The Cluster Cation $[Os_4(CO)_{12}H_4(OH)]^+$:† Preparation and Crystal Structure

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The cluster cation $[Os_4(CO)_{12}H_4(OH)]^+$ has been prepared in high yields by the reaction of $[Os_4(CO)_{12}H_4]$ with NOX (X = NO_3, PF_6, BF_4, or Cl) in MeCN or CH_2Cl_2. The cation is also isolated as the $[Os(CO)_3(NO_3)_3]^-$ salt from the reaction with N_2O_4 in toluene. The salt $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ crystallises in the triclinic space group P_1, with cell dimensions a = 9.701(5), b = 11.504(6), c = 14.352(6) Å, α = 83.03(2), β = 84.79(2), γ = 85.38(2)°, and Z = 2. The structure has been solved by a combination of direct methods and Fourier-difference techniques and refined by blocked-cascade least squares to R = 0·037 for 5 538 observed reflections. The four osmium atoms in the cation define a ' butterfly ' configuration with two triangles sharing a common edge but which are not coplanar. The space above the butterfly is occupied by the OH group. The hydrido-ligands are not located directly but the carbonyl arrangement suggests that they bridge each of the four wing-tip–hinge Os–Os ' bonds.'

In recent papers we have described the synthesis and structure of the nitrosyl clusters $[Os_3(CO)_9(NO)_2]$ [1] and $[M_3(CO)_{10}H(\mu\text{-}NO)]$ (M = Ru or Os).[2] These have been found to react readily with a range of substrates under mild conditions to yield a range of cluster products. The tetrahydride $[Os_4(CO)_{12}H_4]$ undergoes reactions with substrates such as ethylene only under moderately vigorous conditions to yield organometallic clusters in low yield. It was with this in mind that we set out to prepare more reactive tetranuclear nitrosyl clusters.

In this paper we report the reaction of $[Os_4(CO)_{12}H_4]$ with NOX (X = NO_3, PF_6, BF_4, or Cl) to give $[Os_4(CO)_{12}H_4(OH)]^+$. No nitrosyl-containing species have, as yet, been characterised as products of this reaction. A single-crystal X-ray analysis of $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ has established the structural characteristics of this cation.

RESULTS AND DISCUSSION

The Reaction of $[Os_4(CO)_{12}H_4]$ *with* N_2O_4.—Dodecacarbonyltetrahydridotetraosmium, $[Os_4(CO)_{12}H_4]$, reacts in toluene with dinitrogen tetraoxide, N_2O_4, at room temperature or with liquid N_2O_4 at 0 °C to yield two products $[Os_4(CO)_{12}H_3(OH)]$ and $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$. In an independent experiment we have established that the neutral complex readily and irreversibly reacts with H^+ to form the same cluster cation [equation (1)]. The salt $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ is obtained as yellow tablets which are stable over long periods under nitrogen. The i.r. and ^1H Fourier-transform (F.t.) n.m.r. spectroscopic data are presented in Table 1. In the i.r. spectrum only bands which may be associated with terminally bound CO ligands are observed and an O–H stretching vibration appears at 3 365 cm^{-1}. The ^1H F.t. n.m.r. exhibits a single resonance at τ 25.05 (singlet) at 35 °C indicating that all four H ligands are in an equivalent environment at that temperature.

$$[Os_4(CO)_{12}H_3(OH)] \xrightarrow{+H^+} [Os_4(CO)_{12}H_4(OH)]^+ \quad (1)$$

The corresponding PF_6^-, BF_4^-, or Cl^- salts have been prepared from $[Os_4(CO)_{12}H_4]$ with NOX. We believe that in the reaction of $[Os_4(CO)_{12}H_4]$ with NOX the NO^+ species functions as an oxidant, a role well established.[3]

TABLE 1

Spectroscopic data for $[Os_4(CO)_{12}H_3(OH)]$ and $[Os_4(CO)_{12}H_4(OH)][Os_3(CO)_3(NO_3)_3]$

		$[Os_4(CO)_{12}H_3(OH)]$	$[Os_4(CO)_{12}H_4(OH)]$-$[Os_3(CO)_3(NO_3)_3]$
i.r.	ν(CO)	2 082s, 2 062vs, 2 014vs, 2 004 (sh), 1 994s, 1 980w [a]	2 129s, 2 108s, 2 100 (sh), 2 083vs, 2 071w, 2 047vs 2 020m [b]
	$\nu(NO_3)$		1 520s, 1 295s, 1 275vs, 1 000m, 990vs, 970s
	ν(OH)	Not observed	3 365m, br
^1H n.m.r. (τ) (at room temperature)		25.12(s) 24.02(s), 27.74(s) (2 : 1 ratio)	25.05(s) [c] *d*

[a] Acetone solvent. [b] Cyclohexane solvent. [c] CH_3I solvent. [d] No signal due to OH proton was observed.

