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THE REDUCTION OF TRIOSMIUM DODECACARBONYL BY SODIUM BOROHYDRIDE. THE PREPARATION AND X-RAY STRUCTURE OF THE CLUSTER ANION $[H_2Os_4(CO)_{12}]^{2-}$

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Summary

The reduction of $Os_3(CO)_{12}$ by $NaBH_4$ in tetrahydrofuran has been studied, and the formation of the anionic clusters $[HOs_3(CO)_{11}]^-$, $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ observed. The previously unreported dianion $[H_2Os_4(CO)_{12}]^{2-}$ was prepared in satisfactory yield, and characterised as the bis(triphenylphosphine)iminium salt. This compound crystallizes in the space group $P\bar{1}$, with $Z = 1$, and cell dimensions of a 11.014(2), b 14.751(3), c 15.168(3) Å, α 123.95(2)°, β 95.77(2)°, γ 98.73(2)°. The structure was solved by a combination of multisolution sign expansion and Fourier methods, and final residuals were R 0.067 and R_w 0.066 for 5972 observed intensity data. The dianion comprises a distorted tetrahedron of osmium atoms, each metal also bonding to three terminal carbonyl ligands, which are staggered with respect to the metal—metal bonds. Unlike the cation, the cluster anion is statistically disordered between two centrosymmetrically related sites.

Previous studies [1] have shown that the reaction of triosmium dodecacarbonyl with sodium tetrahydroborate in refluxing tetrahydrofuran yields a mixture of salts which were described as 'uncharacterised anions'. Reinvestigation of this reaction has now established that the reaction mixture contains the cluster anions $[HOs_3(CO)_{11}]^-$ (I), $[H_3Os_4(CO)_{12}]^-$ (II) and $[H_2Os_4(CO)_{12}]^{2-}$ (III), which can be separated and isolated by careful fractional crystallization of the bis(triphenylphosphine)iminium salts from methanol.

$$Os_3(CO)_{12} \xrightarrow[\text{reflux}]{NaBH_4\text{—THF}} \underset{(I,\ 56\%)}{[HOs_3(CO)_{11}]^-} + \underset{(II,\ 4\%)}{[H_3Os_4(CO)_{12}]^-} + \underset{(III,\ 11\%)}{[H_2Os_4(CO)_{12}]^{2-}}$$

The anions I and II have been obtained previously by different routes, and have been reported recently [2,3]. The dianionic tetranuclear cluster $[H_2Os_4(CO)_{12}]^{2-}$ is new, and can be obtained as the main product of the reaction by using dioxane as the solvent.

$$Os_3(CO)_{12} \xrightarrow[\text{reflux}]{\text{NaBH}_4\text{—dioxane}} \underset{(\text{II, }7\%)}{[H_3Os_4(CO)_{12}]^-} + \underset{(\text{III, }39\%)}{[H_2Os_4(CO)_{12}]^{2-}}$$

The salt $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ is obtained as an analytically pure orange precipitate, which decomposes at 163°C. The compound is slightly air-sensitive and dissolves in methanol, dichloromethane, tetrahydrofuran and acetonitrile.

The IR spectrum of III shows five absorptions in the carbonyl stretching region at 2012vw, 1978vs, 1948s, 1928s and 1871m cm^{-1} (in CH_2Cl_2), which are indicative of only terminal carbonyl groups. The full range IR spectrum, recorded with a KBr pellet, also reveals the characteristic vibrations of the bis(triphenylphosphine)iminium cations. The FT ^1H NMR spectrum shows the aromatic multiplet, due to the $[N(PPh_3)_2]^+$ cation, at δ 7.59 ppm, and only one hydrido singlet, at δ −20.58 ppm (in CD_3COCD_3).

