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Structural studies on polynuclear osmium carbonyl hydrides. XXXVI *. The crystal structure of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO)$, a case wherein internally inconsistent Os–Os bond lengths can be explained by the presence of both ordered and disordered molecular sites in the crystal

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Abstract

The complex $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO)$ crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with a 9.2721(15), b 14.2272(21), c 12.6005(19) Å, β 92.423(13)°, V 1660.7(4) Å^3 and $Z = 4$. Diffraction data (Mo-K_α, $2\theta = 4.0\text{–}45.0°$) were collected on a Syntex $P2_1$/XTL system and the structure refined to R 6.5% for all 2292 reflections (R 4.9% for those 1805 data with $|F_o| > 3\sigma(|F_o|)$). Molecules are bisected by crystallographic mirror planes; the asymmetric unit therefore consists of two independent half molecules. Site "A" contains ordered molecules (Os–Os 2.760(1) Å, 2 × Os–(H)–Os 2.870(1) Å) but site "B" is associated with anomalous Os–Os distances (2 at 2.813(1) Å, 1 at 2.875(1) Å) which can be explained successfully by a two-fold pattern of disorder; other anomalies in interatomic parameters at site B are consistent with this explanation.

Introduction

The species $H_2Os_3(CO)_9CCO$ was originally isolated [6] from pyrolysis of $Os_3(CO)_{11}(CH_2)$ [7–10]. Subsequently it was shown that $HOs_3(CO)_{10}(CH)$ [11] rearranges under milder conditions to form $H_2Os_3(CO)_9CCO$ [12]. We have previously reported the identification of this material as $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO)$ [12]. We now present a detailed account of the crystal structure, which has a very interesting problem involving partial disorder.

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[*] For recent previous publications in this series see refs. 1–5.

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Experimental

Collection of X-ray diffraction data

A few crystals of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$, synthesized and characterized as described previously [12], were provided by Professor J.R. Shapley. For the diffraction study, a rather irregular fragment (ca. 0.15 × 0.1 × 0.1 mm) was cleaved from a larger crystal. This was sealed under Ar into a thin-walled glass capillary and was aligned and centered (with its extended direction parallel with the ϕ-axis) on a Syntex $P2_1$ automated four-circle diffractometer. All set-up operations and data collection were carried out as described previously [13]. Details are provided in Table 1.

The observed diffraction symmetry (C_{2h}, $2/m$) indicated that the crystal belonged to the monoclinic system. The systematic absences ($0k0$ for $k = 2n + 1$) are consistent with either the non-centrosymmetric monoclinic space group $P2_1$ (C_2^2; No. 4) or its centrosymmetric supergroup $P2_1/m$ (C_{2h}^2; No. 11). With $Z = 4$, the crystallographic asymmetric unit could therefore be either two entire molecules in $P2_1$ or one molecule in $P2_1/m$.

Table 1

Experimental data for the X-ray diffraction study of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$

(A) *Crystal data* [a]

Cryst. system: monoclinic	V 1660.7(4) Å^3
Space group: $P2_1/m$ (No. 11)	Formula: $\text{C}_{11}\text{H}_2\text{O}_{10}\text{Os}_3$
a 9.2721(15) Å	Mol. wt.: 864.7
b 14.2272(21) Å	Z 4
c 12.6005(19) Å	D(calc'd) 3.46 g cm^{-3}
β 92.423(13)°	T 24°C (297K)

(B) *Data collection*

Diffractometer: Syntex $P2_1$/XTL

Radiation: Mo-K_α(λ 0.710730 Å)

Monochromator: pyrolytic graphite; equatorial mode with $2\theta(\text{mono}) = 12.16°$; assumed to be 50% perfect/50% mosaic for polarization correction.

Reflections measured: $+h$, $\pm k$, $\pm l$ for $2\theta = 4.0\text{–}45.0°$; 4696 reflections were collected and merged to a unique set (under C_{2h} ($2/m$) symmetry) of 2292 reflections. $R(I) = 4.2\%$ for 2090 pairs of averaged reflections.

Scan conditions: coupled θ(crystal)–2θ(counter) scan from $[2\theta(K_{\alpha_1}) - 0.9]°$ through $[2\theta(K_{\alpha_2}) + 0.9]°$ at 2.5 deg/min in 2θ. Backgrounds counted (for one-half of total scan time) at each extreme of the 2θ scan.

Standard reflections: 3 approximately mutually orthogonal reflections ($5\ \bar{1}\ 0$, $0\ 10\ 0$, $1\ 1\ \bar{7}$) collected after each batch of 97 data points. No significant fluctuations or decay were observed.