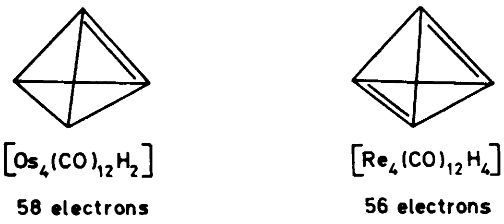
The initial reaction is therefore considered to be as in equation (2). The dication, which is expected to be

$$[Os_4(CO)_{12}H_4] + 2NOX \longrightarrow [Os_4(CO)_{12}H_4]X_2 + 2NO \quad (2)$$

strongly acidic, then undergoes proton dissociation to the basic solvent to yield $[Os_4(CO)_{12}H_2]$ [equation (3)].

$$[Os_4(CO)_{12}H_4]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Os_4(CO)_{12}H_3]^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Os_4(CO)_{12}H_2] \quad (3)$$

This neutral intermediate complex has not been observed or identified but as a 58-electron species may be represented (Scheme 1) as possessing an unsaturated cluster geometry related to $[Re_4(CO)_{12}H_4]$.[4] It is therefore expected to readily undergo reaction (oxida-



SCHEME 1

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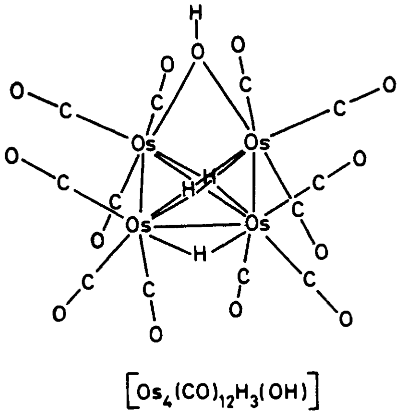
† Tetrahydrido-1,4-μ-hydroxo-tetrakis[tricarbonylosmium(I)] (3 *Os–Os*).

tive addition) to produce the more stable 60-electron species. The next step of the reaction is thereby visualised as (4). The compound $[Os_4(CO)_{12}H_3(OH)]$

$$[Os_4(CO)_{12}H_2] + H_2O \longrightarrow [Os_4(CO)_{12}H_3(OH)] \quad (4)$$



SCHEME 2

has been characterised as a reaction product but the source of water is difficult to explain. Considerable efforts were made to exclude water from the reaction but the same products were always obtained. This type of behaviour has been observed in other reactions of carbonyl clusters and it is tempting to speculate that sufficient water is generated by the reduction of CO. The final step, the protonation of $[Os_4(CO)_{12}H_3(OH)]$, has been established (see above) to give $[Os_4(CO)_{12}H_4(OH)]^+$.

The compound $[Os_4(CO)_{12}H_3(OH)]$ was identified on the basis of its mass spectrum and its i.r. and ^1H F.t. n.m.r. spectra, which are similar to the established compound $[Os_4(CO)_{12}H_3I]$;[5] it was not, as a consequence, examined further. Its structure, based on the known structure of the iodo-compound, is shown in Scheme 2.

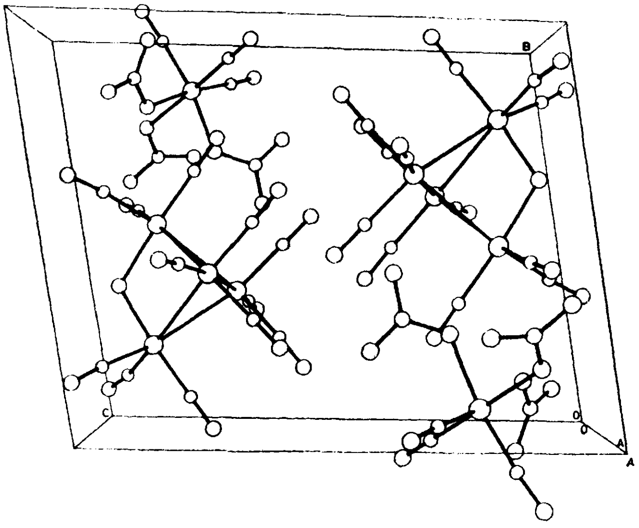


FIGURE 1 Molecular packing diagram of $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ projected on to the (100) plane

