between pairs of positions in the neodymium complex and between the two 4-bipy ligands.

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Low-Temperature X-ray and Neutron Diffraction Studies of Tetra-*n*-butylammonium Octadecacarbonyl-μ_3-hydrido-*octahedro*-hexaosmium*

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Abstract. $[NBu^n_4][Os_6(\mu_3\text{-}H)(CO)_{18}]$, $C_{16}H_{36}N^+.[Os_6(CO)_{18}H]^-$, $M_r = 1888{\cdot}86$, monoclinic, $I2$; at 200 K (X-ray), $a = 13{\cdot}759\ (11)$, $b = 15{\cdot}034\ (9)$, $c = 22{\cdot}093\ (9)$ Å, $\beta = 93{\cdot}16\ (5)°$, $V = 4563\ (5)$ Å^3, $Z = 4$, $D_x = 2{\cdot}75$ Mg m^{-3}, Mo $K\alpha$, $\bar{\lambda} = 0{\cdot}71069$ Å, $\mu = 16{\cdot}7$ mm^{-1}, $F(000) = 3392$, $R = 0{\cdot}049$ for 2847 unique observed reflections with $(\sin\theta)/\lambda \le 0{\cdot}60$ Å^{-1}; at 20 K (neutron), $a = 13{\cdot}743\ (4)$, $b = 14{\cdot}780\ (4)$, $c = 21{\cdot}430\ (8)$ Å, $\beta = 93{\cdot}15\ (3)°$, $V = 4346\ (3)$ Å^3, $Z = 4$, $D_x = 2{\cdot}89$ Mg m^{-3}, $\lambda_N = 1{\cdot}1617\ (1)$ Å, $\mu = 0{\cdot}154$ mm^{-1}, $F(000) = 1062{\cdot}5$ fm, $R = 0{\cdot}123$ for 2780 unique observed reflections with $(\sin\theta)/\lambda \le 0{\cdot}56$ Å^{-1}. The neutron diffraction study of the title compound confirms the μ_3 site proposed for the hydride ligand in the $[Os_6(\mu_3\text{-}H)(CO)_{18}]^-$ anion. The average Os—H distance is 1·93 (2) Å, and is the first such distance to be determined; the mean Os—H—Os angle is 100·4 (7)°.

Introduction. The title compound was prepared by protonation of the $[Os_6(CO)_{18}]^{2-}$ dianion as described by Eady, Johnson & Lewis (1976). A brief report of the X-ray crystal structure of the $[(PPh_3)_2N]$ salt of $[Os_6(\mu_3\text{-}H)(CO)_{18}]$ was published in 1976 (McPartlin, Eady, Johnson & Lewis, 1976). In order to confirm the assignment of a μ_3 site for the hydride ligand we have undertaken a neutron diffraction study of this anion, as its $[NBu^n_4]$ salt. The dimensions of the Os—(μ_3-H) unit, which has not previously been characterized by neutron diffraction, are of interest to allow comparison with the more widely studied Os—(μ_2-H) and Os—H moieties. Further, as a class, very few μ_3-H complexes have been studied by neutron diffraction.

Experimental. *X-ray study:* red/orange irregular block (approx. 0·15 × 0·25 × 0·30 mm); Nicolet *P*3*m* diffractometer, 12 reflections centred ($17 < 2\theta < 25°$), graphite-monochromated Mo $K\alpha$; temperature 200 K by LT-1 N_2 gas-flow apparatus; for data collection $3{\cdot}5 < 2\theta < 50°$, ω–2θ scans, width in $2\theta = 2{\cdot}4° + \Delta_{\alpha_1\alpha_2}$, 2 s prescan after which reflections with >30 counts remeasured at rates between 1·5 and 29·3° min^{-1}, 2 octants of data (*hkl*, *hk*–*l*, 4094 reflections, $h\ 0\rightarrow16$, $k\ 0\rightarrow17$, $l\ -26\rightarrow26$) measured over 110 X-ray hours, corrected for *ca* 10% decay from check reflections; systematic absences *hkl*: $h+k+l = 2n+1$, space group $I2$ (No. 5) determined by Laue symmetry, solution and refinement. 3038 unique data, $R_{\text{int}} = 0{\cdot}035$ (186 pairs of intensities averaged); for structure solution and refinement 2847 with $F > 4\sigma(F)$ retained, absorption correction by 238 azimuthal scan

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data, transmission coefficients 0·010–0·031; direct (Os atoms) and difference Fourier methods; blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0{\cdot}0008F^2]^{-1}$, $\sigma(F) = \sigma(F^2)/2F$ with $\sigma(F^2)$ from counting statistics, anisotropic displacement parameters for Os atoms, isotropic for C, N, O, fixed isotropic for alkyl H (in idealized geometries, C—H 0·96 Å), $R = 0{\cdot}049$, $wR = 0{\cdot}061$, $S = 1{\cdot}40$; data:parameter ratio 10·3:1, max. peak and min. trough in final ΔF synthesis +1·69 and −1·73 e Å^{-3} respectively, mean shift/e.s.d. in final cycle 0·066; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Absolute structure assignment by η refinement [$\eta = 1{\cdot}19$ (8)] (Rogers, 1981).