Absorption correction: $\mu(\text{Mo-}K_\alpha) = 243.1\ \text{cm}^{-1}$; all data were corrected empirically by interpolation (in 2θ and ϕ) between the normalized transmission curves of 5 close-to-axial ψ-scan reflections
($0\bar{5}2$, $2\theta = 15.7°$, $T_{\min}/T_{\max} = 0.444$;
$1\bar{6}3$, $2\theta = 20.2°$, $T_{\min}/T_{\max} = 0.439$;
$0\bar{8}4$, $2\theta = 26.5°$, $T_{\min}/T_{\max} = 0.486$;
$0\overline{10}4$, $2\theta = 31.7°$, $T_{\min}/T_{\max} = 0.488$;
$1\bar{9}7$, $2\theta = 34.9°$, $T_{\min}/T_{\max} = 0.486$)

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[a] Cell parameters were based on the Mo-$K_{\bar{\alpha}}$ components of 25 reflections with $2\theta = 20\text{–}30°$ ({092}, {057}, {$11\bar{7}$}, {$44\bar{4}$}, {$64\bar{2}$}, {$51\bar{6}$} and $26\bar{2}$).

Table 2

Intensity statistics on diffraction data for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$

	Number	Observed	Theoretical	
			Centric	Acentric
$\|E\| > 1.0$	651	28.40%	31.73%	36.79%
$\|E\| > 2.0$	155	6.76%	4.55%	1.89%
$\|E\| > 2.5$	55	2.40%	1.24%	0.19%
$\|E\| > 3.0$	9	0.35%	0.27%	0.01%
$\langle \|E\| \rangle$		0.754	0.798	0.886
$\langle \|E\| \rangle$		1.003	1.000	1.000
$\langle \|E\|^2 - 1 \rangle$		1.094	0.968	0.736

Because of the possibility that the true space group might be polar (i.e., $P2_1$), we elected to collect diffraction data from the hemisphere defined by $+h$, $\pm k$, $\pm l$. This provides two point-group equivalent forms for space group $P2_1/m$ ($I(hkl) = I(h\bar{k}l)$ and $I(hk\bar{l}) = I(h\bar{k}\bar{l})$) but only a single point-group unique form for the polar space group $P2_1$, thereby facilitating (should it be necessary) the determination of crystal polarity via differences caused by anomalous dispersion ($\Delta f'(\text{Os}) = -1.816\text{e}^-$ and, more importantly, $\Delta f''(\text{Os}) = 7.605\text{e}^-$ for Mo-K_α radiation) [14]. All data were corrected for Lorentz and polarization factors and for the effects of absorption. Data were reduced to unscaled $|F_o|$ values and were placed on an approximately absolute scale by means of a Wilson plot. Intensity statistics now strongly suggested that the structure was centric (Table 2). The 4696 data were therefore merged to a unique set of 2292 reflections. Averaging statistics were $R(I) = 4.2\%$ and $R(wI) = 4.9\%$ for 2090 pairs of averaged reflections.

Solution and refinement of the structure

All calculations were performed on a Syntex XTL system with a locally modified version of the Syntex XTL set of crystallographic programs. The analytical form of the scattering factors (neutral atoms assumed) was corrected for both the real ($\Delta f'$) and imaginary ($i\,\Delta f''$) components of anomalous dispersion [14]. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(|F_o|) + (0.015|F_o|)^2]^{-1}$. Discrepancy indices are defined as follows:

$$R_F(\%) = 100\Sigma \| F_o| - |F_c\| / \Sigma |F_o|$$

$$R_{wF}(\%) = 100\left[\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2\right]^{1/2}$$

$$\text{GOF} = \left[\Sigma w(|F_o| - |F_c|)^2 / (\text{NR} - \text{NV})\right]^{1/2}.$$

In the last equation, NR is the number of reflections, and NV is the number of variables.

The positions of the osmium atoms were determined by direct methods (MULTAN) [15] in space group $P2_1/m$. Subsequent difference-Fourier syntheses revealed the locations of all non-hydrogen atoms and some hydride ligands (those of one molecule only). Full-matrix least-squares refinement converged with $R_F = 6.5\%$, $R_{wF} = 6.3\%$ and GOF = 1.32 for all 2292 reflections and $R_F = 4.9\%$ and $R_{wF} = 6.0\%$ for those 1805 reflections with $|F_o| > 3\sigma(|F_o|)$. A correction for secondary extinc-

Table 3

Final atomic coordinates and thermal parameters for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$