Structure of the Cluster Complex.—The salt $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ consists of discrete cationic and anionic species separated by typical van der Waals distances. A molecular packing diagram is shown in Figure 1. There is only one intermolecular contact significantly shorter than the sum of the van der Waals radii [O(6)–O′(10) **2.806 Å**, where O′(10) is generated from O(10) by the transformation $1 + x,y,z - 1$]. This may indicate the presence of a weak hydrogen bond between the hydroxyl group of the cation and a nitrate oxygen atom of the anion.

Interatomic distances and angles appear in Tables 2 and 3, respectively. Figure 2 shows the cation, Figure 3 the anion; both include the atom-numbering scheme adopted.

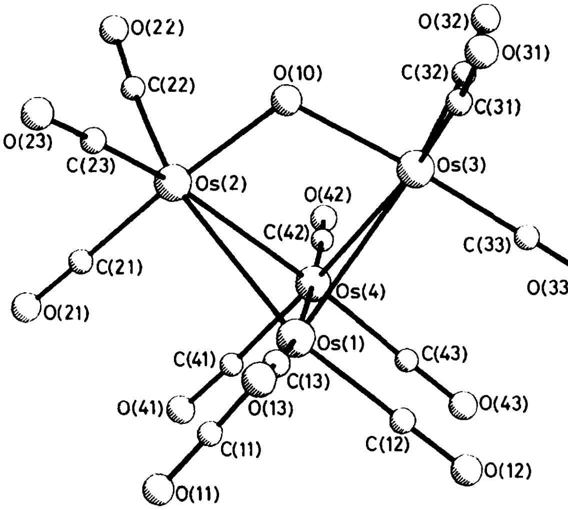


FIGURE 2 PLUTO plot of $[Os_4(CO)_{12}H_4(OH)]^+$

In the cation the four osmium atoms define a ' butterfly ' configuration in which two triangles share a common

TABLE 2

Bond lengths (Å)

Os(1)–Os(2)	3.045(2)	Os(3)–Os(4)	3.048(2)
Os(1)–Os(3)	3.033(2)	Os(2)–O(10)	2.080(7)
Os(1)–Os(4)	2.831(2)	Os(3)–O(10)	2.102(6)
Os(2)–Os(4)	3.025(2)	O(10)–Os(3)	2.102(6)
Os(1)–C(11)	1.906(11)	C(11)–O(11)	1.143(15)
Os(1)–C(12)	1.900(11)	C(12)–O(12)	1.150(14)
Os(1)–C(13)	1.907(13)	C(13)–O(13)	1.164(17)
Os(2)–C(21)	1.886(12)	C(21)–O(21)	1.145(16)
Os(2)–C(22)	1.914(11)	C(22)–O(22)	1.120(15)
Os(2)–C(23)	1.902(11)	C(23)–O(23)	1.143(15)
Os(3)–C(31)	1.907(12)	C(31)–O(31)	1.152(16)
Os(3)–C(32)	1.929(11)	C(32)–O(32)	1.126(14)
Os(3)–C(33)	1.890(11)	C(33)–O(33)	1.152(14)
Os(4)–C(41)	1.891(13)	C(41)–O(41)	1.148(16)
Os(4)–C(42)	1.889(13)	C(42)–O(42)	1.163(17)
Os(4)–C(43)	1.891(11)	C(43)–O(43)	1.151(14)
Os(5)–C(51)	1.863(14)	N(1)–O(1)	1.307(15)
Os(5)–C(52)	1.890(14)	N(1)–O(2)	1.199(16)
Os(5)–C(53)	1.863(13)	N(1)–O(3)	1.194(15)
C(51)–O(51)	1.190(19)	N(2)–O(4)	1.307(14)
C(52)–O(52)	1.148(17)	N(2)–O(5)	1.209(14)
C(53)–O(53)	1.121(18)	N(2)–O(6)	1.232(12)
Os(5)–O(1)	2.077(8)	N(3)–O(7)	1.291(15)
Os(5)–O(4)	2.089(7)	N(3)–O(8)	1.213(15)
Os(5)–O(7)	2.096(8)	N(3)–O(9)	1.219(16)