Neutron study: red/orange prism (approx. 0·7 × 0·9 × 1·8 mm); BNL H6S four-circle diffractometer, 32 reflections centred ($46 < 2\theta < 63°$), germanium (220) monochromator, $\lambda = 1{\cdot}1617$ (1) Å, temperature 20 (1) K by Displex® model CS-202 closed-cycle refrigerator; for data collection $4 < 2\theta < 104°$, ω–2θ step scans (47–81 steps, 2 × 10^5 incident-beam monitor counts/step, ~4·2 s) of width 2·88° for $2\theta < 55°$, $(1{\cdot}5 + 3{\cdot}20\tan\theta)°$ for $55 < 2\theta < 75°$ and $(1{\cdot}65 + 3{\cdot}51\tan\theta)°$ for $75 < 2\theta < 104°$, 2 octants of data measured ($-hkl$, $-hk-l$, 5950 reflections, h −23→0, k 0→25, l −35→35) over 20 d, no decay or crystal movement. 5502 data, $R_{\text{int}} = 0{\cdot}048$ (309 pairs of intensities averaged); for structure refinement 2780 with $F > 2\sigma(F)$ and $(\sin\theta)/\lambda < 0{\cdot}56$ Å^{-1} [showing better resolved profiles than $(\sin\theta)/\lambda > 0{\cdot}56$ Å^{-1}] retained; absorption correction by Gaussian quadrature on crystal faces (distances in mm): (010) 0·35, $(0\bar{1}0)$ 0·35, (001) 0·46, $(00\bar{1})$ 0·46, $(01\bar{1})$ 0·50, (101) 0·80, $(10\bar{1})$ 0·60, transmission 0·84–0·90; blocked-cascade least-squares refinement on F, $w = [\sigma^2(F) + 0{\cdot}0002F^2]^{-1}$ [$\sigma(F)$ as for X-ray], all atoms isotropic without constraints, $R = 0{\cdot}123$, $wR = 0{\cdot}120$, $S = 3{\cdot}27$; data:parameter ratio 7·2:1, max. peak and min. trough +3·8 and −2·2 fm Å^{-3} respectively (*cf.* H-atom trough −5·7 fm Å^{-3}), max. shift/e.s.d. in final cycle 0·060. Neutron scattering lengths from Koester (1977), neutron absorption values of μ/p from *International Tables for X-ray Crystallography* (1974) for C, N, O and Os and from McMullan & Koetzle (1979) for H. Isotropic extinction correction to neutron data by the method of Larson (1967), $F_c^* = F_c(1 + xF_c^2/\sin 2\theta)^{-1/4}$ where $x = 4{\cdot}0\,(7) \times 10^{-5}$. Computer program *SHELXTL* (Sheldrick, 1985).

Discussion. The final fractional coordinates and isotropic displacement parameters are listed in Table 1† for the neutron study at 20 K; in this table and throughout this paper the e.s.d.'s in the least-significant digit are given in parentheses. Derived bond lengths and selected bond angles are given in Table 2. The results of the X-ray study, which is less precise than the neutron for all molecular dimensions except Os—Os distances, have been deposited.* In addition, the molecular

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (Å^2 ×10^3)

