CO)$_{10}$], while with an equimolar quantity of PPh$_3$, [Os$_3$RhH$_3$(PPh$_3$)(CO)$_{11}$] is obtained. These products have previously been synthesised by the direct reaction of substituted rhodium complexes with [Os$_3$(μ-H)$_2$(CO)$_{10}$], in moderate yield [24].

Experimental

All reactions were carried out under dry and oxygen-free atmospheres, by standard Schlenk techniques. The solvents were dried by molecular sieves and degassed prior to use. The progress of the reactions was monitored by IR spectroscopy, and TLC separation procedures were employed. IR spectra were run on a Perkin–Elmer PE 580 spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer, and the X-ray photoelectron spectra were recorded using an AEI MS 200 electron spectrometer. The starting materials used were either purchased or synthesised using literature techniques [25].

Preparation of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ *(1)*

In a typical reaction $[Os_3H_2(CO)_{10}]$ (100 mg, 0.12 mmol) and $[(Rh(CO)_2Cl)_2]$ (23 mg, 0.06 mmol) were mixed in toluene (10 cm^3), under an atmosphere of hydrogen. A yellow precipitate separated and the solution was centrifuged after stirring for 20 h. The precipitate was then washed twice with dichloromethane. The compound was recrystallised from a dichloromethane/hexane mixture, and crystals suitable for X-ray analysis obtained. Yield of compound **1** was 60%.

Preparation of $[Os_3Ir(\mu\text{-}H)_3(CO)_{12}]$ *(2)*

$Tl[PF_6]$ (22 mg) and $[(PPh_3)_2N]$ $[Os_3H(CO)_{11}[$ (94 mg) were mixed in dichloromethane solution, under a hydrogen atmosphere. $[(Ir(COD)Cl)_2]$ (27 mg) was added and the reaction mixture stirred for 4 h. The solution was then filtered and stirred

Table 3

Atomic co-ordinates ($\times 10^4$) for **1**

Atom	*x*	*y*	*z*
Os(1)	−141(1)	3786(1)	2846(1)
Os(2)	2005(1)	498(1)	2650(1)
Os(3)	3364(1)	2562(1)	3422(1)
Rh(1)	2800(2)	2866(1)	1453(1)
C(11)	−1991(20)	4136(19)	3916(11)
O(11)	−3104(19)	4283(19)	4556(10)
C(12)	−277(23)	5955(19)	2596(11)
O(12)	−354(20)	7210(14)	2491(10)
C(13)	−1609(22)	4000(20)	1891(11)
O(13)	−2620(19)	4153(20)	1330(11)
C(21)	1196(26)	−838(23)	3648(13)
O(21)	648(23)	−1618(16)	4264(11)
C(22)	4202(22)	−1047(19)	2183(14)
O(22)	5500(18)	−1979(15)	1935(12)
C(23)	924(24)	96(19)	1629(12)
O(23)	251(20)	−102(19)	1030(10)
C(31)	3555(24)	2225(20)	4831(12)
O(31)	3695(25)	2036(19)	5651(9)
C(32)	5748(21)	1392(20)	3027(14)
O(32)	7171(21)	737(19)	2822(13)
C(33)	3738(23)	4531(21)	3232(11)
O(33)	3956(20)	5706(15)	3135(10)
C(41)	1542(22)	2900(20)	390(13)
O(41)	878(21)	2976(19)	−291(10)
C(42)	5046(22)	1576(23)	864(12)
O(42)	6371(20)	805(19)	496(11)
C(43)	3009(23)	4940(20)	1119(12)
O(43)	3260(22)	6059(18)	892(11)

for 12 h under a carbon monoxide atmosphere, to give a precipitate of **2**. This precipitate was washed with dichloromethane, and recrystallised from dichloromethane/hexane to give a microcrystalline product. Yield of **2** 30 mg (40%).

Both compounds **1** and **2** exhibited low solubility in a range of solvents, and **2** decomposed if left in solution over a period of days. It was not possible to purify either of the compounds by TLC techniques since decomposition occurred on silica plates.

Substitution reactions of 1

A dichloromethane solution of **1** (10 mg) was treated with an excess of cyclooctadiene, in the presence of Me_3NO (1 cm^3), to afford $[Os_3RhH_3(COD)(CO)_{10}]$ (6 mg). The reaction of **1** (10 mg) with an equimolar amount of PPh_3, in dichloromethane afforded $[Os_3RhH_3(PPh_3)(CO)_{11}]$ (5 mg).