TABLE 3

Bond angles (°)

Os(2)–Os(1)–Os(3)	71.2(1)	Os(4)–C(43)–O(43)	179.7(12)
Os(2)–Os(1)–Os(4)	61.8(1)	Os(2)–Os(1)–C(11)	94.0(3)
Os(3)–Os(1)–Os(4)	62.5(1)	Os(3)–Os(1)–C(11)	153.5(4)
Os(1)–Os(2)–Os(4)	55.6(1)	Os(4)–Os(1)–C(11)	91.3(4)
Os(1)–Os(3)–Os(4)	55.5(1)	Os(2)–Os(1)–C(12)	154.1(4)
Os(1)–Os(4)–Os(2)	62.5(1)	Os(3)–Os(1)–C(12)	92.2(4)
Os(1)–Os(4)–Os(3)	62.0(1)	Os(4)–Os(1)–C(12)	93.0(4)
Os(2)–Os(4)–Os(3)	71.3(1)	Os(2)–Os(1)–C(13)	111.3(3)
Os(1)–Os(2)–O(10)	83.0(2)	Os(3)–Os(1)–C(13)	113.1(4)
Os(4)–Os(2)–O(10)	81.7(2)	Os(4)–Os(1)–C(13)	172.4(3)
Os(1)–Os(3)–O(10)	82.9(2)	Os(1)–Os(2)–C(21)	95.2(3)
Os(4)–Os(3)–O(10)	80.8(2)	Os(4)–Os(2)–C(21)	92.8(3)
C(21)–Os(2)–O(10)	174.2(4)	Os(1)–Os(2)–C(22)	162.3(3)
C(22)–Os(2)–O(10)	87.0(4)	Os(4)–Os(2)–C(22)	108.6(3)
C(23)–Os(2)–O(10)	95.3(4)	Os(1)–Os(2)–C(23)	104.3(3)
C(31)–Os(3)–O(10)	91.3(4)	Os(4)–Os(2)–C(23)	159.8(3)
C(32)–Os(3)–O(10)	90.0(4)	Os(1)–Os(3)–C(31)	108.7(3)
C(33)–Os(3)–O(10)	176.1(4)	Os(4)–Os(3)–C(31)	162.9(3)
Os(2)–O(10)–Os(3)	115.5(3)	Os(1)–Os(3)–C(32)	159.8(4)
C(11)–Os(1)–C(12)	92.8(5)	Os(4)–Os(3)–C(32)	104.8(4)
C(11)–Os(1)–C(13)	92.5(5)	Os(1)–Os(3)–C(33)	94.3(3)
C(12)–Os(1)–C(13)	93.3(5)	Os(4)–Os(3)–C(33)	95.4(4)
C(21)–Os(2)–C(22)	93.3(5)	Os(1)–Os(4)–C(41)	92.6(4)
C(21)–Os(2)–C(22)	93.3(5)	Os(2)–Os(4)–C(41)	92.1(3)
C(21)–Os(2)–C(23)	90.5(5)	Os(3)–Os(4)–C(41)	153.8(4)
C(22)–Os(2)–C(23)	91.1(5)	Os(1)–Os(4)–C(42)	173.9(3)
C(31)–Os(3)–C(32)	90.3(5)	Os(2)–Os(4)–C(42)	112.9(3)
C(31)–Os(3)–C(33)	92.2(5)	Os(3)–Os(4)–C(42)	113.2(4)
C(32)–Os(3)–C(33)	91.7(5)	Os(1)–Os(4)–C(43)	91.8(4)
C(41)–Os(4)–C(42)	91.7(5)	Os(2)–Os(4)–C(43)	154.1(5)
C(41)–Os(4)–C(43)	92.8(5)	Os(3)–Os(4)–C(43)	94.1(4)
C(42)–Os(4)–C(43)	92.4(5)	Os(1)–C(11)–O(11)	177.9(11)
Os(2)–C(21)–O(21)	179.2(8)	Os(1)–C(12)–O(12)	178.5(13)
Os(2)–C(22)–O(22)	171.8(12)	Os(1)–C(13)–O(13)	177.6(10)
Os(2)–C(23)–O(23)	176.4(11)	Os(3)–C(31)–O(31)	174.0(9)
Os(4)–C(41)–O(41)	176.9(10)	Os(3)–C(32)–O(32)	175.8(9)
Os(4)–C(42)–O(42)	175.8(11)	Os(3)–C(33)–O(33)	176.7(11)
C(51)–Os(5)–C(52)	90.0(6)	C(51)–Os(5)–O(1)	171.2(5)
C(51)–Os(5)–C(53)	90.5(6)	C(51)–Os(5)–O(4)	90.1(4)
C(52)–Os(5)–C(53)	91.0(6)	C(51)–Os(5)–O(7)	95.6(5)
Os(5)–C(51)–O(51)	175.4(11)	C(52)–Os(5)–O(1)	96.2(5)
Os(5)–C(52)–O(52)	175.5(12)	C(52)–Os(5)–O(4)	97.1(4)
Os(5)–C(53)–O(53)	178.6(13)	C(52)–Os(5)–O(7)	173.2(5)
Os(5)–O(1)–N(1)	124.1(7)	C(53)–Os(5)–O(1)	95.7(5)
Os(5)–O(4)–N(2)	122.3(6)	C(53)–Os(5)–O(4)	171.9(5)
Os(5)–O(7)–N(3)	122.1(7)	C(53)–Os(5)–O(7)	93.0(5)
O(1)–Os(5)–O(5)	82.8(3)	O(1)–N(1)–O(2)	116.4(11)
O(1)–Os(5)–O(7)	77.9(3)	O(1)–N(1)–O(3)	119.4(11)
O(4)–Os(5)–O(7)	78.9(3)	O(2)–N(1)–O(3)	124.1(13)
O(4)–N(2)–O(5)	120.1(9)	O(7)–N(3)–O(8)	120.5(11)
O(4)–N(2)–O(6)	116.3(9)	O(7)–N(3)–O(9)	117.0(10)
O(5)–N(2)–O(6)	123.6(11)	O(8)–N(3)–O(9)	122.5(13)