	x	*y*	*z*	*U*
Os(1)	437 (4)	−250	1862 (3)	3 (1)
Os(2)	970 (5)	−1207 (5)	2990 (3)	8 (1)
Os(3)	1295 (4)	742 (4)	2898 (3)	1 (1)
Os(4)	−102 (5)	55 (5)	3696 (3)	7 (1)
Os(5)	−707 (5)	1027 (5)	2514 (3)	11 (2)
Os(6)	−1057 (5)	−934 (5)	2626 (3)	10 (1)
C(11)	20 (8)	−1254 (8)	1377 (6)	16 (3)
O(11)	−198 (10)	−1853 (10)	1065 (7)	19 (3)
C(12)	155 (7)	542 (7)	1187 (5)	5 (2)
O(12)	11 (11)	960 (11)	747 (7)	23 (3)
C(13)	1767 (8)	−447 (8)	1697 (5)	13 (3)
O(13)	2569 (10)	−549 (9)	1591 (6)	14 (3)
C(21)	1249 (10)	−2102 (10)	2379 (7)	27 (3)
O(21)	1407 (10)	−2676 (10)	2029 (7)	20 (3)
C(22)	2307 (8)	−1201 (8)	3210 (5)	10 (2)
O(22)	3151 (9)	−1277 (9)	3346 (6)	12 (3)
C(23)	698 (8)	−2076 (8)	3618 (5)	9 (2)
O(23)	502 (10)	−2594 (10)	3990 (6)	13 (3)
C(31)	2520 (7)	633 (7)	3354 (5)	4 (2)
O(31)	3256 (10)	612 (10)	3649 (7)	17 (3)
C(32)	1062 (8)	1835 (8)	3326 (5)	14 (3)
O(32)	979 (11)	2536 (11)	3590 (7)	25 (4)
C(33)	1920 (8)	1271 (7)	2215 (5)	8 (2)
O(33)	2293 (10)	1621 (10)	1821 (6)	15 (3)
C(41)	−785 (8)	−844 (9)	4147 (6)	18 (3)
O(41)	−1163 (11)	−1356 (11)	4452 (7)	27 (4)
C(42)	−589 (10)	985 (9)	4194 (6)	22 (3)
O(42)	−847 (12)	1531 (11)	4504 (8)	27 (4)
C(43)	1045 (8)	−83 (8)	4193 (5)	13 (2)
O(43)	1739 (9)	−145 (10)	4538 (6)	15 (3)
C(51)	−1912 (8)	1073 (8)	2042 (5)	15 (3)
O(51)	−2629 (12)	1116 (12)	1763 (8)	30 (4)
C(52)	−134 (7)	1952 (7)	2024 (5)	7 (2)
O(52)	145 (9)	2506 (9)	1724 (5)	7 (3)
C(53)	−1152 (10)	1941 (11)	3046 (7)	30 (3)
O(53)	−1450 (15)	2524 (15)	3309 (10)	47 (5)
C(61)	−2148 (10)	−1248 (10)	3083 (7)	28 (3)
O(61)	−2836 (14)	−1506 (14)	3341 (9)	44 (5)
C(62)	−811 (10)	−2182 (10)	2519 (6)	24 (3)
O(62)	−747 (13)	−2951 (12)	2428 (8)	34 (4)
C(63)	−1844 (8)	−832 (8)	1877 (6)	17 (3)
O(63)	−2358 (11)	−806 (12)	1432 (8)	28 (4)
C(1)	6398 (20)	4249 (21)	5071 (16)	76 (7)
C(2)	7305 (9)	3599 (9)	5031 (6)	20 (3)
C(3)	8143 (9)	4285 (10)	5031 (6)	22 (3)
C(4)	9110 (10)	3812 (10)	4989 (7)	32 (3)
N(1)	10000	4438 (10)	5000	24 (3)
C(6)	9996 (9)	4580 (9)	3798 (6)	16 (3)
C(5)	9963 (11)	5065 (10)	4436 (7)	27 (3)
C(7)	10109 (10)	5282 (9)	3266 (6)	21 (3)
C(8)	10123 (10)	4810 (10)	2635 (6)	23 (3)
C(01)	−1789 (15)	5632 (16)	1367 (10)	56 (5)
C(02)	−1282 (13)	6105 (13)	921 (8)	43 (4)
C(03)	−1155 (14)	5469 (13)	360 (9)	48 (4)
C(04)	−320 (9)	4814 (9)	536 (6)	23 (3)
N(2)	0	4180 (9)	0	16 (3)
C(05)	834 (8)	3622 (8)	277 (5)	15 (3)
C(06)	1266 (9)	2920 (9)	−163 (6)	16 (3)
C(07)	2093 (10)	2451 (10)	223 (6)	25 (3)
C(08)	2585 (10)	1751 (9)	−196 (6)	23 (3)
H(456)	−1214 (18)	185 (18)	3071 (12)	27 (6)
H(1*A*)	5810 (34)	3681 (34)	5083 (22)	82 (12)
H(1*B*)	6281 (38)	4497 (39)	4680 (28)	95 (15)
H(1*C*)	6369 (31)	4473 (31)	5346 (23)	66 (11)
H(2*A*)	7458 (26)	3257 (26)	5516 (18)	59 (9)
H(2*B*)	7308 (20)	3148 (20)	4614 (14)	36 (6)
H(3*A*)	7989 (20)	4713 (21)	4649 (13)	37 (6)
H(3*B*)	8129 (25)	4694 (26)	5464 (17)	58 (9)

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† Lists of structure factors, anisotropic displacement parameters and full bond lengths and angles for both studies have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44176 (65 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 1 (*cont.*)

	x	*y*	*z*	*U*
H(4*A*)	9135 (20)	3419 (19)	4554 (13)	32 (6)
H(4*B*)	9223 (23)	3336 (22)	5355 (15)	46 (8)
H(5*A*)	9296 (23)	5471 (22)	4437 (15)	46 (8)
H(5*B*)	10576 (18)	5494 (18)	4513 (12)	27 (6)
H(6*A*)	9321 (19)	4176 (19)	3697 (12)	33 (6)
H(6*B*)	10603 (19)	4152 (19)	3817 (12)	31 (6)
H(7*A*)	10803 (18)	5622 (18)	3385 (12)	28 (5)
H(7*B*)	9496 (25)	5749 (24)	3259 (16)	53 (8)
H(8*A*)	10201 (21)	5296 (20)	2269 (14)	38 (7)
H(8*B*)	9461 (22)	4407 (22)	2541 (15)	45 (7)
H(8*C*)	10787 (22)	4367 (22)	2639 (14)	42 (7)
H(01*A*)	−1957 (46)	6063 (45)	1782 (30)	113 (17)
H(01*B*)	−1310 (31)	5292 (30)	1549 (20)	67 (10)
H(01*C*)	−2512 (34)	5277 (32)	1184 (22)	80 (12)
H(02*A*)	−1862 (24)	6730 (23)	659 (16)	49 (8)
H(02*B*)	−579 (26)	6384 (24)	1104 (17)	53 (8)
H(03*A*)	−1739 (32)	5220 (31)	122 (21)	73 (11)
H(03*B*)	−924 (31)	5853 (29)	−58 (20)	71 (11)
H(04*A*)	−655 (16)	4298 (16)	857 (11)	21 (5)
H(04*B*)	276 (21)	5084 (22)	735 (14)	42 (7)
H(05*A*)	1402 (17)	4078 (17)	424 (11)	25 (5)
H(05*B*)	559 (22)	3317 (21)	651 (14)	40 (7)
H(06*A*)	705 (21)	2436 (21)	−321 (14)	39 (7)
H(06*B*)	1558 (18)	3310 (18)	−566 (12)	28 (6)
H(07*A*)	2647 (18)	2946 (18)	372 (12)	27 (6)
H(07*B*)	1779 (18)	2156 (18)	603 (12)	29 (6)
H(08*A*)	3147 (26)	1386 (25)	62 (17)	56 (9)
H(08*B*)	2834 (26)	2042 (26)	−595 (18)	59 (9)
H(08*C*)	2023 (21)	1246 (21)	−390 (14)	39 (7)

