

Fig. 2. Numbering scheme of the molecule, excluding perchlorate ion and H atoms.

atom which is equal to $11.06 \text{ \AA}^3/\text{atom}$. The Fe atom and each cyanide are almost in a line and the angle $C(N5)-Fe-C(N6)$ is $85.6(3)^\circ$. The coordination bond

distances of iron and carbon atoms are shorter than those of iron and nitrogen atoms. Other bond lengths and bond angles are normal.

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Structure of 1,2- μ -Acetato-(*O,O'*)-1,1,1,2,2,2,3,3,3,3-decacarbonyl- μ -hydrido-triangulo-triosmium: A Redetermination and Normal Probability Plot Analysis

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Abstract. $[\text{Os}_3(\text{C}_2\text{H}_3\text{O}_2)\text{H}(\text{CO})_{10}]$, $M_r = 910.76$, monoclinic, $P2_1/m$, $a = 7.882(3)$, $b = 12.622(3)$, $c = 9.908(2) \text{ \AA}$, $\beta = 109.73(2)^\circ$, $U = 927.8 \text{ \AA}^3$, $Z = 2$, $D_m = 3.26(2)$, $D_x = 3.259 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 205.4 \text{ cm}^{-1}$, $F(000) = 800$, room temperature, final $R = 0.029$ for 1488 reflections [$F > 3\sigma(F)$]. The structure is fully consistent with that previously reported [Lausarot, Vaglio, Valle, Tiripicchio, Camellini & Gariboldi (1985). *J. Organomet. Chem.* **291**, 221–229]. In addition to the random error present for the positional parameters of the two independent sets of data, systematic errors have been found in the thermal parameters associated with the Os atoms.

Introduction. As part of a study on model compounds of trinuclear osmium clusters grafted on oxide surfaces

(i.e. with bridging oxygen donors), the title compound was studied. The composition of the crystals examined only became clear during the structure solution when it was quickly realized that the structure had already been reported (Lausarot, Vaglio, Valle, Tiripicchio, Camellini & Gariboldi, 1985). These two independent determinations thus provide an opportunity for the application of a normal probability plot analysis to the atomic coordinates and thermal parameters (Abrahams & Keve, 1971).

Experimental. Air-stable yellow crystals from cyclohexane; density by flotation ($\text{CHBr}_3/\text{CH}_2\text{I}_2$). Preliminary data from photographic X-ray examination and accurate cell dimensions from 25 accurately centred reflections using an Enraf-Nonius CAD-4 diffractometer fitted with graphite monochromator and $\text{Mo } K\alpha$ radiation. Intensities of 1846 reflections were recorded ($1.5 < \theta < 25^\circ$; $h 0-9$, $k 0-15$, $l -11-11$)

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using a crystal of dimensions $0.45 \times 0.2 \times 0.08$ mm. Two intensity controls (644, 053) indicated no decay of the sample with time. An empirical ψ -scan absorption correction was applied from three reflections (40 $\bar{1}$, 50 $\bar{1}$, 61 $\bar{2}$) (transmission: max. 99.9, min. 27.0%). Systematic absences: $h0l$, none; $0k0$, $k \neq 2n$. After data reduction 1712 unique reflections remained of which 1491 with $F > 3\sigma(F)$ were used in the analysis. The structure was solved by conventional means from the Patterson synthesis. Evidence for the methyl H atoms (one on the mirror plane) came from a difference electron-density synthesis; geometrical constraints were applied to the interatomic distances in the methyl group (C—H = 0.95, H...H = 1.55, C...H = 2.04 Å) in order to position the H atoms, and these coordinates were used without refinement in subsequent calculations. Three reflections (310, 011, $\bar{1}03$) appeared to suffer extinction and were removed from the analysis. Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ converged to $R = 0.029$ {133 parameters, 1488 reflections, anisotropic Os, O, C atoms, $w = 1/[\sigma^2(F) + 0.0001F^2]$, max. shift/e.s.d. 0.11, $wR = 0.033$ }. The residual electron density was in the range 1.33 to $-1.42 e \text{ \AA}^{-3}$, but no convincing case could be advanced for the position of the hydride H atom. Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, pp. 99–101, 149–150). All calculations were carried out using *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965) on an IBM 3090 computer. The atomic parameters are presented in Table 1.*

Half-normal probability plot analysis has been applied to compare the present study and the earlier results of Lausarot *et al.* (1985) ($R = 0.040$, $wR = 0.053$, 1484 reflections). The combined data were divided into two sets: (i) the positional parameters only, which consisted of 44 data points; and (ii) the combined positional and thermal parameters comprising 132 data points. The δm_i (observed) values were determined using the expression given in (1).

$$\delta m(\text{observed}) = [|p(1)| - |p(2)|] / [\sigma^2 p(1) + \sigma^2 p(2)]^{1/2}, \quad (1)$$

where $p(1)$ and $p(2)$ are the corresponding parameters for the two data sets. The δm_i (expected) values were obtained from *International Tables for X-ray Crystallography* (1974, pp. 293–310).