edge but are not coplanar. The dihedral angle between the two triangles is 82.3°. There is no direct metal–metal bond across the 'wing-tips' [Os(2) · · · Os(3) 3.537 Å], but the tips are bridged by a hydroxyl group. Each Os atom is also bonded to three terminal carbonyl ligands. Although the hydrides were not located in the structure determination the carbonyl arrangement suggests that the hydrogen atoms bridge the four Os(hinge)–Os(wing-tip) bonds.

The osmium atom in the anion displays octahedral co-ordination with *cis* ligand–Os–ligand angles in the range 77.9—97.1°. The arrangement of the ligands around the metal defines the *fac* geometrical isomer. The three carbonyl ligands are linear and the unidentate nitrate groups are planar at nitrogen.

Cationic transition-metal clusters are relatively uncommon and there has been no previous report of a structurally characterised cationic osmium cluster. There is only one example of a tetranuclear osmium complex which displays the 'butterfly' geometry[5] although several ruthenium species have been reported.[6] In $[Os_4(CO)_{12}H_3I]$ [5] the 'hinge' Os–Os bond is bridged by a hydride. The metal–metal distance of 2.927(4) Å is significantly longer than the value found in the present cation, which suggests that this bond is not hydride-bridged. This 'hinge' bond is also shorter than the unbridged Os–Os bond length of 2.876(1) Å in the iodide and is similar in length to the average value of 2.816 Å found for the unbridged edges in $[Os_4(CO)_{12}H_4]$.[7] The four Os(hinge)–Os(wing-tip) distances have an average length of 3.038(11) Å which is in good agreement with the value of 3.052(1) Å for the long hydride-bridged bonds in $[Os_4(CO)_{12}H_3I]$.[5] The *cis* Os–Os–C(carbonyl) angles involving the long Os–Os edges have a mean value of 110(4)° which compares well with the similar bonds in the iodide,[5] and are significantly wider than the *cis* Os–Os–C angles involving the hinge bond in our cation [mean 92(1)°]. It has been shown [8] for a large number of cluster compounds that a lengthening of metal–metal bonds and a widening of Os–Os–C angles is indicative of hydrides bridging the metal–metal edges. In the present complex the Os–H–Os systems are best considered as three-centre two-electron bonds and there may be little direct Os–Os interaction.