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

Os(1)—Os(2)	2·860 (9)	Os(1)—Os(3)	2·861 (8)
Os(1)—Os(5)	2·868 (9)	Os(1)—Os(6)	2·878 (9)
Os(1)—C(11)	1·882 (13)	Os(1)—C(12)	1·885 (12)
Os(1)—C(13)	1·904 (13)	Os(2)—Os(3)	2·923 (10)
Os(2)—Os(4)	2·861 (10)	Os(2)—Os(6)	2·879 (9)
Os(2)—C(21)	1·914 (16)	Os(2)—C(22)	1·871 (12)
Os(2)—C(23)	1·912 (13)	Os(3) Os(4)	2·829 (9)
Os(3)—Os(5)	2·860 (9)	Os(3)—C(31)	1·905 (11)
Os(3)—C(32)	1·893 (14)	Os(3)—C(33)	1·906 (13)
Os(4)—Os(5)	2·989 (10)	Os(4)—Os(6)	2·964 (9)
Os(4)—H(456)	1·984 (25)	Os(4)—C(41)	1·919 (14)
Os(4)—C(42)	1·885 (15)	Os(4)—C(43)	1·865 (13)
Os(5)—Os(6)	2·950 (10)	Os(5)—H(456)	1·885 (27)
Os(5)—C(51)	1·893 (13)	Os(5)—C(52)	1·920 (13)
Os(5)—C(53)	1·891 (17)	Os(6)—H(456)	1·928 (27)
Os(6)—C(61)	1·894 (16)	Os(6)—C(62)	1·891 (16)
Os(6)—C(63)	1·892 (13)	C(11)—O(11)	1·141 (19)
C(12)—O(12)	1·135 (19)	C(13)—O(13)	1·146 (17)
C(21)—O(21)	1·160 (21)	O(22)—C(22)	1·186 (16)
C(23)—O(23)	1·148 (18)	C(31)—O(31)	1·164 (16)
C(32)—O(32)	1·189 (20)	C(33)—O(33)	1·137 (18)
C(41)—O(41)	1·141 (21)	C(42)—O(42)	1·116 (22)
C(43)—O(43)	1·178 (17)	C(51)—O(51)	1·127 (20)
C(52)—O(52)	1·121 (17)	C(53)—O(53)	1·119 (27)
C(61)—O(61)	1·185 (25)	C(62)—O(62)	1·156 (23)
C(63)—O(63)	1·155 (20)	C(1)—H(1*A*)	1·17 (6)
C(1)—H(1*B*)	0·92 (7)	C(1)—H(1*C*)	0·68 (6)
C(1)—C(2)	1·579 (32)	C(2)—H(2*A*)	1·16 (4)
C(2)—H(2*B*)	1·12 (3)	C(2)—C(3)	1·535 (18)
C(3)—H(3*A*)	1·05 (3)	C(3)—H(3*B*)	1·11 (4)
C(3)—C(4)	1·509 (19)	C(4)—H(4*A*)	1·01 (3)
C(4)—H(4*B*)	1·06 (4)	C(4)—N(1)	1·533 (17)
N(1)—C(5)	1·522 (17)	N(1)—C(4′)	1·533 (17)
N(1)—C(5′)	1·521 (17)	C(6)—H(6*A*)	1·12 (3)
C(6)—H(6*B*)	1·05 (3)	C(6)—C(5)	1·546 (19)
C(6)—C(7)	1·556 (18)	C(5)—H(5*A*)	1·10 (4)
C(5)—H(5*B*)	1·06 (3)	C(7)—H(7*A*)	1·10 (3)
C(7)—H(7*B*)	1·09 (4)	C(7)—C(8)	1·522 (19)
C(8)—H(8*A*)	1·07 (3)	C(8)—H(8*B*)	1·10 (3)
C(8)—H(8*C*)	1·12 (3)	C(01)—H(01*A*)	1·13 (7)
C(01)—H(01*B*)	0·90 (5)	C(01)—H(01*C*)	1·17 (5)
C(01)—C(02)	1·400 (29)	C(02)—H(02*A*)	1·323 (38)
C(02)—H(02*B*)	1·10 (4)	C(02)—C(03)	1·545 (26)
C(03)—H(03*A*)	1·00 (5)	C(03)—H(03*B*)	1·12 (5)
C(03)—C(04)	1·532 (23)	C(04)—H(04*A*)	1·14 (3)
C(04)—H(04*B*)	0·99 (3)	C(04)—N(2)	1·564 (15)
N(2)—C(05)	1·507 (13)	N(2)—C(04′)	1·564 (15)
N(2)—C(05′)	1·507 (13)	C(05)—H(05*A*)	1·07 (3)
C(05)—H(05*B*)	1·01 (3)	C(05)—C(06)	1·543 (18)
C(06)—H(06*A*)	1·09 (3)	C(06)—H(06*B*)	1·13 (3)
C(06)—C(07)	1·534 (18)	C(07)—H(07*A*)	1·09 (3)
C(07)—H(07*B*)	1·04 (3)	C(07)—C(08)	1·549 (20)