The structure determination is in agreement with the molecular configuration predicted from spectroscopic data. The dianion is statistically disordered, sitting on a crystallographic centre of symmetry. The four osmium atoms define a distorted tetrahedron, with four short (mean Os—Os 2.798 Å) and two long

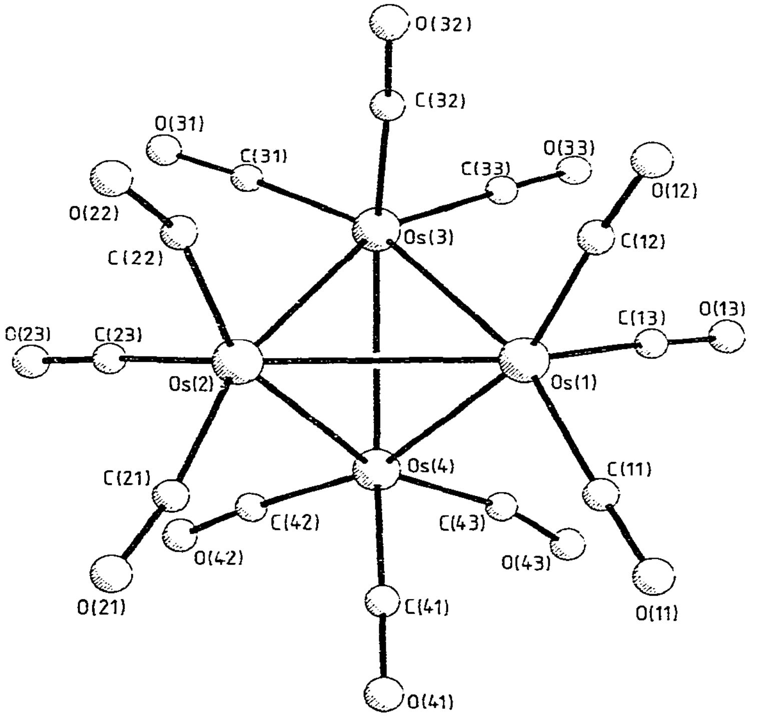

Fig. 1. The $[H_2Os_4(CO)_{12}]^{2-}$ anion, showing the atom numbering scheme. Only one orientation of the disordered molecule has been shown for clarity.

TABLE 1

BOND LENGTHS (Å)

Os(2)—Os(1)	2.937(2)	Os(3)—Os(2)	2.792(2)
Os(3)—Os(1)	2.797(2)	Os(4)—Os(2)	2.792(2)
Os(4)—Os(1)	2.811(2)	Os(4)—Os(3)	2.931(2)
P(1)—N(1)	1.593(9)	C(121)—P(1)	1.792(5)
P(2)—N(1)	1.579(9)	C(201)—P(2)	1.813(8)
C(101)—P(1)	1.796(9)	C(211)—P(2)	1.787(9)
C(111)—P(1)	1.788(9)	C(221)—P(2)	1.803(7)

TABLE 2

BOND ANGLES (°)