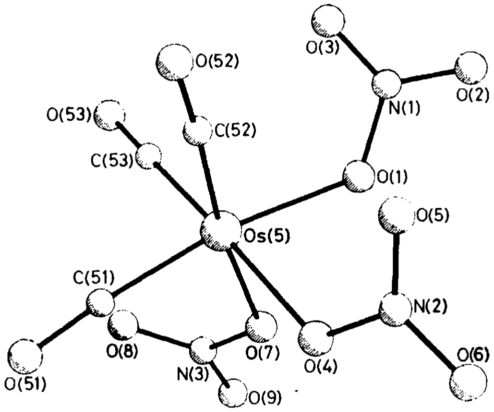


FIGURE 3 PLUTO plot of $[Os(CO)_3(NO_3)_3]^-$

The distribution of the hydride ligands in $[Os_4(CO)_{12}H_4(OH)]^+$ differs from that in $[Os_4(CO)_{12}H_3I]$.[5] Now all the hydrides bridge Os(hinge)–Os(wing-tip) edges and the Os(hinge)–Os(hinge) bond is unbridged. The reason for this 'hydride migration' is unclear but the ligand polyhedron in $[Os_4(CO)_{12}H_4(OH)]^+$ is more symmetric than would be the case if the Os(hinge)–Os(hinge) bond and three Os(hinge)–Os(wing-tip) edges were bridged.

The hydroxyl group bridges the two wing-tip Os atoms symmetrically within experimental error [mean 2.091(16) Å]. This length is similar to the average Os–O distance of 2.06(2) Å in $[Os_4(CO)_{12}O_4]$ [9] where the oxygen atoms, which act as four-electron donors, cap triangular faces of the tetrahedron and there is no direct metal–metal bonding. As with bridging iodine in $[Os_4(CO)_{12}H_3I]$, the hydroxyl group in the present cation acts as a three-electron donor. This gives a 62-electron system, with two more electrons than is required for the ' closed-shell ' 60-electron system of $[Os_4(CO)_{12}H_4]$. In these clusters an additional pair of electrons results in the breaking of a metal–metal bond to give the open ' butterfly ' metal geometry.

The carbonyl ligands are all approximately linear with an average Os–C–O angle of 177(2)°. The Os–C and C–O distances do not vary significantly from their respective means of 1.90(1) and 1.15(1) Å. These values agree with the average Os–C distance of 1.901 Å and C–O distance of 1.145 Å in the iodide.[5] The light-atom positions have not been located with sufficient accuracy, because of the dominance of the heavy metal atoms in the *X*-ray scattering, to ascertain the exact nature of the bonding in the complex or the *trans* influence of the hydroxyl group compared to a carbonyl group or another metal atom.

The anion obeys the ' 18-electron rule ' with each carbonyl ligand donating two electrons and each nitrate group one. The average Os–C and C–O distances of 1.872(16) and 1.169(30) Å are respectively shorter and longer than the corresponding distances in the cluster cation. The carbonyls are essentially linear and the average Os–C–O angle is 177(2)° as found in the cation. The Os–O(nitrate) bonds have an average length of 2.087(9) Å which suggests that there is little multiple bonding. This distance is similar to the value of the Os–O bond [2.09(1) Å] in $[Os_3(CO)_9H_2(\mu_2\text{-}OC_6H_3CH_2\text{-}Ph)]$ [10] where the oxygen ligand is also *trans* to a carbonyl group. The mean value for the Os–O–N angle is 123(1)°. The nitrogen atoms display the expected sp^2 hybridisation with only small deviations from the idealised O–N–O angle of 120°. The N–O(Os) bond lengths [mean 1.302(9) Å] are significantly longer than the remaining six N–O bonds [mean 1.211(14) Å]. These latter distances are indicative of N–O multiple bonding.

EXPERIMENTAL

All operations were carried out under a nitrogen atmosphere. Solvents were distilled over drying agents and saturated with purified nitrogen.

Reactions of $[Os_4(CO)_{12}H_4]$.—*With* N_2O_4. Dinitrogen tetraoxide (*ca.* 8 cm³) was added to $[Os_4(CO)_{12}H_4]$ (100 mg) at 0 °C. After stirring for 2 h the excess of N_2O_4 was removed and the buff-coloured residue crystallised from acetone. Yield 90% (Found: C, 11.5; H, 0.5; N, 2.65. Calc. for $C_{15}H_5N_3O_{25}Os_5$: C, 11.5; H, 0.5; N, 2.60%).