Discussion. Selected bond lengths and angles for the title compound are listed in Table 2. A single molecule

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and the data for the normal probability plots have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44831 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($\text{\AA}^2 \times 10^3$)

	$U_{\text{eq}} = \frac{1}{3}(\text{trace of diagonalized } U)$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Os(1)	0.06684 (5)	0.13536 (2)	0.22419 (3)	32.9 (2)
Os(2)	0.39979 (7)	0.2500	0.33771 (6)	41.6 (3)
C(1)	0.0669 (13)	0.1175 (6)	0.4116 (10)	40 (4)
O(1)	0.0617 (12)	0.1108 (5)	0.5248 (7)	62 (4)
C(2)	0.2101 (14)	0.0116 (8)	0.2333 (10)	51 (5)
O(2)	0.2962 (12)	-0.0622 (6)	0.2395 (9)	77 (5)
C(3)	-0.1595 (15)	0.0642 (8)	0.1438 (10)	50 (5)
O(3)	-0.2958 (11)	0.0198 (7)	0.1037 (9)	81 (5)
C(4)	0.3838 (17)	0.2500	0.5318 (15)	48 (7)
O(4)	0.3874 (17)	0.2500	0.6440 (12)	81 (8)
C(5)	0.4161 (21)	0.2500	0.1447 (17)	56 (8)
O(5)	0.4336 (18)	0.2500	0.0354 (13)	84 (8)
C(6)	0.5604 (16)	0.1317 (10)	0.3931 (12)	62 (6)
O(6)	0.6517 (13)	0.0594 (9)	0.4227 (11)	104 (7)
C(7)	0.0481 (20)	0.2500	-0.0513 (13)	45 (7)
C(8)	0.0323 (27)	0.2500	-0.2063 (15)	67 (9)
O(7)	0.0558 (10)	0.1609 (5)	0.0092 (7)	47 (3)
H(81)	-0.0941	0.2500	-0.2660	80*
H(82)	0.0834	0.1855	-0.2287	80*

* Fixed isotropic temperature factor.

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

	Present study	Previous study*
Os(1)—Os(1 ¹)	2.894 (2)	2.875 (3)
Os(1)—Os(2)	2.873 (1)	2.857 (2)
Os(1)—O(7)	2.127 (6)	2.13 (1)
C(7)—O(7)	1.266 (8)	1.25 (2)
C(7)—C(8)	1.50 (2)	1.52 (4)
Os—C(carbonyl)		
Max.	1.97 (1)	1.97 (2)
Min.	1.87 (1)	1.83 (2)
Av.	1.92	1.89
C—O(carbonyl)		
Max.	1.16 (1)	1.18 (2)
Min.	1.10 (2)	1.06 (2)
Av.	1.14	1.16
Os(1)—Os(2)—Os(1 ¹)	60.5 (1)	60.4 (1)
O(7)—Os(1)—Os(2)	92.2 (2)	91.4 (4)
Os(1)—O(7)—C(7)	126.0 (6)	124.5 (7)
O(7)—C(7)—C(8)	117.3 (5)	116.1 (5)
O(7)—Os(1)—C(1)	177.2 (3)	177.8 (6)
O(7)—Os(1)—C(2)	89.7 (3)	89.0 (6)
O(7)—Os(1)—C(3)	86.4 (3)	88.0 (6)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

* Lausarot, Vaglio, Valle, Tiripicchio, Camellini & Gariboldi (1985).

showing the mirror symmetry is illustrated in Fig. 1. On symmetry grounds the hydride H atom must be located on the mirror plane (unless disordered) and indeed several weak features in the difference electron-density map were found. However, none of these seemed to be chemically reasonable and the justification for selecting one feature from several would be hard to defend. Unrefined coordinates for the hydride were, however, suggested in the previous study but must be regarded with some reservation. A comparison of crystal parameters reveals a large difference of 0.08 Å in the

two evaluations of the unit cell *b* parameter (Taylor & Kennard, 1986) which must give rise to differences in molecular geometry. It is apparent that the e.s.d. values associated with the bond lengths in the present study are smaller than those of Lausarot *et al.* (1985).