Os(3)—Os(1)—Os(2)	58.2(1)	C(11)—Os(1)—Os(2)	111.2(4)
Os(4)—Os(1)—Os(2)	58.1(1)	C(11)—Os(1)—Os(3)	161.4(6)
Os(4)—Os(1)—Os(3)	63.0(1)	C(11)—Os(1)—Os(4)	98.5(7)
Os(3)—Os(2)—Os(1)	58.4(1)	C(12)—Os(1)—Os(2)	109.5(5)
Os(4)—Os(2)—Os(1)	58.7(1)	C(12)—Os(1)—Os(3)	99.4(4)
Os(4)—Os(2)—Os(3)	63.3(1)	C(12)—Os(1)—Os(4)	161.7(4)
Os(2)—Os(3)—Os(1)	63.4(1)	C(13)—Os(1)—Os(2)	141.1(6)
Os(4)—Os(3)—Os(1)	58.7(1)	C(13)—Os(1)—Os(3)	87.7(4)
Os(4)—Os(3)—Os(2)	58.3(1)	C(13)—Os(1)—Os(4)	91.3(7)
Os(2)—Os(4)—Os(1)	63.2(1)	C(21)—Os(2)—Os(1)	109.8(4)
Os(3)—Os(4)—Os(1)	58.3(1)	C(21)—Os(2)—Os(3)	162.4(6)
Os(3)—Os(4)—Os(2)	58.3(1)	C(21)—Os(2)—Os(4)	99.8(7)
C(12)—Os(1)—C(11)	98.7(8)	C(22)—Os(2)—Os(1)	106.6(6)
C(13)—Os(1)—C(11)	95.5(6)	C(22)—Os(2)—Os(3)	95.5(6)
C(13)—Os(1)—C(12)	93.0(10)	C(22)—Os(2)—Os(4)	158.2(6)
C(22)—Os(2)—C(21)	100.6(10)	C(23)—Os(2)—Os(1)	139.1(8)
C(23)—Os(2)—C(21)	95.9(10)	C(23)—Os(2)—Os(3)	88.2(8)
C(23)—Os(2)—C(22)	98.9(10)	C(23)—Os(2)—Os(4)	86.6(8)
C(32)—Os(3)—C(31)	95.8(8)	C(31)—Os(3)—Os(1)	160.7(7)
C(33)—Os(3)—C(31)	101.6(8)	C(31)—Os(3)—Os(2)	97.6(7)
C(33)—Os(3)—C(32)	97.4(10)	C(31)—Os(3)—Os(4)	109.7(6)
C(42)—Os(4)—C(41)	98.4(10)	C(32)—Os(3)—Os(1)	88.2(5)
C(43)—Os(4)—C(41)	95.8(10)	C(32)—Os(3)—Os(2)	91.3(6)
C(43)—Os(4)—C(42)	99.5(11)	C(32)—Os(3)—Os(4)	141.8(6)
O(11)—C(11)—Os(1)	173.1(21)	C(33)—Os(3)—Os(1)	96.5(4)
O(12)—C(12)—Os(1)	175.4(16)	C(33)—Os(3)—Os(2)	158.0(4)
O(13)—C(13)—Os(1)	177.3(12)	C(33)—Os(3)—Os(4)	104.4(6)
O(21)—C(21)—Os(2)	170.4(18)	C(41)—Os(4)—Os(1)	86.6(9)
O(22)—C(22)—Os(2)	157.3(20)	C(41)—Os(4)—Os(2)	87.5(8)
O(23)—C(23)—Os(2)	175.3(22)	C(41)—Os(4)—Os(3)	138.4(10)
O(31)—C(31)—Os(3)	173.2(20)	C(42)—Os(4)—Os(1)	161.8(6)
O(32)—C(32)—Os(3)	177.1(15)	C(42)—Os(4)—Os(2)	99.3(7)
O(33)—C(33)—Os(3)	179.3(22)	C(42)—Os(4)—Os(3)	109.2(6)
O(41)—C(41)—Os(4)	171.3(29)	C(43)—Os(4)—Os(1)	97.4(10)
O(42)—C(42)—Os(4)	176.9(17)	C(43)—Os(4)—Os(2)	160.2(10)
O(43)—C(43)—Os(4)	169.9(25)	C(43)—Os(4)—Os(3)	109.1(9)
P(2)—N(1)—P(1)	135.6(6)	C(102)—C(101)—P(1)	116.9(4)
C(101)—P(1)—N(1)	114.2(4)	C(106)—C(101)—P(1)	123.0(5)
C(111)—P(1)—N(1)	109.8(4)	C(112)—C(111)—P(1)	120.9(6)
C(111)—P(1)—C(101)	110.2(4)	C(116)—C(111)—P(1)	119.1(5)
C(121)—P(1)—N(1)	108.5(3)	C(122)—C(121)—P(1)	118.4(4)
C(121)—P(1)—C(101)	106.1(3)	C(126)—C(121)—P(1)	121.6(4)
C(121)—P(1)—C(111)	107.8(3)	C(202)—C(201)—P(2)	121.9(4)
C(201)—P(2)—N(1)	114.5(4)	C(206)—C(201)—P(2)	117.4(6)
C(211)—P(2)—N(1)	107.6(5)	C(212)—C(211)—P(2)	119.1(4)
C(211)—P(2)—C(201)	109.6(3)	C(216)—C(211)—P(2)	120.7(7)
C(221)—P(2)—N(1)	110.9(3)	C(222)—C(221)—P(2)	118.7(5)
C(221)—P(2)—C(201)	108.4(4)	C(226)—C(221)—P(2)	121.2(3)
C(221)—P(2)—C(211)	105.4(3)		