Table 2 (*cont.*)

C(08)—H(08*A*)	1·07 (4)	C(08)—H(08*B*)	1·03 (4)
C(08)—H(08*C*)	1·14 (3)		
Os(2)—Os(1)—Os(3)	61·4 (2)	Os(2)—Os(1)—Os(5)	92·0 (3)
Os(3)—Os(1)—Os(5)	59·9 (2)	Os(2)—Os(1)—Os(6)	60·2 (2)
Os(3)—Os(1)—Os(6)	90·9 (3)	Os(5)—Os(1)—Os(6)	61·8 (2)
Os(2)—Os(1)—C(11)	97·6 (4)	Os(3)—Os(1)—C(11)	158·8 (4)
Os(5)—Os(1)—C(11)	129·0 (5)	Os(6)—Os(1)—C(11)	80·3 (4)
Os(2)—Os(1)—C(12)	171·1 (4)	Os(3)—Os(1)—C(12)	109·6 (4)
Os(5)—Os(1)—C(12)	82·5 (4)	Os(6)—Os(1)—C(12)	122·2 (4)
C(11)—Os(1)—C(12)	91·3 (6)	Os(2)—Os(1)—C(13)	82·9 (4)
Os(3)—Os(1)—C(13)	82·1 (4)	Os(5)—Os(1)—C(13)	138·5 (4)
Os(6)—Os(1)—C(13)	140·7 (4)	C(11)—Os(1)—C(13)	92·4 (5)
C(12)—Os(1)—C(13)	96·4 (5)	Os(1)—Os(2)—Os(3)	59·3 (2)
Os(1)—Os(2)—Os(4)	90·5 (3)	Os(3)—Os(2)—Os(4)	58·6 (2)
Os(1)—Os(2)—Os(6)	60·2 (2)	Os(3)—Os(2)—Os(6)	89·6 (3)
Os(4)—Os(2)—Os(6)	62·2 (2)	Os(1)—Os(2)—C(21)	79·4 (5)
Os(3)—Os(2)—C(21)	126·7 (5)	Os(4)—Os(2)—C(21)	160·1 (5)
Os(6)—Os(2)—C(21)	98·0 (5)	Os(1)—Os(2)—C(22)	114·4 (5)
Os(3)—Os(2)—C(22)	82·0 (4)	Os(4)—Os(2)—C(22)	113·0 (5)
Os(6)—Os(2)—C(22)	171·6 (5)	C(21)—Os(2)—C(22)	86·8 (6)
Os(1)—Os(2)—C(23)	151·1 (5)	Os(3)—Os(2)—C(23)	138·2 (5)
Os(4)—Os(2)—C(23)	86·5 (4)	Os(6)—Os(2)—C(23)	93·5 (4)
C(21)—Os(2)—C(23)	94·1 (6)	C(22)—Os(2)—C(23)	93·0 (6)
Os(1)—Os(3)—Os(2)	59·3 (2)	Os(1)—Os(3)—Os(4)	91·1 (2)
Os(2)—Os(3)—Os(4)	59·6 (2)	Os(1)—Os(3)—Os(5)	60·2 (2)
Os(2)—Os(3)—Os(5)	90·9 (3)	Os(4)—Os(3)—Os(5)	63·4 (2)
Os(1)—Os(3)—C(31)	132·0 (4)	Os(2)—Os(3)—C(31)	91·0 (4)
Os(4)—Os(3)—C(31)	105·7 (4)	Os(5)—Os(3)—C(31)	165·6 (5)
Os(1)—Os(3)—C(32)	137·7 (4)	Os(2)—Os(3)—C(32)	141·1 (5)
Os(4)—Os(3)—C(32)	82·8 (4)	Os(5)—Os(3)—C(32)	80·1 (4)
C(31)—Os(3)—C(32)	89·5 (5)	Os(1)—Os(3)—C(33)	78·3 (4)
Os(2)—Os(3)—C(33)	122·2 (4)	Os(4)—Os(3) C(33)	164·0 (4)
Os(5)—Os(3)—C(33)	100·7 (4)	C(31)—Os(3)—C(33)	90·3 (5)
C(32)—Os(3)—C(33)	96·7 (6)	Os(2)—Os(4)—Os(3)	61·8 (2)
Os(2)—Os(4)—Os(5)	89·6 (3)	Os(3)—Os(4)—Os(5)	58·8 (2)
Os(2)—Os(4)—Os(6)	59·2 (2)	Os(3)—Os(4)—Os(6)	89·8 (3)
Os(5)—Os(4)—Os(6)	59·4 (2)	Os(2)—Os(4)—H(456)	96·1 (8)
Os(3)—Os(4)—H(456)	94·7 (8)	Os(5)—Os(4)—H(456)	38·2 (8)
Os(6)—Os(4)—H(456)	40·0 (8)	Os(2)—Os(4)—C(41)	95·5 (5)
Os(3)—Os(4)—C(41)	157·0 (5)	Os(5)—Os(4)—C(41)	129·7 (5)
Os(6)—Os(4)—C(41)	80·8 (4)	H(456)—Os(4)—C(41)	91·6 (9)
Os(2)—Os(4)—C(42)	169·7 (5)	Os(3)—Os(4)—C(42)	110·7 (5)
Os(5)—Os(4)—C(42)	92·2 (5)	Os(6)—Os(4)—C(42)	129·9 (5)
H(456)—Os(4)—C(42)	91·6 (9)	C(41)—Os(4)—C(42)	91·2 (6)