Structure determination of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (1)

Crystal data. $C_{12}H_3O_{12}Os_3Rh$, *M* 1 012.7, triclinic, *a* 8.288(2), *b* 9.185(2), *c* 13.655(2) Å, α 82.26(2), β 80.10(1), γ 68.91(1)°, *V* 952.4 $Å^3$ (by least-squares

Table 4

Anisotropic thermal parameters ($Å^2 \times 10^3$) for **1** [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	27(1)	28(1)	25(1)	−2(1)	−3(1)	−9(1)
Os(2)	30(1)	25(1)	28(1)	−1(1)	−3(1)	−12(1)
Os(3)	30(1)	29(1)	26(1)	0(1)	−7(1)	−12(1)
Rh(1)	31(1)	32(1)	20(1)	0(1)	−1(1)	−13(1)
C(11)	29(8)	45(9)	19(7)	−4(6)	8(6)	−1(7)
O(11)	50(8)	90(11)	37(7)	−10(7)	−5(7)	−7(8)
C(12)	51(11)	33(8)	25(8)	−13(6)	−4(7)	7(7)
O(12)	74(10)	33(6)	61(9)	−1(6)	1(7)	−23(6)
C(13)	35(9)	51(10)	23(7)	2(7)	2(7)	−20(7)
O(13)	50(8)	91(11)	51(8)	−6(8)	−14(7)	−24(8)
C(21)	54(11)	54(11)	33(9)	−11(8)	−13(8)	−14(9)
O(21)	101(12)	47(8)	61(9)	20(7)	4(8)	−38(8)
C(22)	33(9)	30(8)	56(10)	−8(7)	3(8)	−16(7)
O(22)	41(8)	39(7)	102(12)	−13(7)	19(7)	−10(6)
C(23)	49(10)	32(8)	37(9)	−4(7)	−4(8)	−22(7)
O(23)	67(10)	84(10)	52(8)	−2(7)	−16(7)	−48(9)
C(31)	54(11)	40(9)	26(8)	−2(7)	−8(7)	−17(8)
O(31)	117(14)	82(11)	21(6)	1(6)	−14(7)	−38(10)
C(32)	17(8)	42(9)	58(11)	11(8)	−16(7)	−11(7)
O(32)	65(11)	65(10)	91(12)	10(9)	−35(9)	−20(9)
C(33)	45(10)	48(10)	22(8)	−14(7)	−6(7)	−8(8)
O(33)	80(10)	38(7)	58(8)	5(6)	−20(7)	−32(7)
C(41)	34(9)	39(9)	39(9)	3(7)	4(7)	−10(7)
O(41)	81(11)	78(10)	38(7)	2(7)	−21(7)	−29(9)
C(42)	33(9)	66(12)	31(9)	−23(8)	20(7)	−17(8)
O(42)	56(9)	87(11)	49(8)	−7(7)	1(7)	−18(8)
C(43)	46(10)	36(9)	30(8)	2(7)	−1(7)	−14(8)
O(43)	88(12)	55(9)	70(10)	9(7)	−17(8)	−42(8)

[a] The temperature factor takes the form $\exp[-2\pi^2(h^2a^{\star 2}U_{11} + k^2b^{\star 2}U_{22} + \ldots 2klb^{\star}c^{\star}U_{23})]$.

refinement on diffractometer angles for 48 automatically centred reflections in the range $15 < 2\theta < 25°$, λ 0.71069 Å), space group $P\bar{1}$ (No. 2), $Z = 2$, D_x 3.32 g cm^{-3}, $F(000)$ 888. Orange multifaceted block. Crystal dimensions: 0.310 × 0.228 × 0.171 mm, μ(Mo-K_α) 208.38 cm^{-1}, μR 2.61.

Data collection and processing. Stoe-Siemens four-circle diffractometer, graphite monochromated Mo-K_α radiation, 24 step ω–θ scans with step width 0.04°, scan speeds 0.0133–0.0533° s^{-1}; 3503 reflections measured ($5 < 2\theta < 50°$, $\pm h$, $\pm k$, $+l$), 3351 unique [merging $R = 0.027$ after empirical absorption correction (max., min. transmission factors = 0.055, 0.022)], giving 2897 reflections with $F > 5\sigma(F)$. No significant variation in intensities of three standard reflections.

Structure analysis and refinement. Automatic centrosymmetric direct methods (SHELX76: EEES) for Os and Rh atom positions, followed by Fourier difference techniques for C and O atoms. Blocked-cascade least-squares with all non-hydrogen atoms anisotropic. Hydrides were not directly located. The weighting scheme $w = [\sigma^2(F_o) + 0.0012F_o^2]^{-1}$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.055 and 0.058. Programs and computers used are given in [10]. Final atomic co-ordinates and thermal parameters are listed in Tables 3 and 4, respectively. Copies of the structure factors tables may be obtained from the authors.

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