(mean Os—Os 2.943 Å) edges. Each metal atom is also bonded to three terminal carbonyl ligands. The two long metal—metal bonds are opposite to each other, and the distribution of the carbonyl ligands is in keeping with the anion having idealised D_{2d} symmetry. Figure 1 shows a single dianion, and some bond lengths and angles for the dianion and the unique cation are listed in Tables 1 and 2, respectively.

The ^{1}H NMR spectrum is consistent with the two hydrides being equivalent, and they are considered to bridge the two long metal—metal (Os(1)—Os(2) and Os(3)—Os(4)) edges, from the carbonyl configuration. The carbonyl ligands are staggered with respect to the metal—metal bond, in contrast to the eclipsed geometry in $H_4Re_4(CO)_{12}$ [4], where the hydrides probably triply bridge the faces of the Re_4 tetrahedron. The *cis* Os—Os—C (carbonyl) angles involving Os(1)—Os(2) and Os(3)—Os(4) bonds average 109°, compared to an angle of 93° for the remainder. A similar bending away of the carbonyl ligands from

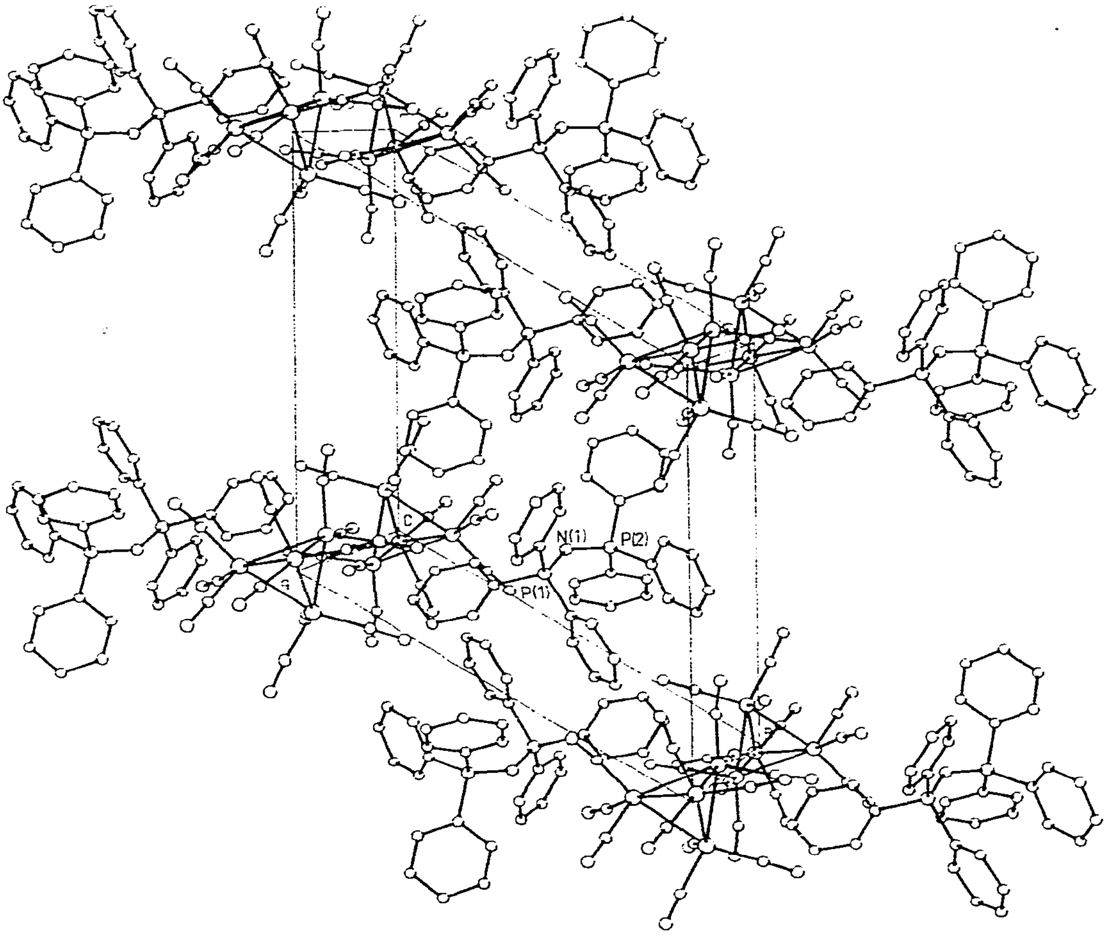

Fig. 2. The unit cell contents for $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$.

ostensibly hydrido-bridged edges has been observed in the tetranuclear clusters $[(\mu\text{-H})_6Re_4(CO)_{12}]^{2-}$ [5], $Os_3Pt(\mu\text{-H})_2(CO)_{10}P(C_6H_{11})_3$ [6], and $(\mu\text{-H})_3CoOs_3(CO)_{12}$ [7]. The lengthening of the metal—metal bonds has also been taken as an indication of the presence of bridging hydrides [5], and the long Os—Os bond lengths are similar to the mean value of 2.964 Å for the edge bridged metal—metal bonds in $H_4Os_4(CO)_{12}$ [8]. The unbridged Os—Os distances in the dianion $[H_2Os_4(CO)_{12}]^{2-}$ are also in good agreement with the value of 2.816 Å of the neutral complex.