Os(2)—Os(4)—C(43)	77·7 (4)	Os(3)—Os(4)—C(43)	78·7 (4)
Os(5)—Os(4)—C(43)	136·4 (5)	Os(6)—Os(4)—C(43)	135·4 (5)
H(456)—Os(4)—C(43)	172·5 (9)	C(41)—Os(4)—C(43)	93·3 (6)
C(42)—Os(4)—C(43)	94·1 (6)	Os(1)—Os(5)—Os(3)	59·9 (2)
Os(1)—Os(5)—Os(4)	87·8 (3)	Os(3)—Os(5)—Os(4)	57·8 (2)
Os(1)—Os(5)—Os(6)	59·3 (2)	Os(3)—Os(5)—Os(6)	89·4 (3)
Os(4)—Os(5)—Os(6)	59·9 (2)	Os(1)—Os(5)—H(456)	96·1 (8)
Os(3)—Os(5)—H(456)	95·9 (8)	Os(4)—Os(5)—H(456)	40·6 (8)
Os(6)—Os(5)—H(456)	39·8 (8)	Os(1)—Os(5)—C(51)	104·5 (5)
Os(3)—Os(5)—C(51)	163·4 (5)	Os(4)—Os(5)—C(51)	131·6 (5)
Os(6)—Os(5)—C(51)	86·4 (5)	H(456)—Os(5)—C(51)	91·1 (9)
Os(1)—Os(5)—C(52)	87·1 (4)	Os(3)—Os(5)—C(52)	81·1 (4)
Os(4)—Os(5)—C(52)	134·6 (4)	Os(6)—Os(5)—C(52)	144·9 (5)
H(456)—Os(5)—C(52)	173·9 (9)	C(51)—Os(5)—C(52)	93·1 (6)
Os(1)—Os(5)—C(53)	165·4 (6)	Os(3)—Os(5)—C(53)	105·6 (5)
Os(4)—Os(5)—C(53)	85·2 (5)	Os(6)—Os(5)—C(53)	126·4 (6)
H(456)—Os(5)—C(53)	87·0 (10)	C(51)—Os(5)—C(53)	89·7 (6)
C(52)—Os(5)—C(53)	88·7 (6)	Os(1)—Os(6)—Os(2)	59·6 (2)
Os(1)—Os(6)—Os(4)	88·1 (2)	Os(2)—Os(6)—Os(4)	58·6 (2)
Os(1)—Os(6)—Os(5)	59·0 (2)	Os(2)—Os(6)—Os(5)	90·0 (3)
Os(4)—Os(6)—Os(5)	60·7 (2)	Os(1)—Os(6)—H(456)	94·8 (8)
Os(2)—Os(6)—H(456)	96·8 (8)	Os(4)—Os(6)—H(456)	41·4 (7)
Os(5)—Os(6)—H(456)	38·8 (8)	Os(1)—Os(6)—C(61)	171·9 (6)
Os(2)—Os(6)—C(61)	127·4 (5)	Os(4)—Os(6)—C(61)	92·9 (5)
Os(5)—Os(6)—C(61)	114·8 (6)	H(456)—Os(6)—C(61)	80·8 (9)
Os(1)—Os(6)—C(62)	97·9 (5)	Os(2)—Os(6)—C(62)	73·7 (5)
Os(4)—Os(6)—C(62)	120·0 (5)	Os(5)—Os(6)—C(62)	156·6 (6)
H(456)—Os(6)—C(62)	157·2 (10)	C(61)—Os(6)—C(62)	88·6 (7)
Os(1)—Os(6)—C(63)	83·2 (5)	Os(2)—Os(6)—C(63)	137·8 (5)
Os(4)—Os(6)—C(63)	145·6 (5)	Os(5)—Os(6)—C(63)	86·6 (5)
H(456)—Os(6)—C(63)	106·1 (9)	C(61)—Os(6)—C(63)	91·5 (6)
C(62)—Os(6)—C(63)	94·2 (6)	Os(4)—H(456)—Os(5)	101·2 (12)
Os(4)—H(456)—Os(6)	98·5 (12)	Os(5)—H(456)—Os(6)	101·4 (12)
Os(1)—C(11)—O(11)	176·8 (12)	Os(1)—C(12)—O(12)	174·0 (12)
Os(1)—C(13)—O(13)	178·6 (11)	Os(2)—C(21)—O(21)	176·7 (14)
Os(2)—C(22)—O(22)	174·3 (11)	Os(2)—C(23)—O(23)	177·7 (11)
Os(3)—C(31)—O(31)	176·2 (11)	Os(3)—C(32)—O(32)	175·7 (12)
Os(3)—C(33)—O(33)	177·0 (12)	Os(4)—C(41)—O(41)	175·4 (13)
Os(4)—C(42)—O(42)	177·3 (13)	Os(4)—C(43)—O(43)	175·8 (12)
Os(5)—C(51)—O(51)	178·8 (14)	Os(5)—C(52)—O(52)	175·8 (10)
Os(5)—C(53)—O(53)	173·2 (16)	Os(6)—C(61)—O(61)	174·7 (15)
Os(6)—C(62)—O(62)	173·7 (14)	Os(6)—C(63)—O(63)	176·3 (13)