Atom	x	y	z	B, Å^2
(A) *Positional parameters for molecule A*				
Os(1A)	0.20141(11)	0.25000(0)	0.12297(8)	
Os(2A)	0.46686(8)	0.15300(5)	0.17345(5)	
O(11A)	−0.0186(22)	0.25000(0)	0.3002(17)	
O(12A)	0.0550(15)	0.0944(11)	−0.0108(13)	
O(21A)	0.7885(16)	0.1296(12)	0.1363(12)	
O(22A)	0.5030(22)	0.1086(18)	0.4083(11)	
O(23A)	0.3861(19)	−0.0438(11)	0.0948(13)	
O(1A)	0.4797(23)	0.25000(0)	−0.1321(17)	
C(11A)	0.0559(29)	0.25000(0)	0.2285(21)	2.4(5)
C(12A)	0.1097(24)	0.1518(16)	0.0422(17)	3.8(5)
C(21A)	0.6652(21)	0.1425(13)	0.1512(14)	2.4(4)
C(22A)	0.4919(23)	0.1257(16)	0.3209(16)	3.6(4)
C(23A)	0.4128(21)	0.0295(15)	0.1239(15)	2.7(4)
C(1A)	0.4077(28)	0.25000(0)	0.0500(21)	2.5(5)
C(2A)	0.4438(28)	0.25000(0)	−0.0455(21)	2.3(5)
H(12A)	0.263(10)	0.147(7)	0.194(7)	3.0
(B) *Apparent (composite) positional parameters for molecule B*				
Os(1B)	0.08022(11)	0.25000(0)	0.67697(9)	
Os(2B)	−0.17424(8)	0.14895(6)	0.62658(6)	
O(11B)	0.250(5)	0.25000(0)	0.474(4)	16.6(17)
O(12B)	0.2430(18)	0.0924(14)	0.7944(13)	
O(21B)	−0.4970(16)	0.1189(13)	0.6499(12)	
O(22B)	−0.1627(27)	0.0468(19)	0.4165(15)	
O(23B)	−0.0769(19)	−0.0222(11)	0.7550(15)	
O(1B)	−0.1990(24)	0.25000(0)	0.9357(16)	
C(11B)	0.198(5)	0.25000(0)	0.549(4)	8.1(12)
C(12B)	0.1872(23)	0.1503(16)	0.7494(17)	3.4(4)
C(21B)	−0.3787(24)	0.1295(15)	0.6450(16)	3.3(4)
C(22B)	−0.1727(27)	0.0862(19)	0.4914(20)	5.2(6)
C(23B)	−0.1180(25)	0.0405(18)	0.7055(18)	4.3(5)
C(1B)	−0.1288(27)	0.25000(0)	0.7481(20)	1.9(5)
C(2B)	−0.1614(31)	0.25000(0)	0.8462(23)	3.1(6)

(C) *Anisotropic thermal parameters*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1A)	1.20(5)	2.24(5)	2.16(5)	0	0.044(35)	0
Os(2A)	1.52(4)	2.29(4)	2.22(4)	0.276(27)	0.021(25)	0.145(27)
O(11A)	3.5(10)	6.3(14)	4.5(11)	0	1.9(9)	0
O(12A)	3.8(7)	4.2(8)	6.3(9)	−2.0(7)	0.7(7)	−2.4(7)
O(21A)	3.3(7)	5.2(9)	6.0(9)	1.4(7)	0.2(6)	1.2(7)
O(22A)	11.2(15)	14.3(18)	1.2(6)	5.1(15)	0.6(8)	0.8(9)
O(23A)	8.4(12)	3.2(8)	5.6(9)	−1.8(8)	2.5(9)	−1.5(7)
O(1A)	4.4(11)	4.9(12)	3.7(10)	0	−0.2(9)	0
Os(1B)	1.40(5)	3.02(6)	2.67(5)	0	0.42(4)	0
Os(2B)	1.63(4)	3.38(5)	2.51(4)	−0.017(29)	0.258(27)	−0.050(29)
O(12B)	5.8(10)	6.6(11)	5.5(9)	0.5(9)	−0.7(8)	0.5(9)
O(21B)	3.3(7)	6.9(10)	4.6(8)	−0.9(8)	0.3(6)	−1.0(7)
O(22B)	13.3(18)	14.4(21)	4.3(9)	4.4(16)	2.2(10)	−4.4(11)
O(23B)	5.8(10)	4.0(9)	8.4(12)	1.7(8)	0.5(8)	3.6(8)
O(1B)	4.3(11)	9.1(17)	2.4(9)	0	0.5(8)	0

tion was included; the correction applied was very small, with $g = 5.66 \times 10^{-7}$ in the modified Zachariasen expression shown below.

$$|F_{o,corr}| = |F_{o,uncorr}|(1.0 + gI_o)$$

Final atomic parameters are collected in Table 3.

Discussion

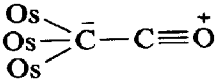
The crystal is composed of discrete molecular units of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO)$, which are separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. The crystal contains two sites for molecules (referred to hereafter as A and B), each lying about a crystallographic mirror plane. The crystallographic asymmetric unit thus consists of two independent half-molecules. Molecules at site A are completely normal, with bond lengths which are consistent with the known stoichiometry. Details of this site will be discussed first. Molecules at site B yields a pattern of bond lengths (and other geometric features) which are inconsistent with those at site A; this pattern can be explained in terms of disorder at site B.

