low coordination numbers of the cation favour the development of the intramolecular hydrogen bond. The planes of the carboxylic groups make the following angles with the least-squares planes through the C atoms:

[C(1) to C(8)]	with C(7)O(1)O(2)	23·4°
[C(1) to C(8)]	with C(8)O(3)O(4)	31·7
[C(11) to C(18)]	with C(17)O(11)O(12)	20·7
[C(11) to C(18)]	with C(18)O(13)O(14)	16·6.

The larger torsion angles of the first two carboxylic groups seem to cause the hydrogen bond O(2)···O(3) = 2·400 (2) to be longer than O(12)···O(13) = 2·390 (2) Å. Similar to the other acid lithium phthalates, the distances and angles within the benzene ring and the carboxylic groups are modified by the stress exerted by the short hydrogen bond.

The fact that H(2) is found to be located closer to O(2) than to O(3) within the hydrogen bond seems quite reasonable with regard to the environment of the carboxylic groups of molecule (I). The distances Li(1)—O(1) and Li(1)—O(4) are equal within the standard deviations. But O(4) and O(3) are involved in the hydrogen bonds to the water molecules previously mentioned. H(1), therefore, should be more closely attached to O(2) than to O(3) because O(2) shows no intermolecular linkages. Thus, O(2)—C(7) is longer than O(3)—C(8) and, consequently, O(1)—C(7) is shorter than O(4)—C(8).

In molecule (II), the higher symmetry with respect to linked neighbours makes it difficult to decide which of O(12) or O(13) the hydrogen H(11) should be closer to. A neutron diffraction study is in progress.

The quasi-planar hydrogen phthalate ions are packed in the crystal structure in a layer-like fashion. The angle between the two least-squares planes through molecules (I) and (II) is 15·5°. These mean planes have very roughly the orientation of the cleavage plane (110).

The topological configuration of the constituent groups in the present structure shows a close resemblance to that of $LiHC_8O_4H_4 \cdot CH_3OH$ if the methanol molecules are replaced by water molecules. This replacement causes an increase in density (from 1·474 to 1·524 Mg m^{-3}) and a distortion of the unit cell. If the lattice parameters in $LiHC_8O_4H_4 \cdot CH_3OH$ as reported by Adiwidjaja & Küppers (1978) are properly interchanged ($a \rightarrow -a, b \rightarrow c, c \rightarrow b$) to allow a comparison, the values to be compared with the present lattice parameters are: $a = 13·692, b = 8·467, c = 8·023$ Å, $\alpha = 95·29, \beta = 93·28, \gamma = 83·69°$.

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Tetramethylammonium Tri-μ-hydrido-dodecacarbonyltetraosmate

By BRIAN F. G. JOHNSON, JACK LEWIS, PAUL R. RAITHBY
AND CAMILLO ZUCCARO

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Abstract. $[(CH_3)_4N][Os_4(CO)_{12}H_3]$, orthorhombic, *Pccn*, $a = 11·647$ (8), $b = 12·742$ (2), $c = 16·865$ (3) Å, $U = 2502·9$ Å^3, $Z = 4$, $D_c = 3·115$ Mg m^{-3}, μ(Mo $K\alpha$) = 20·29 mm^{-1}. The structure was refined to an R of 0·037 for 1034 unique observed diffractometer data. The Os atoms define a distorted tetrahedron with crystallographic C_2 symmetry. The carbonyl ligands are all terminal, and their arrangement suggests that the hydrides bridge three Os—Os edges.

Introduction. Low-temperature IR and NMR studies on $[H_3Os_4(CO)_{12}]^-$ have indicated the existence of two

isomers in solution (Johnson, Lewis, Raithby, Sheldrick, Wong & McPartlin, 1978). Our structural studies on $[H_2Os_4(CO)_{12}]^{2-}$ (Johnson, Lewis, Raithby, Sheldrick & Süss, 1978) and $H_4Os_4(CO)_{12}$ (Raithby, 1978) have established that the hydrides edge-bridge Os—Os bonds in both compounds. A single-crystal X-ray analysis of the title compound was undertaken to investigate the possible existence of isomers in the solid state, since isomer formation is thought to be due to different hydride arrangements.

Treatment of $H_4Os_4(CO)_{12}$ with methanolic KOH gives a deep-yellow solution, from which $[H_3Os_4(CO)_{12}]^-$ can be precipitated as the $[NMe_4]^+$ salt (Johnson, Lewis, Raithby, Sheldrick, Wong & McPartlin, 1978). Recrystallization from hexane/dichloromethane yielded, as the major component, yellow platelets; some small block-shaped crystals were also obtained, but none of these was suitable for a single-crystal analysis. 1674 intensities (layers 0–13,k,l) were measured on an automated Stoe STADI-2 two-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, and a crystal $0.273 \times 0.110 \times 0.050$ mm. Lp and numerical absorption corrections were applied. The b and c dimensions were determined by a least-squares fit to the ω medians of the zero-layer reflections; a was determined from diffractometer μ-angle measurements. Equivalent reflections were averaged to give 1034 unique observed $[I > 1.5\sigma(I)]$ intensities.