The carbonyl ligands are all approximately linear, the large deviation of the Os(2)—C(22)—O(22) unit is thought to be an artifact arising from the disorder rather than a true structural feature. There is no evidence for incipient bridge bonding between terminal carbonyls and adjacent metal atoms, as reported for some polynuclear osmium clusters [9]. This suggests an even distribution of electrons at the metal centres, and in terms of electron counting the dianion may be considered as a 'closed' 60 electron system.

The dimensions of the cation shown in the packing diagram (Fig. 2) are similar to those reported by Rivera et al. [10], with staggered PPh_3 groups. The dianion and the centrosymmetrically related cations are separated by normal van der Waals' distances, and there are no abnormally short intramolecular contacts in either species.

Experimental

All operations were carried out under rigorous exclusion of air by using Schlenk-techniques. The solvents were distilled over drying agents such as sodium—potassium alloy or calcium hydride, and saturated with purified nitrogen.

Reaction of $Os_3(CO)_{12}$ with $NaBH_4$ in tetrahydrofuran

A solution of 450 mg (ca. 0.5 mmol) $Os_3(CO)_{12}$ and 200 mg (ca. 5.0 mmol) $NaBH_4$ in 50 ml tetrahydrofuran was refluxed for 1 h. Then the red coloured reaction mixture was filtered through filter floc, and the filtrate evaporated to dryness. The residue was dissolved in 20 ml methanol, and after addition of 350 mg (ca. 0.6 mmol) $[(PPh_3)_2N]Cl$ in 10 ml methanol the solution was refluxed for 15 min, and concentrated to 20 ml. During cooling to room temperature the salt $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ precipitated in analytically pure form; it was washed with a little cold methanol and dried (yield 90 mg, 11%). The filtered solution was concentrated to 15 ml and cooled to −25°C, and the salt $[H_3Os_4(CO)_{12}][N(PPh_3)_2]$ was obtained as a precipitate, which was separated and recrystallized from methanol (yield 25 mg; 4%). The solution was evaporated to dryness, the residue washed twice with 20 ml water in order to remove excess $[(PPh_3)_2N]Cl$, and the remaining $[HOs_3(CO)_{11}][N(PPh_3)_2]$ dried under high vacuum (yield 395 mg; 56%).