structure of the anion appears to be more accurately determined by the neutron study since the range of Os—C—O angles is smaller [173·2 (16)–178·8 (14) *vs* 166·5 (34)–176·2 (14)° for X-ray] and the mean angle is closer to linear [176·0 (4) *vs* 172·0 (7)°] as would be expected {*cf.* a very precise structure of $[\mathrm{Os_3}(\mu\text{-H})_3(\mu_3\text{-CH})(\mathrm{CO})_9]$ showed mean Os—C—O 178·0 (1)° (Orpen & Koetzle, 1984)}. The rather poor residual indices and goodness-of-fit obtained for the neutron study are attributable to overlap of diffraction peaks at high 2θ and the presence of some disorder in the cations, notably affecting methyl groups C(1) and C(01). Attempts to improve the accuracy of integrated intensities by profile analysis failed to give significantly improved residuals. Anisotropic refinement led to physically meaningless displacement parameter values, although residuals were considerably reduced. Despite these inadequacies, the data suffice to define the crystal and molecular structure of both the cluster anion and the cations.

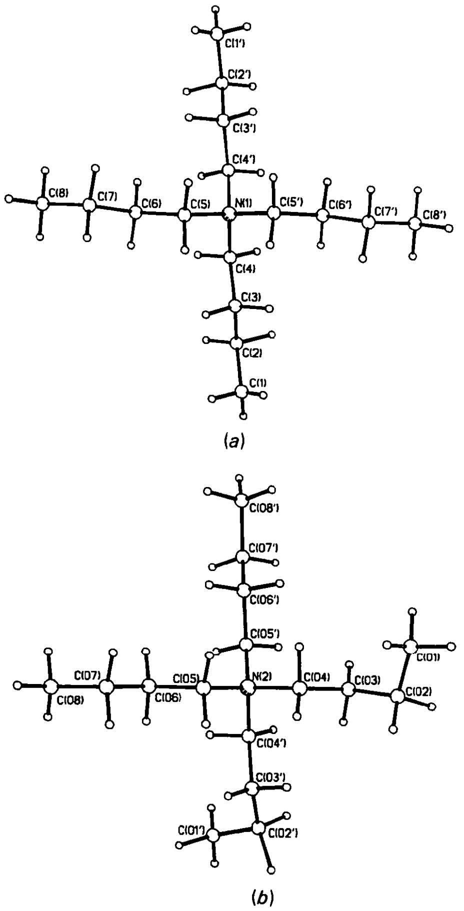

Fig. 1. (*a*) Perspective view of one cation of $[\mathrm{NBu}^n_4][\mathrm{Os_6}(\mu_3\text{-H})(\mathrm{CO})_{18}]$ along the crystallographic twofold axis, showing the labelling scheme; for clarity atoms are drawn as spheres of arbitrary radius. (*b*) Perspective view of the second independent $[\mathrm{NBu}^n_4]^+$ cation approximately orthogonal to the crystallographic twofold axis; drawn as for (*a*).

The crystal structure consists of isolated anions and cations linked by rather weak C—H···O interactions (see Taylor & Kennard, 1982) between the *n*-butyl and carbonyl groups [shortest H···O distances are H(03*A*)···O(43′) 2·435 Å and H(04*B*)···O(31$^{\rm ii}$) 2·474 Å, the O atoms being related to positions given in Table 1 by the transformations $-\frac{1}{2}+x$, $\frac{1}{2}+y$, $-\frac{1}{2}+z$ and $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$ respectively]. While the anions are in general positions, there are two independent cations at sites of crystallographic C_2 (2) symmetry; N(1) lies at Wyckoff site (*b*) and N(2) at Wyckoff site (*a*). The geometries of the $[\mathrm{NBu}^n_4]^+$ cations are illustrated in Fig. 1. They have normal dimensions except where distorted by the unresolved disorder (or high-amplitude motion) at and near C(1) and C(01). The butyl chains are all in extended conformations with the exception of C(01)—C(04) which has a *gauche* conformation about the C(02)—C(03) bond [torsion angle C(01)—C(02)—C(03)—C(04) −78·1 (18)°]. It is notable that it is this butyl group which is involved in the shortest C—H···O contacts. All other C—C—C—C and C—C—C—N torsion angles are near 180° as expected for an extended conformation.