The two unique Os positions were located by multisolution Σ_2 sign expansion, and the C, N and O atoms from a subsequent difference synthesis. The structure was refined by a full-matrix least-squares method with complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme $w = 4.2197/[\sigma^2(F) + 0.000047|F_o|^2]$. Parameters refined included anisotropic temperature factors for the Os atoms, interlayer scale factors, and an empirical extinction parameter x,

Table 1. *Atom coordinates* $(\times 10^4)$ *and isotropic temperature factors* $(Å^2 \times 10^3)$

	x	y	z	U
Os(1)	2150 (1)	1377 (1)	−774 (1)	
Os(2)	3622 (1)	2123 (1)	421 (1)	
C(11)	3470 (21)	797 (14)	−1212 (13)	55 (5)
O(11)	4300 (15)	423 (10)	−1513 (10)	73 (5)
C(12)	1099 (23)	1109 (15)	−1592 (15)	67 (7)
O(12)	479 (17)	956 (11)	−2133 (11)	92 (5)
C(13)	1762 (20)	164 (14)	−202 (12)	53 (6)
O(13)	1485 (16)	−588 (11)	136 (10)	78 (5)
C(21)	4980 (22)	1473 (14)	137 (13)	58 (6)
O(21)	5884 (17)	1116 (11)	0 (11)	88 (5)
C(22)	4245 (26)	3014 (17)	1204 (16)	82 (7)
O(22)	4662 (20)	3551 (14)	1681 (13)	117 (7)
C(23)	3126 (23)	1113 (16)	1114 (14)	69 (7)
O(23)	2849 (17)	437 (11)	1578 (10)	88 (5)
N(1)	2500	−2500	2258 (15)	61 (7)
C(1)	1478 (26)	−2817 (17)	1740 (15)	89 (8)
C(2)	2167 (27)	−1585 (18)	2778 (16)	93 (8)

Table 2. *Bond lengths* (Å) *and angles* (°)

Primed atoms are related to the reference atoms at (x,y,z) by the symmetry operation $(0.5 − x, 0.5 − y, z)$.

Os(2)—Os(1)	2.811 (2)	Os(1)—Os(1')	2.977 (2)
Os(2)—Os(1')	2.920 (2)	Os(2)—Os(2')	2.785 (2)
C(11)—Os(1)	1.860 (25)	O(11)—C(11)	1.191 (24)
C(12)—Os(1)	1.876 (28)	O(12)—C(12)	1.179 (26)
C(13)—Os(1)	1.876 (20)	O(13)—C(13)	1.160 (20)
C(21)—Os(2)	1.848 (26)	O(21)—C(21)	1.170 (25)
C(22)—Os(2)	1.887 (28)	O(22)—C(22)	1.161 (28)
C(23)—Os(2)	1.832 (24)	O(23)—C(23)	1.208 (24)
C(1)—N(1)	1.531 (29)	C(2)—N(1)	1.509 (28)
Os(2)—Os(1)—Os(1')	60.5 (2)	Os(1)—Os(2)—Os(2')	62.9 (2)
Os(2)—Os(1)—Os(2')	58.1 (2)	Os(1)—Os(2)—Os(1')	62.5 (2)
C(11)—Os(1)—Os(2)	85.1 (7)	C(21)—Os(2)—Os(1)	100.7 (7)
C(12)—Os(1)—Os(2)	170.6 (6)	C(22)—Os(2)—Os(1)	160.0 (8)
C(13)—Os(1)—Os(2)	93.2 (6)	C(23)—Os(2)—Os(1)	91.6 (8)
C(11)—Os(1)—Os(1')	98.9 (7)	C(21)—Os(2)—Os(2')	163.3 (6)
C(12)—Os(1)—Os(1')	110.7 (6)	C(22)—Os(2)—Os(2')	98.8 (7)
C(13)—Os(1)—Os(1')	149.1 (7)	C(23)—Os(2)—Os(2')	86.9 (6)
C(11)—Os(1)—Os(2')	142.1 (6)	C(21)—Os(2)—Os(1')	112.2 (7)
C(12)—Os(1)—Os(2')	115.2 (6)	C(22)—Os(2)—Os(1')	102.0 (7)
C(13)—Os(1)—Os(2')	96.3 (6)	C(23)—Os(2)—Os(1')	86.9 (6)
C(12)—Os(1)—C(11)	100.0 (10)	C(22)—Os(2)—C(21)	97.0 (11)
C(13)—Os(1)—C(11)	94.4 (9)	C(23)—Os(2)—C(21)	96.9 (10)
C(13)—Os(1)—C(12)	94.1 (9)	C(23)—Os(2)—C(22)	95.6 (10)
O(11)—C(11)—Os(1)	178.2 (19)	O(21)—C(21)—Os(2)	174.6 (19)
O(12)—C(12)—Os(1)	176.7 (22)	O(22)—C(22)—Os(2)	177.9 (26)
O(13)—C(13)—Os(1)	177.4 (20)	O(23)—C(23)—Os(2)	177.1 (24)
C(2)—N(1)—C(1)	109.6 (15)	C(1)—N(1)—C(1)	110.4 (25)
C(2)—N(1)—C(2)	109.0 (26)		