The molecular geometry is illustrated in Figs. 1–4, while interatomic distances and angles are collected in Table 4. Distances of atoms from the Os_3 planes are listed in Table 5.

The molecule at site A

All atoms of this molecule, including the two symmetry-related hydride ligands, were located and refined. Atom H(12) (and the symmetry-related H(12′)) lies 0.73(9) Å below the triosmium plane and is associated with the following distances and angles: Os(1)–H(12) = 1.80(9) Å, Os(2)–H(12) = 1.91(9) Å and Os(1)–H(12)–Os(2) = 101(4)°. The hydrido-bridged Os(1)–Os(2) bond length of 2.870(1) Å is ~ 0.09 Å longer than the nonhydrido-bridged Os(2)–Os(2′) distance of 2.760(1) Å. Each of these is shorter than comparable bonds found in such species as $Os_3(CO)_{12}$ (Os–Os(aver.) = 2.877(3) Å) [16] and $(\mu\text{-H})HOs_3(CO)_{11}$ (Os–Os = 2.8574(7)–2.9097(7) Å, Os–(H)–Os = 2.9886(9) Å) [16], presumably due to the presence of the capping $\mu_3\text{-}\eta^1$-CCO ligand.

The $\mu_3\text{-}\eta^1$-CCO ligand caps the Os_3 triangle, with Os(1)–C(1) = 2.157(26) Å and Os(2)–C(1) = Os(2′)–C(1) = 2.133(20) Å. The ligand is linear within the limits of experimental error, the angle C(1)–C(2)–O(1) being 178.6(24)°. The small difference in Os–C distances is mirrored in the Os–C(1)–C(2) angles, with Os(1)–C(1)–C(2) = 133.0(17)° and Os(2)–C(1)–C(2) = Os(2′)–C(1)–C(2) = 128.7(17)°. Bond lengths within the CCO system (C(1)–C(2) = 1.264(37) Å and C(2)–O(1) = 1.154(34) Å) are compatible with ligand being formally described as **1** below.



1

Each osmium atom is associated with three terminal carbonyl ligands (Os–CO = 1.878(19)–1.934(21) Å, C–O = 1.129(25)–1.181(25) Å and Os–C–O = 172.3(19)–

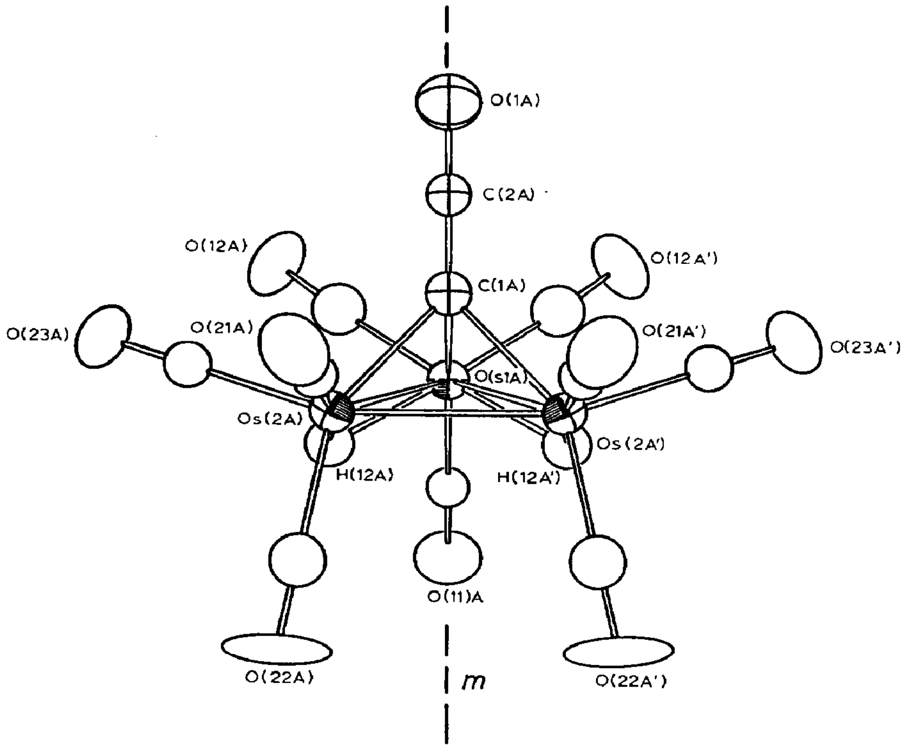


Fig. 1. Geometry for the ordered molecule of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$ at site A (ORTEPII diagram; 30% probability ellipsoids); Os(1A)–Os(2A) = 2.870 Å, Os(2A)–Os(2A′) = 2.760 Å.