Reaction of $Os_3(CO)_{12}$ with $NaBH_4$ in dioxane

A solution of 450 mg (ca. 0.5 mmol) $Os_3(CO)_{12}$ and 200 mg (ca. 5.0 mmol) $NaBH_4$ in 50 ml dioxane was refluxed for 4 h. The resulting light brown suspension was filtered through filter floc and the filtrate discarded. The solid was washed with 10 ml dioxane, removed from the filter by dissolving it in 50 ml tetrahydrofuran and then the solvent drawn off. The residue was taken in 30 ml of methanol, to which a solution of 570 mg (ca. 1.0 mmol) $[PPh_3)_2N]Cl$ in 10 ml methanol was added. After heating and concentration to 25 ml the salt $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ precipitated. The analytically pure precipitate was isolated, washed with little cold methanol and dried (yield 320 mg; 39%). The filtered solution was concentrated to 15 ml and cooled to —25°C. The precipitating salt $[H_3Os_4(CO)_{12}][N(PPh_3)_2]$ was separated and recrystallized from methanol (yield 45 mg; 7%).

$[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ micro-analysis. Found: C, 46.12; H, 3.03; N, 1.18; P, 5.85. $C_{84}H_{62}N_2O_{12}Os_4P_4$ calcd.: C, 46.36; H, 2.88; N, 1.29; P, 5.69%.

The molecular and crystal structure of $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$

Crystal data: $C_{84}H_{62}N_2O_{12}Os_4P_4$, mol. wt. 2176.04, triclinic, a 11.014(2), b 14.751(3), c 15.168(3) Å, α 123.95(2)°, β 95.77(2)°, γ 98.73(2)°, U 1968.2 Å^3, d_c 1.84 g cm^{-3}, $Z = 1$. Space group $P\bar{1}$ from structure solution and refinement. Graphite-monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 65.49 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.245 × 0.350 × 0.560 mm.

Orange tablets of $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ were obtained by slow crystallization from a 1 : 2 dichloromethane/diethyl ether mixture, and mounted in Lindemann capillaries. 8972 intensities were recorded ($3.0 < 2\theta \leqslant 60.0°$) on a Syntex $P2_1$ four-circle diffractometer, using graphite-monochromated Mo-K_α radiation, and a θ—2θ scan procedure. Lp corrections, and semi-empirical absorption corrections, based on a pseudo-ellipsoid model and 490 azimuthal scan data from 16 independent reflections were applied. This gave transmission coefficients which ranged from 0.95 to 0.55 for the full data set. The data were averaged to give 5972 unique observed reflections [$I > 2.5\sigma(I)$]. Cell dimensions were derived from the angular measurements of 15 strong reflections ($25.0 < 2\theta < 35.0°$).

The structure was solved by a combination of multisolution sign expansion and Fourier techniques. The calculated density indicated the presence of one $[H_2Os_4(CO)_{12}][N(PPh_3)_2]_2$ species in the cell. This was in keeping with the molecule crystallizing in the non-centrosymmetric space group $P1$, for if the complex were to crystallize in $P\bar{1}$, it would require the anion to sit on a centre of symmetry. The 'best' E-map obtained from multisolution Σ_2 sign expansion showed four strong peaks around the origin, which together with their symmetry equivalents, defined a cube. Multisolution tangent refinement in $P1$ also revealed a cubic configuration. This could be interpreted in terms of two interlocking tetrahedra, and in the centrosymmetric case represents a statistically disordered model (Fig. 3). Fourier difference synthesis calculated, in $P\bar{1}$, with half osmium atoms at the vertices of one of these tetrahedra, revealed the positions of the carbonyl groups, and of the unique bis(triphenylphosphine)iminium ligand. The structure was refined by blocked full-matrix least-squares with anisotropic Os and P atoms, and isotropic C, N and O atoms. In view of the relatively large uncertainties in light atom positions, the X-ray scattering being dominated by the osmium contribution, and because of refinement problems with the disordered model, all the carbonyl Os—C and C—O bond lengths were constrained to equal