The anion $[\mathrm{Os_6}(\mu_3\text{-H})(\mathrm{CO})_{18}]^-$ has the geometry illustrated in Fig. 2. The $\mathrm{Os_6}$ unit has approximate C_{3v} symmetry, each Os atom being connected to four neighbouring metals to form an octahedral cluster. One face of the cluster [Os(4), Os(5), Os(6)] is symmetrically capped by the hydride ligand H(456). Each Os atom is further ligated by three terminal linear carbonyl groups [mean Os—C = 1·895 (3) Å, mean C—O = 1·150 (6) Å]. The Os—H distances average 1·93 (2) Å, rather longer than have been observed for Os—(μ_2-H) lengths by neutron diffraction [typically 1·83 Å, see *e.g.* Teller & Bau (1981)], which are in turn longer than terminal Os—H (1·66 Å). The individual Os—H—Os angles are close to their mean [100·4 (7)°] and the H atom lies 0·892 (25) Å from the plane of the three Os atoms. These dimensions may be compared with

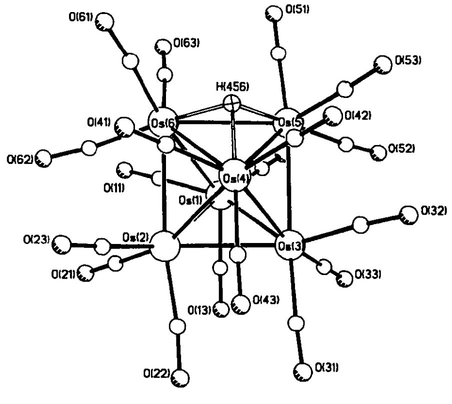

Fig. 2. Perspective view of the $[\mathrm{Os_6}(\mu_3\text{-H})(\mathrm{CO})_{18}]^-$ anion drawn as for Fig. 1.

91·8 (2)° and 0·978 (3) Å in $[FeCo_3(\mu_3\text{-}H)(CO)_9\{P(OMe)_3\}_3]$ (Teller, Wilson, McMullan, Koetzle & Bau, 1978), 93·9 (3)° and 0·907 (6) Å in $[Ni_4(\mu_3\text{-}H)_3(\eta\text{-}C_5H_5)_4]$ (Koetzle, Müller, Tipton, Hart & Bau, 1979) and 95·7° and 0·957 (6) Å for $[Rh_4(\mu_3\text{-}H)_4(\eta\text{-}C_5Me_5)]^{2+}$ (Ricci, Koetzle, Goodfellow, Espinet & Maitlis, 1974). Therefore, the hydride lies closer to the trimetal plane here than in the other examples although the difference is not significant in the case of the Ni_4 cluster. In $[Os_6(\mu_3\text{-}H)(CO)_{18}]^-$ the Os—Os distances in the bridged triangle (mean 2·968 Å) are notably longer than the other Os—Os lengths which may be separated into two classes, distinguishable owing to the near-C_{3v} symmetry of the cluster: those in the Os(1) Os(2) Os(3) triangle (mean 2·881 Å), and those connecting the two triangles (mean 2·863 Å). These values are in good agreement with those obtained at 200 K by X-ray diffraction in this work (2·963, 2·881 and 2·868 Å) and those reported for the $(PPh_3)_2N^+$ salt by McPartlin *et al.* (1976) (2·973, 2·872 and 2·863 Å respectively). These distances reflect the distortions in the Os_6 framework that occur on protonation of $[Os_6(CO)_{18}]^{2-}$ [*cf.* mean Os—Os in the approximate D_3 symmetry dianion 2·863 Å (McPartlin *et al.*, 1976)]. These distortions and those in the surrounding carbonyl coordination sphere (note large Os—Os—C angles involving carbonyls *cis* to the hydride) were the basis for the assignment of the μ_3 site for the hydride in $[Os_6(\mu_3\text{-}H)(CO)_{18}]^-$ (McPartlin *et al.*, 1976; Orpen, 1980). That assignment is fully confirmed by the present study.

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Synthesis and Molecular Structure of Tetrabutylammonium Tetrachloro(pyrimidine-2-thiolato)technetate(IV)

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Abstract. $[N(C_4H_9)_4][Tc(C_4H_3N_2S)Cl_4]$, $M_r = 594{\cdot}3$, triclinic, $P\bar{1}$, $a = 11{\cdot}182\,(6)$, $b = 11{\cdot}505\,(4)$, $c = 12{\cdot}235\,(4)$ Å, $\alpha = 64{\cdot}53\,(4)$, $\beta = 76{\cdot}81\,(3)$, $\gamma = 84{\cdot}10\,(5)$°, $V = 1383{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}427$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}97$ mm^{-1}, $F(000) = 614$, $T = 297$ K, $R = 0{\cdot}058$ for 3670 unique observed reflections. The coordination about Tc is distorted octahedral with Tc—N 2·087 (6), Tc—S 2·429 (2) and Tc—Cl 2·346 (2)–2·396 (2) Å. The N—Tc—S angle is 67·1 (2)°, constituting the major angular distortion from ideal octahedral.

Introduction. The γ-emitting radionuclide ^{99m}Tc is widely used as an imaging agent in diagnostic nuclear medicine. The biodistribution of ^{99m}Tc following administration to the patient may be controlled by incorporating it in a coordination or organometallic compound. Both the nature of the ligand and the Tc oxidation state are important in determining the physical properties of the product complex and thus its

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