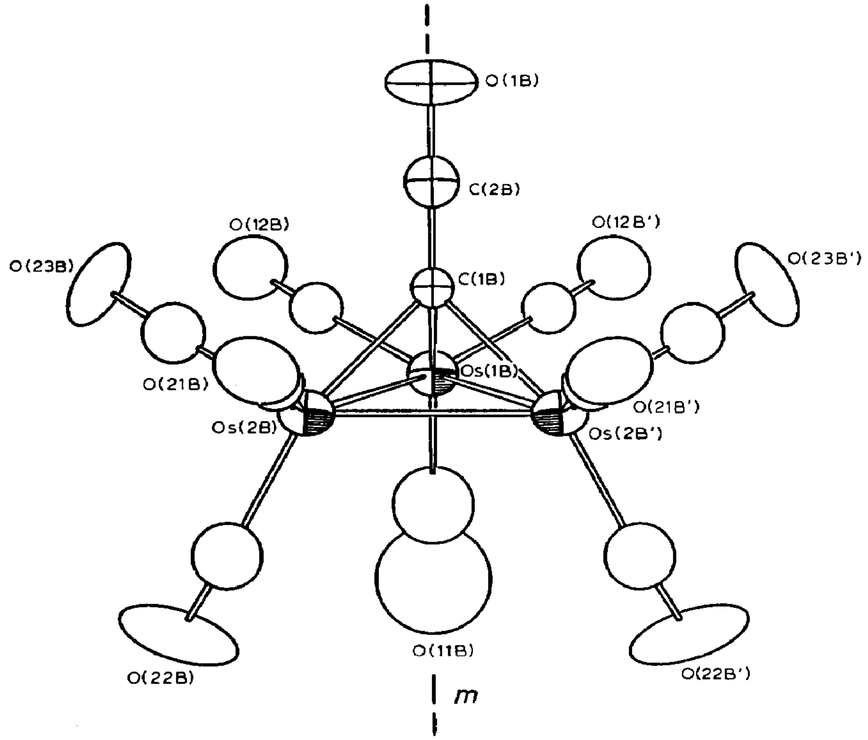


Fig. 2. Overall pattern of atoms belonging to disordered molecules at site B of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CCO})$ (ORTEPII diagram; 30% probability ellipsoids); Os(1B)–Os(2B) = 2.813 Å (?), Os(2B)–Os(2B′) = 2.875 Å.

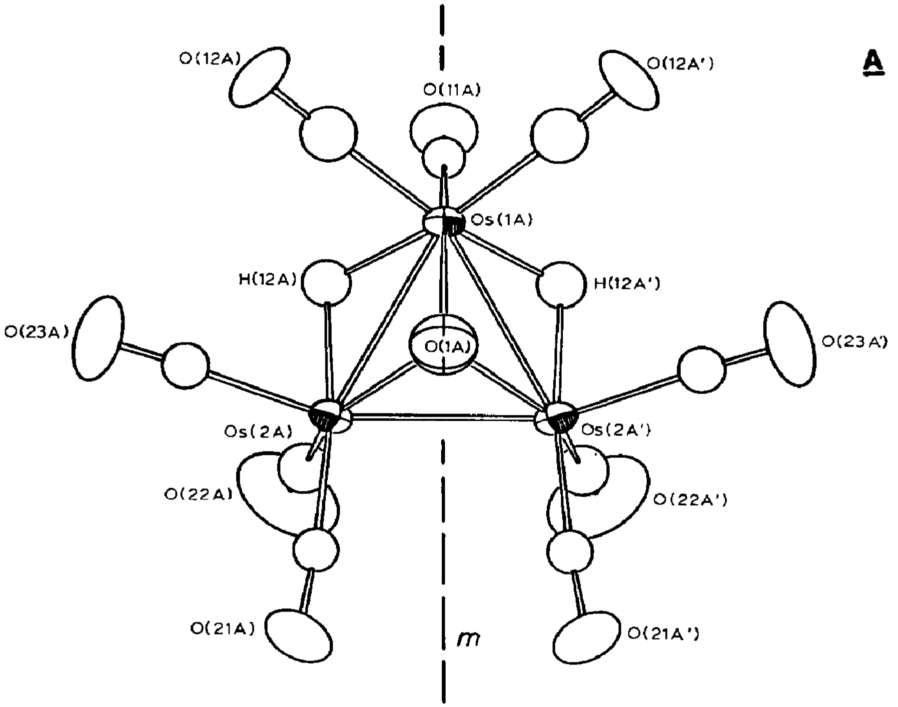


Fig. 3. Molecule at site A projected onto its triosmium plane.