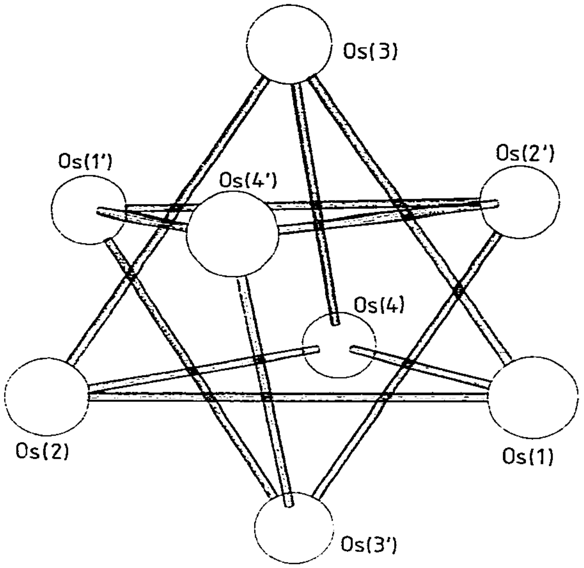

Fig. 3. The nature of the disorder of the metal tetrahedron.

TABLE 3

ATOM COORDINATION (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

	x/a	*y/b*	*z/c*	*U*
Os(1)	—331(1)	—1572(1)	—761(1)	
Os(2)	—813(1)	520(1)	1038(1)	
Os(3)	1603(1)	399(1)	651(1)	
Os(4)	—410(1)	259(1)	—871(1)	
C(11)	—1825(9)	—2577(13)	—1787(11)	57(5)
O(11)	—2744(10)	—3249(12)	—2367(12)	87(5)
C(12)	73(17)	—2423(13)	—266(14)	51(4)
O(12)	332(17)	—2999(12)	—30(14)	76(5)
C(13)	712(17)	—2074(14)	—1754(14)	46(5)
O(13)	1313(12)	—2417(12)	—2395(9)	71(4)
C(21)	—2545(3)	413(15)	842(14)	51(4)
O(21)	—3579(7)	437(17)	879(16)	68(5)
C(22)	—512(18)	523(15)	2275(8)	47(4)
O(22)	—702(18)	617(15)	3050(10)	84(5)
C(23)	—309(22)	2076(4)	1715(18)	55(6)
O(23)	—83(14)	3035(3)	2138(11)	77(4)
C(31)	2428(20)	1912(6)	1736(14)	74(6)
O(31)	2845(16)	2842(5)	2458(10)	85(5)
C(32)	1904(19)	—117(15)	1513(13)	56(5)
O(32)	2081(17)	—392(14)	2080(11)	91(5)
C(33)	2839(13)	—113(15)	—141(13)	55(4)
O(33)	3594(11)	—428(15)	—636(11)	62(5)
C(41)	—2141(4)	—392(18)	—1453(17)	72(6)
O(41)	—3196(6)	—720(14)	—1870(13)	95(5)
C(42)	—392(18)	1714(6)	—467(15)	55(4)
O(42)	—426(18)	2587(7)	—260(14)	76(5)
C(43)	38(25)	—341(20)	—2214(11)	80(7)
O(43)	150(16)	—686(12)	—3085(6)	65(4)
N(1)	—4240(5)	5932(6)	3232(5)	44(2)
P(1)	—3139(2)	5599(2)	2592(2)	

(continued)

TABLE 3 (continued)