which refined to 0.00005 (1); F_c is multiplied by $(1 − 0.0001xF_c^2/\sin \theta)$. The constraint $U_{11} = (U_{22} + U_{33})/2$ was applied to reduce correlation involving interlayer scale factors. The refinement converged to $R = 0.037$ and $R' = \sum w^{1/2} \Delta/\sum w^{1/2}|F_o| = 0.031$. Attempts to locate the hydridic H atoms with various $(\sin \theta)/\lambda$ cut-offs were unsuccessful. The final atomic coordinates and isotropic thermal parameters are given in Table 1, the bond lengths and angles in Table 2.*

Discussion. The $[H_3Os_4(CO)_{12}]^-$ anion (Fig. 1) has crystallographic C_2 symmetry, with the twofold axis bisecting Os(1)—Os(1') and Os(2)—Os(2'). The distortions of the Os$_4$ tetrahedron are consistent with the three hydrides occupying edge-bridging positions. The long and short bond lengths are similar to the bridged (mean 2.934 Å) and unbridged (mean 2.798 Å) distances in $[H_2Os_4(CO)_{12}]^{2-}$ (Johnson, Lewis, Raithby, Sheldrick & Süss, 1978), respectively. The carbonyl ligands bend away from these long bonds, with an average cis Os—Os—C angle of 112.70° for the three carbonyls closest to the three long edges, and an average of 96.74° for the remainder. Similar widening of the Re—Re—C(carbonyl) angles in $[H_6Re_4(CO)_{12}]^{2-}$ (Ciani, Sironi & Albano, 1977) has been ascribed to the presence of edge-bridging hydrides. Our results indicate

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33911 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
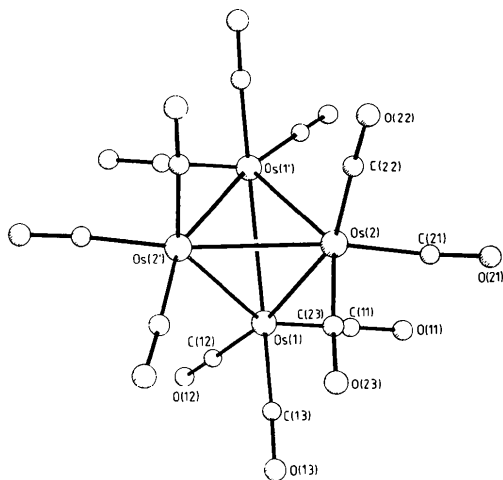
Fig. 1. The [H₃Os₄(CO)₁₂]⁻ anion.

that one hydride lies on the twofold axis, bridging Os(1)–Os(1′), while the other two bridge Os(1)–Os(2′) and Os(2)–Os(1′), respectively. Thus, this anion is essentially isostructural with the C_2 isomer of [H₃Ru₄(CO)₁₂]⁻, for which it has been shown that both C_2 and C_{3v} isomers exist in the solid state (Jackson, Johnson, Lewis, McPartlin & Nelson, 1978).

None of the Os–C or C–O lengths deviate from the respective means of 1·863 and 1·178 Å by more than 1·3σ, and the average Os–C–O angle is 177·0°. These lengths are not significantly different from the mean

Os–C and C–O distances of 1·89 (4) and 1·16 (4) Å in Os₅(CO)₁₆ (Reichert & Sheldrick, 1977).

The tetramethylammonium cation adopts the expected configuration, having a twofold crystallographic axis passing through the N atom.

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Bis(triphenylphosphine)iminium μ₂-Hydrido-μ₃-sulphido-nonacarbonyltriosmate

By Brian F. G. Johnson, Jack Lewis, David Pippard
and Paul R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Abstract. [(C₁₈H₁₅P)₂N] [Os₃(CO)₉HS], monoclinic, $P2_1/c$, $a = 9·600$ (3), $b = 30·074$ (10), $c = 15·946$ (8) Å, $\beta = 101·15$ (3)°, $U = 4516·9$ Å³, $Z = 4$, $D_c = 2·05$ Mg m⁻³, μ(Mo $K\alpha$) = 8·562 mm⁻¹. The structure was refined to an R of 0·057 for 3186 unique diffractometer data. In the anion the three Os atoms define an isosceles triangle, which is capped by the S atom. The carbonyl groups are all terminal, and the ligand distribution suggests that the hydride bridges the long Os–Os edge.

Introduction. The structure determination of the title compound was undertaken as one of a series in our investigations of the changes in cluster geometry in Os₃S systems, due to variations in ionic charge and the number of hydrides present.

The anion was prepared in good yield by treating H₂Os₃(CO)₉S with methanolic KOH, followed by precipitation as the yellow bis(triphenylphosphine)-iminium salt (Johnson, Lewis, Pippard & Raithby, 1978). 5705 intensities were measured ($3·0 < 2\theta \leq$