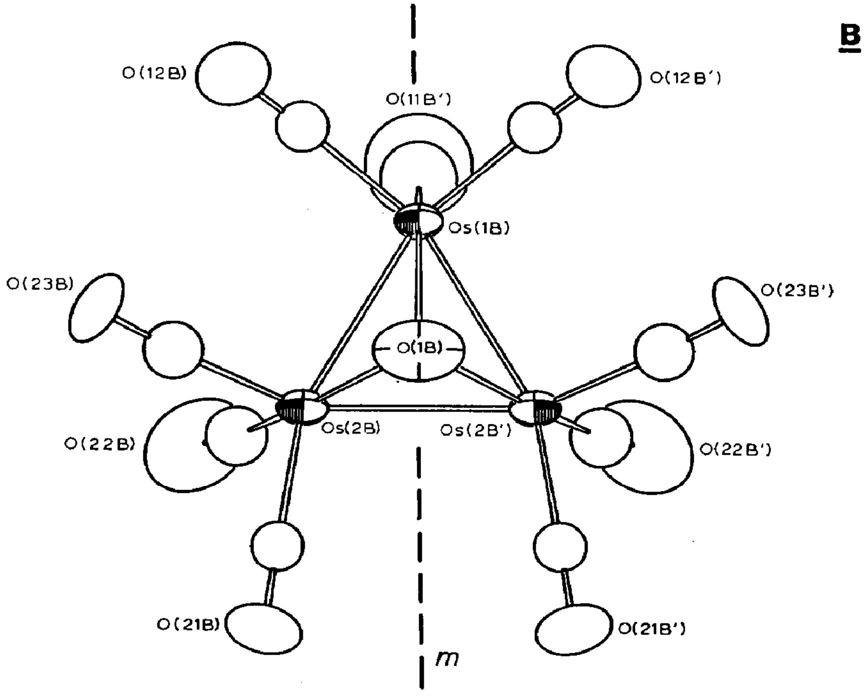


Fig. 4. Composite molecule at site B projected onto its triosmium plane.

Table 4

Apparent interatomic distances (Å) and angles (deg) for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$

Atoms	Molecule A (ordered)	Molecule B (disordered)
(A) *Osmium – osmium distances*		
Os(1)–Os(2)	2.870(1)	2.813(1)
Os(1)–Os(2′)	2.870(1)	2.813(1)
Os(2)–Os(2′)	2.760(1)	2.875(1)
(B) *Distances involving the* μ_3-η^1 *-CCO moiety*		
Os(1)–C(1)	2.157(26)	2.170(25)
Os(2)–C(1)	2.133(20)	2.130(18)
Os(2′)–C(1)	2.133(20)	2.130(18)
C(1)–C(2)	1.264(37)	1.285(38)
C(2)–O(1)	1.154(34)	1.194(35)
(C) *Osmium – carbonyl distances*		
Os(1)–C(11)	1.934(27)	1.989(50)
Os(1)–C(12)	1.907(23)	1.937(22)
Os(1)–C(12′)	1.907(23)	1.937(22)
Os(2)–C(21)	1.878(19)	1.939(22)
Os(2)–C(22)	1.903(21)	1.923(26)
Os(2)–C(23)	1.924(21)	1.897(25)
(D) *C – O(carbonyl) distances*		
C(11)–O(11)	1.161(34)	1.071(72)
C(12)–O(12)	1.158(28)	1.115(29)
C(21)–O(21)	1.181(25)	1.111(27)
C(22)–O(22)	1.129(25)	1.106(34)
C(23)–O(23)	1.129(26)	1.144(30)
(E) *Osmium – hydride distances*		
Os(1)–H(12)	1.80(9)	–
Os(1)–H(12′)	1.80(9)	–
Os(2)–H(12)	1.91(9)	–
Os(2′)–H(12′)	1.91(9)	–
(F) *Os – Os – Os and Os – H – Os angles*		
Os(2)–Os(1)–Os(2′)	57.49(3)	61.48(3)
Os(1)–Os(2)–Os(2′)	61.25(3)	59.26(3)
Os(2)–Os(2′)–Os(1)	61.25(3)	59.26(3)
Os(1)–H(12)–Os(2)	101 (4)	–
(G) *Angles involving the* μ_3-η^1 *-CCO ligand*		
Os(2)–Os(1)–C(1)	47.7(6)	48.5(5)
Os(2′)–Os(1)–C(1)	47.7(6)	48.5(5)
Os(1)–Os(2)–C(1)	48.4(6)	49.8(5)
Os(2′)–Os(2)–C(1)	49.7(6)	47.5(4)
C(11)–Os(1)–C(1)	161.8(9)	150.1(13)
C(12)–Os(1)–C(1)	99.0(9)	104.7(8)
C(12′)–Os(1)–C(1)	99.0(9)	104.7(8)
C(21)–Os(2)–C(1)	99.5(8)	100.1(8)
C(22)–Os(2)–C(1)	149.4(9)	160.3(10)
C(23)–Os(2)–C(1)	107.4(8)	97.5(9)
Os(1)–C(1)–C(2)	133.0(17)	130.4(17)
Os(2)–C(1)–C(2)	128.7(17)	130.1(17)
Os(2′)–C(1)–C(2)	128.7(17)	130.1(17)
C(1)–C(2)–O(1)	178.6(24)	176.6(25)