	x/a	y/b	z/c	U
P(2)	−4845(2)	6974(2)	3772(2)	
C(101)	−2745(5)	6354(4)	2013(4)	36(2)
C(102)	−3683(5)	6184(4)	1209(4)	44(2)
C(103)	−3472(5)	6799(4)	774(4)	54(2)
C(104)	−2321(5)	7582(4)	1142(4)	55(2)
C(105)	−1382(5)	7752(4)	1946(4)	57(2)
C(106)	−1594(5)	7137(4)	2381(4)	48(2)
C(111)	−1768(6)	5781(6)	3470(5)	53(2)
C(112)	−716(6)	5437(6)	3068(5)	89(4)
C(113)	369(6)	5639(6)	3777(5)	117(5)
C(114)	402(6)	6186(6)	4886(5)	124(5)
C(115)	−650(6)	6531(6)	5287(5)	115(5)
C(116)	−1735(6)	6328(6)	4579(5)	83(3)
C(121)	−3647(5)	4134(3)	1470(4)	38(2)
C(122)	−4556(4)	3425(3)	1544(4)	47(2)
C(123)	−4926(5)	2270(3)	713(4)	58(2)
C(124)	−4387(5)	1824(3)	−193(4)	64(3)
C(125)	−3478(5)	2533(4)	−267(4)	64(3)
C(126)	−3108(5)	3689(3)	564(4)	54(2)
C(201)	−3808(6)	8289(5)	4185(5)	47(2)
C(202)	−3873(6)	8689(5)	3542(5)	62(2)
C(203)	−2940(6)	9607(5)	3803(5)	77(3)
C(204)	−1941(6)	10127(5)	4707(5)	85(3)
C(205)	−1875(6)	9727(5)	5351(5)	98(4)
C(206)	−2808(6)	8808(5)	5090(5)	75(3)
C(211)	−5330(6)	7136(6)	4931(5)	49(2)
C(212)	−5635(6)	6193(6)	4947(5)	70(3)
C(213)	−6104(6)	6284(6)	5807(5)	87(3)
C(214)	−6268(6)	7317(6)	6650(5)	84(3)
C(215)	−5963(6)	8261(6)	6634(5)	101(4)
C(216)	−5494(6)	8170(6)	5775(5)	84(3)
C(221)	−6269(5)	6694(5)	2867(4)	46(2)
C(222)	−6809(5)	5588(5)	1957(4)	59(2)
C(223)	−7951(5)	5333(5)	1279(4)	75(3)
C(224)	−8552(5)	6185(5)	1511(4)	74(3)
C(225)	−8012(5)	7291(5)	2421(4)	73(3)
C(226)	−6870(5)	7545(5)	3099(4)	61(2)

1.87 and 1.15 Å, respectively; the constraints did not significantly increase R. The cation phenyl rings were refined as rigid groups with idealised geometry (C—C 1.395 Å, C—C—C 120°). An empirical extinction parameter x, which refined to 0.0029(20), was included [F_c is multiplied by $(1 - 0.0001\,xF_c^2/\sin\theta)$], and a weighting scheme of the form $w = 1.435/(\sigma^2(F) + 0.0009|F|^2)$, for which $w\Delta^2$ was fairly independent of $|F_0|$ and $\sin\theta$, introduced. The refinement converged to $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0| = 0.066$ and $R = 0.067$. A Fourier differenc synthesis calculated at this stage showed ripples of ca. 1 eÅ^{-3} close to the metal atom positions, but did not reveal the location of the hydrides. Phenyl hydrogens were not included.

Refinement of a similarly disordered model in $P1$, including site occupancy refinement, produced unreasonable bond parameters in the cation, and did not reduce R significantly.

The final atomic coordinations and isotropic temperature factors are given in Table 3, while the anisotropic thermal parameters are listed in Table 4.

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS (Å^2 × 10^3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	39(1)	30(1)	36(1)	18(1)	12(1)	5(1)
Os(2)	46(1)	32(1)	39(1)	21(1)	15(1)	10(1)
Os(3)	36(1)	37(1)	43(1)	21(1)	5(1)	2(1)
Os(4)	47(1)	47(1)	44(1)	34(1)	11(1)	6(1)
P(1)	42(1)	33(1)	34(1)	21(1)	7(1)	10(1)
P(2)	52(1)	39(1)	34(1)	21(1)	14(1)	16(1)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^*)$

Complex neutral-atom scattering factors [11] were employed. Calculations were performed with the University of Cambridge IBM 370/165 computer using programs written by G.M.S., and the PLUTO plotting program written by Dr. W.D.S. Motherwell.

Structure factors may be obtained from the authors.

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