The normal probability plot analysis has been put forward (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) as a concise and sensitive method for comparing independent sets of crystallographic data, but examples of this technique are uncommon (Kratky & Dunitz, 1975). The half-normal probability plot derived from the positional parameters is shown in Fig. 2. Excluding one data point [O(6), *z* coordinate] it is close to linear and passes through the origin, indicating only random error in the data. The array has a slope of about 1.37 indicating either that the Δp_i are too large, the σp_i too small, or that both conditions are applicable (Abrahams & Keve, 1971). The half-normal probability plot for the case when Δp_i are too large cannot be linear, but the alternative hypothesis, that σp_i are too small, may be accounted for if both sets of data are fitted by least squares to the calculated structure factors better than is warranted, leading to an underestimation of σp_i values. If the distribution of error between $\sigma p(1)_i$ and $\sigma p(2)_i$ is equal, then both sets of standard deviations are too small by 37%. This accords well with an extensive analysis of estimated errors (Taylor & Kennard, 1986). The half-normal probability plot presented in Fig. 3, for both positional and thermal parameters, shows deviation from linearity for high δm values. The linear part of the plot has a slope of 1.27 and passes through the origin, again indicating the presence of only random errors in these parameters. The points deviating severely from linearity correspond to one positional coordinate [O(6), *z* coordinate] and eight of the thermal parameters associated with the Os atoms. The possible origins of curvature and a slope different to unity in normal probability plots have been discussed (Abrahams & Keve, 1971; Kratky & Dunitz,

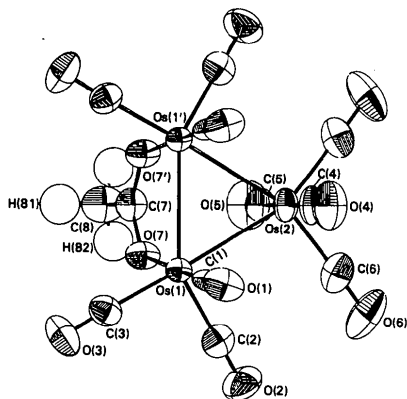


Fig. 1. [(μ -H)(μ -O₂CMe)Os₃(CO)₁₀] drawn with 50% probability surfaces. Primed atoms (') are related by $x, \frac{1}{2}-y, z$ to the unprimed atoms.

1975). In the present case the different absorption corrections [ψ scan in this work and one based on *DIFABS* (Walker & Stuart, 1983) in the previous study] must be regarded as a major contributor. This analysis supports the view that for routine structure determination it is the thermal parameters that are more likely to be subject to errors.

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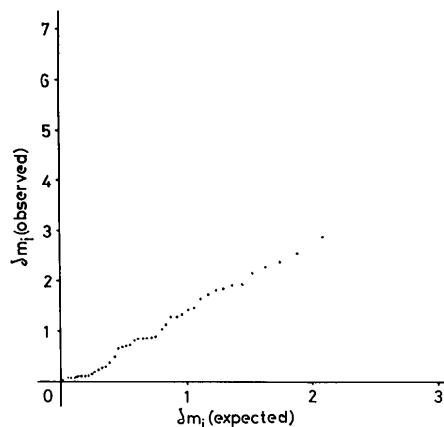


Fig. 2. Half-normal probability plot of δm_i from 44 positional coordinates.

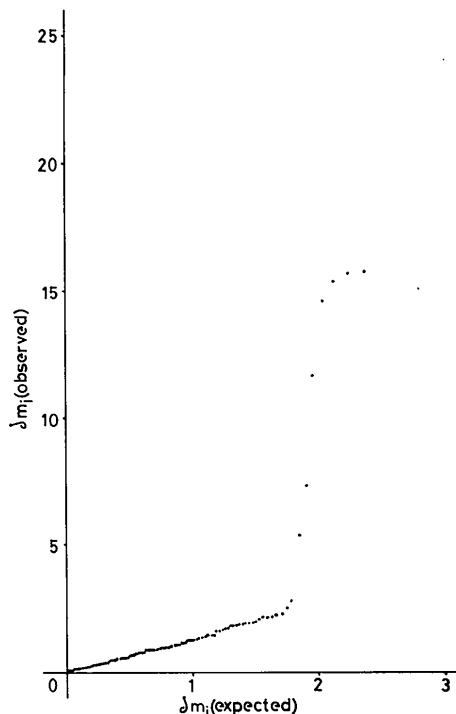


Fig. 3. Half-normal probability plot of δm_i from 132 thermal and positional parameters.