Table 4 (continued)

Atoms	Molecule A (ordered)	Molecule B (disordered)
(H) *Os–Os–CO angles*		
Os(2)–Os(1)–C(11)	117.7(7)	107.5(12)
Os(2)–Os(1)–C(12)	97.2(7)	98.0(6)
Os(2)–Os(1)–C(12′)	146.1(7)	152.7(6)
Os(1)–Os(2)–C(21)	147.2(6)	149.4(6)
Os(1)–Os(2)–C(22)	112.5(7)	113.5(8)
Os(1)–Os(2)–C(23)	99.1(6)	95.1(7)
Os(2′)–Os(2)–C(21)	94.6(6)	98.2(6)
Os(2′)–Os(2)–C(22)	101.8(7)	117.6(8)
Os(2′)–Os(2)–C(23)	156.0(6)	144.4(7)
(I) *OC–Os–CO angles*		
C(11)–Os(1)–C(12)	93.4(9)	95.4(13)
C(11)–Os(1)–C(12′)	93.4(9)	95.4(13)
C(12)–Os(1)–C(12′)	94.2(10)	94.2(9)
C(21)–Os(2)–C(22)	92.8(9)	94.8(10)
C(21)–Os(2)–C(23)	97.0(8)	94.0(10)
C(22)–Os(2)–C(23)	98.6(9)	94.3(11)
(J) *Os–C–O angles*		
Os(1)–C(11)–O(11)	172.3(19)	173.1(40)
Os(1)–C(12)–O(12)	177.0(20)	176.4(20)
Os(1)–C(12′)–O(12′)	177.0(20)	176.4(20)
Os(2)–C(21)–O(21)	175.5(17)	176.3(19)
Os(2)–C(22)–O(22)	178.1(20)	174.7(25)
Os(2)–C(23)–O(23)	177.5(18)	176.0(21)

178.1(20)°). The $Os(CO)_3$ group centered on Os(1) appears to have approximately C_{3v} symmetry (OC–Os–CO = 93.4(9)–94.2(10)°), while that on Os(2) has only approximate C_s symmetry (C(21)–Os(2)–C(22) = 92.8(9)° as compared to C(21)–Os(2)–C(23) = 97.0(8)° and C(22)–Os(2)–C(23) = 98.6(9)°).

Table 5

Distances of atoms from the Os_3 planes

Atom	Molecule A (ordered)	Molecule B (disordered)
C(1)	1.38(3)	1.38(2)
C(2)	2.64(3)	2.67(3)
O(1)	3.79(2)	3.86(2)
H(12)	−0.73(9)	–
C(11)	−1.64(3)	−1.86(5)
C(12)	0.78(2)	0.63(2)
C(21)	0.74(2)	0.72(2)
C(22)	−1.76(2)	−1.66(3)
C(23)	0.48(2)	0.83(2)
O(11)	−2.70(2)	−2.90(5)
O(12)	1.31(2)	1.05(2)
O(21)	1.21(2)	1.07(1)
O(22)	−2.81(1)	−2.61(2)
O(23)	0.78(2)	1.34(2)

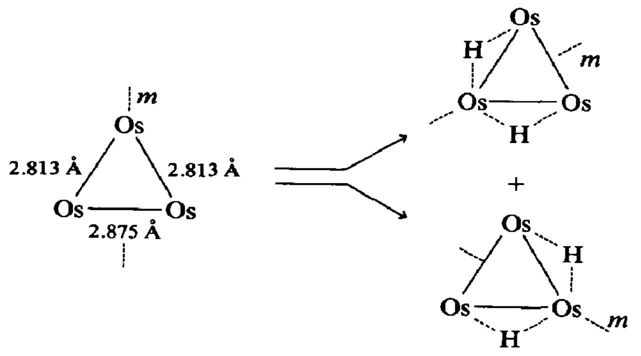
Molecules at site B

Firstly, it should be noted that we were unable to locate the hydride ligands at site B, whereas there was no such problem at site A. However, the first unambiguous indication of problems came when we noticed that the osmium–osmium distances of "molecule B" (Os(1B)–Os(2B) = Os(1B)–Os(2B′) = 2.813(1) Å and Os(2B)–Os(2B′) = 2.875(1) Å) were not compatible with those determined for molecule A (i.e., 2.870(1), 2.870(1) and 2.760(1) Å. Since the senior author of this paper (M.R.C.) had studied hydrido-bridged metal-metal bonds extensively and had concluded that (in the absence of an additional stereochemically active bridging ligand) hydrido-bridged metal-metal distances were longer than normal metal–metal distances [17–18; see also ref. 19], these data initially were a cause of some confusion and incipient alarm. However, a complete explanation of the observed anomalies was obtained by the following analysis. (Note that we were not willing to consider the possibility of so-called "distortion isomerism" [20].)