With N_2O_4 *in toluene*. Liquid N_2O_4 (*ca.* 10 cm³) was added to a suspension of $[Os_4(CO)_{12}H_4]$ (100 mg) in toluene (60 cm³) at 0 °C. After stirring for 5 h the solvent was removed. The residue was extracted with hot hexane which, after separation by t.l.c. yielded $[Os_4(CO)_{12}H_3(OH)]$, yield 5% [Found: C, 13.0; H, 0.50%; *M* (mass spectral) 1 117. Calc. for $C_{12}H_4O_{13}Os_4$: C, 13.0; H, 0.35%; *M* 1 117]. The hexane-insoluble residue was crystallised from dichloromethane–hexane to give $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$, yield 90%.

With $[NO][PF_6]$. To a suspension of $[Os_4(CO)_{12}H_4]$ (50 mg) in MeCN (30 cm³) was added $[NO][PF_6]$ (8 mg). After stirring for 3 h the solvent was removed *in vacuo* and the product crystallised from CH_2Cl_2–Et_2O. Yield 90% (Found: C, 11.5; H, 0.50. Calc. for $C_{12}H_5F_6O_{13}Os_5P$: C, 11.4; H, 0.40%).

With [NO]Cl. To a suspension of $[Os_4(CO)_{12}H_4]$ (50 mg) in CH_2Cl_2 (50 cm³) was added a solution of [NO]Cl (2.5 cm³) in CH_2Cl_2 (40 cm³). The reaction was monitored by i.r. spectroscopy and the addition of [NO]Cl solution stopped when all $[Os_4(CO)_{12}H_4]$ had disappeared. The solvent was removed *in vacuo* and the brown residue dissolved in CH_2Cl_2. After filtration through Kieselguhr the solvent was partially removed *in vacuo*. On addition of Et_2O white microcrystals of the product were obtained, yield 70% (Found: C, 12.3; H, 0.55. Calc. for $C_{12}H_5ClO_{13}Os_4$: C, 12.5; H, 0.45%).

X-*Ray Structural Analysis*.—Yellow tablets of $[Os_4(CO)_{12}H_4(OH)][Os(CO)_3(NO_3)_3]$ were obtained from dichloromethane–hexane. Intensities were recorded on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation, a θ—2θ scan technique, and a single crystal of overall dimensions 0.192 × 0.128 × 0.080

TABLE 4

Atom co-ordinates ($\times 10^4$)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Os(1)	4 972(1)	3 984(1)	7 332(1)
Os(2)	3 404(1)	2 117(1)	8 692(1)
Os(3)	2 488(1)	5 192(1)	8 304(1)
Os(4)	2 303(1)	3 516(1)	6 898(1)
C(11)	5 832(12)	2 886(10)	6 569(7)
O(11)	6 382(10)	2 223(9)	6 129(6)
C(12)	5 121(13)	5 283(11)	6 320(8)
O(12)	5 233(10)	6 080(9)	5 718(6)
C(13)	6 689(13)	4 229(11)	7 796(8)
O(13)	7 741(11)	4 337(9)	8 092(7)
C(21)	4 109(12)	845(10)	8 080(8)
O(21)	4 524(10)	66(9)	7 713(6)
C(22)	1 942(12)	1 244(10)	9 398(8)
O(22)	1 100(11)	812(9)	9 892(7)
C(23)	4 603(12)	1 602(10)	9 681(8)
O(23)	5 323(10)	1 233(9)	10 265(6)
C(31)	3 123(12)	5 982(10)	9 231(9)
O(31)	3 457(10)	6 384(8)	9 851(6)
C(32)	591(12)	5 553(10)	8 746(8)
O(32)	−512(9)	5 701(8)	9 043(6)
C(33)	2 489(12)	6 583(10)	7 384(8)
O(33)	2 557(10)	7 432(9)	6 828(6)
C(41)	3 029(13)	2 349(11)	6 174(8)
O(41)	3 451(11)	1 603(9)	5 768(7)
C(42)	462(13)	3 202(11)	6 746(8)
O(42)	−639(11)	2 953(9)	6 625(7)
C(43)	2 340(13)	4 733(11)	5 827(8)
O(43)	2 359(11)	5 476(9)	5 176(7)
O(10)	2 508(7)	3 578(6)	9 251(4)
Os(5)	11 430(1)	1 146(1)	2 670(1)
C(51)	11 996(15)	−239(12)	2 195(9)
O(51)	12 361(12)	−1 077(10)	1 830(7)
C(52)	12 875(14)	846(12)	3 496(9)
O(52)	13 726(11)	590(10)	4 015(7)
C(53)	10 224(15)	318(13)	3 587(8)
O(53)	9 476(14)	−168(11)	4 130(8)
N(1)	10 901(13)	3 134(10)	3 800(8)
O(1)	10 780(9)	2 809(7)	2 984(5)
O(2)	10 707(15)	4 171(9)	3 825(8)
O(3)	11 256(17)	2 413(11)	4 452(7)
N(2)	13 409(11)	2 895(8)	1 643(6)
O(4)	12 541(8)	2 129(7)	1 527(5)
O(5)	13 852(11)	2 857(9)	2 409(6)
O(6)	13 764(9)	3 604(8)	932(6)
N(3)	8 949(12)	995(10)	1 615(8)
O(7)	9 869(8)	1 692(7)	1 739(6)
O(8)	8 988(13)	−25(10)	2 015(7)
O(9)	8 033(12)	1 421(10)	1 106(8)