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Structure of a Calcium Ethylenediammonium Cyclotetraphosphate Hydrate

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Abstract. $\text{Ca}[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{P}_4\text{O}_{12}\cdot 15/2\text{H}_2\text{O}$, $M_r = 553.19$, orthorhombic, $Pnma$, $a = 14.611$ (3), $b = 18.709$ (3), $c = 7.861$ (2) Å, $V = 2149$ (1) Å³, $Z = 4$, $D_x = 1.710$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.672$ mm⁻¹, $F(000) = 1148$, $T = 295$ K, final $R = 0.031$ for 2677 independent reflexions. The P_4O_{12} ring anion has a rather rare configuration, with two of the bonding O atoms located on a mirror plane. Organic groups are centrosymmetrical and all located in $y = 0.0$ and 0.5 planes. Ten of the 30 water molecules are statistically distributed on three general positions. The hydrogen-bond scheme is described.

Introduction. A monophosphate of ethylenediammonium, $\text{C}_2\text{H}_{10}\text{N}_2^{2+}\cdot\text{HPO}_4^{2-}$, has recently been described (Averbuch-Pouchot & Durif, 1987). Up to now no condensed phosphate containing the $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$ group has been reported. The title compound is the first description of a series of *cyclo*-tetraphosphates characterized in the systems $(\text{C}_2\text{H}_{10}\text{N}_2)_2\text{P}_4\text{O}_{12}-M^{II}_2\text{P}_4\text{O}_{12}-\text{H}_2\text{O}$ ($M^{II} = \text{Ba}, \text{Sr}, \text{Pb}, \text{Ca}, \text{Mn}, \text{Cd}, \text{Co}, \text{Cu}, \text{Mg}, \text{Ni}$) (Averbuch-Pouchot, Durif & Guitel, 1988).

Experimental. Crystals were obtained by adding calcium carbonate and ethylenediamine in stoichiometric ratio to an aqueous solution of *cyclo*-tetraphosphoric acid kept at low temperature ($T < 278$ K); they appear as large orthorhombic prisms with various morphologies. Density not measured. Crystal size: $0.37 \times 0.30 \times 0.32$ mm. Nicolet XRD diffractometer, graphite monochromator. Systematic absences: $0kl$ ($k + l = 2n$), $hk0$ ($h = 2n$). 18 reflexions ($14 < \theta < 16^\circ$) for refining the

unit cell. ω scan; variable scan speed between 1 and 4° min^{-1} ; scan width: 1.20° ; background measured for a time corresponding to 10% of the scan time; intensity and orientation reflexions: 0,14,0, 0,14,0, 10,0,0 with no significant variation; θ range $3\text{--}35^\circ$; 4767 reflexions measured (h,k,l); $h_{\text{max}} = 22$, $k_{\text{max}} = 28$, $l_{\text{max}} = 12$.

Lorentz and polarization corrections; no absorption correction. Direct methods: *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) used for structure determination; H atoms located by difference-Fourier synthesis; anisotropic full-matrix least-squares refinements on F for non-H atoms, isotropic for H atoms; unitary weighting scheme; final refinements with a set of 2677 ($I > 4\sigma_I$); extinction not taken into account; final R value 0.031 ($wR = 0.031$); R factor for the 4767 independent reflexions: 0.068. Scattering factors for neutral atoms, f' and f'' from *International Tables for X-ray Crystallography* (1974). *SDP* (Enraf-Nonius, 1977) used for all calculations. $S = 0.977$; max. $\Delta/\sigma = 0.03$; max $\Delta\rho = 0.29 \text{ e } \text{Å}^{-3}$. Computer used: microVAX II.

Discussion. Table 1 reports the final atomic coordinates.* The P_4O_{12} ring anion is built up of two crystallographically independent PO_4 tetrahedra and

* Lists of structure factors, anisotropic thermal parameters and additional bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44897 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.