(1) The Os(2B)–Os(2B′) distance of 2.875(1) Å is entirely consistent with its being hydrido-bridged (cf. Os(1A)–Os(2A) = Os(1A)–Os(2A′) = 2.870(1) Å in molecule A).

(2) The Os(1B)–Os(2B) and Os(1B)–Os(2B′) distances of 2.813(1) Å are very close to the average of hydrido-bridged and normal Os–Os distances in molecule A: $\frac{1}{2}$[Os(1A)–Os(2A) + Os(2A)–Os(2A′)] = $\frac{1}{2}$(2.870 + 2.760) = 2.815 Å.

(3) The isolated $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$ molecule has an overall configuration which has approximate (but not exact) C_{3v} symmetry. The Os–Os distances at site B can be explained as resulting from a pattern of disorder in which individual molecules are aligned with their microscopically precise molecular mirror planes no longer coincident with the macroscopically precise crystallographic mirror plane, but rotated (about the (Os$_3$ centroid)–CCO axis) on a statistical basis by either a pseudo-$C_3^{\,1}$ or pseudo-$C_3^{\,2}$ operation. The deconvolution of the disordered ensemble is shown in Scheme 1:



Scheme 1

Further evidence for this model is provided by the following additional observations.

(4) Thermal ellipsoids for atoms in molecule B are generally larger than those in molecule A, presumably since there is not perfect overlap between carbonyl groups on Os(1) and Os(2) [and Os(2′)] upon subjecting the molecule to rotations of $2\pi/3$ and $4\pi/3$ radians. Furthermore, anisotropic refinement of O(11B) gave physically meaningless results and it was treated isotropically (B(O(11B)) = 16.6(17) Å^2).

(5) Os–Os–CO angles in molecule B are not equivalent to those in molecule A, but are close to the average of those two angles related by a pseudo-C_3^1 and pseudo-C_3^2 rotation of molecule A. The most obvious example (cf. Figs. 3 and 4) is the Os(2′)–Os(2)–C(22) angle. In molecule B, the observed (composite) angle is 117.6(8)°. This is substantially larger than the value of 101.8(7)° found in molecule A. However, it is close to the average of the pseudo-C_3^1 and -C_3^2 related angles Os(2A)–Os(1A)–C(11A) = 117.7(7)° and Os(1A)–Os(2A′)–C(22A′) = 112.5(7)° (average = 115.1°).

(6) In a similar fashion, C(1)–Os–CO angles in molecule B are not equivalent to those in molecule A, but are close to the average of those two angles of molecule A related by pseudo-C_3^1 and -C_3^2 rotations. For example C(1B)–Os(1B)–C(11B) = 150.1(13)° (distinctly different from C(1A)–Os(1A)–C(1A) = 161.8(9) Å, but close to the equivalent C_3^1- and C_3^2-related angles in molecule A, i.e., C(1A)–Os(2A)–C(22A) = C(1A)–Os(2A′)–C(22A′) = 149.4(9)°). Other angles can be analyzed in a similar fashion.

(7) Deviations of atoms of molecule B from their Os_3 plane are intermediate between those in molecule A related by rotations of $2\pi/3$ and $4\pi/3$ radians. Thus, O(23B′) lies 1.34(2) Å above the Os_3(molecule B) plane. In contrast, O(23A′) lies only 0.78(2) Å from the Os_3(molecule A) plane. However O(21A) (related to O(23A′) by a $2\pi/3$ rotation) is 1.21(2) Å from its triosmium plane and O(12A) (related to O(23A′) by a $4\pi/3$ rotation) is 1.31(2) Å from its triosmium plane; thus dev.(O(23B′)) $\simeq \frac{1}{2}$[dev.(O(21A)) + dev.(O(12A))]. Again, similar analyses can be performed for other atoms of molecules A and B.

We conclude therefore that metric features of molecule B must be treated with the utmost caution, but can, in each case, be explained as the average of two such measurements (ψ-C_3^1 and ψ-C_3^2 related) from molecule A.

Finally we note that $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-CCO})$ is closely related to the symmetrical (C_{3v}) species $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-BCO})$, in which Os–(H)–Os distances are 2.913(1)–2.919(1) Å [21], and to the cationic species $(\mu\text{-H})_3Os_3(CO)_9(CCO)^+$ [12] and $Co_3(CO)_9(CCO)^+$ [22].

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