mm. Unit-cell dimensions were determined from the angular measurements of 25 strong reflections in the range $15 < 2\theta < 25°$. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were omitted, where I_t is the intensity at the top of the peak and I_b the mean background. Data were collected with a constant scan speed of 0.05° s^{-1} and a variable reflection width [θ range of $(0.80 + 0.05\tan\theta)°$]. The background measurement time was proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan. The $10\bar{3}$, $\bar{1}\bar{1}3$, and 330 reflections were measured at 6-h intervals throughout the data collection and showed no significant variation in intensity. Data were corrected for Lorentz polarization factors and $\sigma^2(I)$ was calculated as the sum of the variance due to counting statistics and $(0.03I)^2$. Semiempirical absorption corrections were applied based on a pseudo-ellipsoid model; six parameters were refined to minimise the variation in intensity of 18 strong reflections and their symmetry equivalents measured at various azimuthal settings. The value of R for the 436 data decreased from 0.144 before correction to 0.043 after: for the full data set the transmission factors ranged from 0.753 to 0.406. A total of 10 866 intensities was measured out to $2\theta_{max.} = 60°$; equivalent reflections were averaged to give 5 549 unique data with $F > 5\sigma(F)$.

Crystal data. $[C_{12}H_3O_{13}Os_4][C_3N_3O_{12}Os]$, $M = 1\,576.21$, Triclinic, $a = 9.701(5)$, $b = 11.504(6)$, $c = 14.352(6)$ Å, $\alpha = 80.03(2)$, $\beta = 84.79(2)$, $\gamma = 85.38(2)°$, $U = 1\,567.6$ Å^3, $Z = 2$, $D_c = 3.338$ g cm^{-3} (D_m not measured), $F(000) = 1\,375.51$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 202.77 cm^{-1}, space group $P\bar{1}$ from successful structure refinement.

The five Os atoms in the asymmetric unit were located by multisolution Σ_2 sign expansion, and all the non-hydrogen atoms from a subsequent difference synthesis. The structure was refined by blocked-cascade least squares, with anisotropic thermal parameters assigned to the Os atoms and the N and O atoms of the nitrate groups, and individual isotropic temperature factors for the carbonyl C and O atoms. An empirical extinction parameter x refined to 0.000 18(2), where F_c is multiplied by $[1 - (0.000\,1\,xF_c^2/\sin\theta)]$. In the final stages of refinement 11 low-angle reflections which were considered to suffer from severe extinction were zero weighted and a weighting scheme of the form $w = 1/\sigma^2F$ introduced. With this scheme $w\Delta^2$ was fairly independent of $|F_o|$ and $\sin\theta$. In the final cycle of refinement the mean shift-to-error ratio was 0.002, and the residuals on the 5 538 reflections were R 0.037 and $R' = 0.040$ $(=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|)$. A final difference synthesis did not reveal the positions of the hydrogen atoms.

Complex neutral-atom scattering factors [11] were employed. Table 4 lists the final atomic positional parameters, while details of temperature factors, molecular planes, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22706 (36 pp.).* After initial data processing on the ICL computer at North London Polytechnic, all the computing was carried out on the IBM 370/165 computer at the University of Cambridge, using programs written by Professor G. M. Sheldrick. The diagrams were drawn using the PLUTO program written by Dr. W. D. S. Motherwell.

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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