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Structural and Vibrational Analysis of Nonacarbonyltri-μ-hydrido-μ_3-methylidyne-*triangulo*-triosmium. X-ray and Neutron Diffraction Studies*

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Abstract

X-ray and neutron diffraction studies on the complex $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ have been carried out at 200 and 11 K respectively. The structure is triclinic, space group $P\bar{1}$, with $a = 9{\cdot}399\,(3)$, $b = 11{\cdot}665\,(4)$, $c = 15{\cdot}651\,(7)$ Å, $\alpha = 112{\cdot}32\,(3)$, $\beta = 90{\cdot}11\,(3)$, $\gamma = 97{\cdot}80\,(3)°$, $R(F) = 0{\cdot}044$ for 4121 observed reflections at 200 K, and $a = 9{\cdot}295\,(2)$, $b = 11{\cdot}457\,(3)$, $c = 15{\cdot}622\,(4)$ Å, $\alpha = 111{\cdot}66\,(2)$, $\beta = 90{\cdot}32\,(2)$, $\gamma = 96{\cdot}93\,(2)°$, $R(F) = 0{\cdot}022$ for 4962 observed reflections at 11 K. The structure contains two crystallographically independent molecules, each of which shows $3m$ (C_{3v}) symmetry to within experimental error. All carbonyl ligands are terminal and near linear, the hydride H atoms bridge the Os–Os vectors symmetrically, and the Os_3 triangle is bridged by a methylidyne group. Molecular geometric parameters averaged over $3m$ symmetry and both molecules, at 11 K, are: bond lengths Os–Os 2·893 (2), Os–H 1·834 (3), Os–C(H) 2·101 (2), Os–C(*trans* to H) 1·911 (2), Os–C(*trans* to C) 1·964 (2), C–O 1·141 (1), and C–H 1·086 (2) Å; bond angles Os–H–Os 104·2 (2), Os–C–Os 87·0 (1), and Os–C–O 178·0 (3)°. The neutron data provide a measure of the vibrational behaviour of the H atoms and allow estimation of the frequencies of the internal hydrogen vibrational modes. The hydride hydrogen frequencies calculated assuming the modes to be harmonic and uncoupled are 1395 (30), 1332 (45) and 625 (5) cm^{-1} for the symmetric and antisymmetric stretch and deformation vibrations, respectively. The methylidyne hydrogen ν_{C-H} and δ_{C-H} frequencies are calculated to be 2870 (150) and 867 (20) cm^{-1}. The Fourier transform IR spectrum of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ was measured at low temperature giving frequencies in agreement with those calculated from the diffraction data.

Introduction

Organometallic cluster complexes containing a μ_3-alkylidyne ligand have been amongst the most intensively studied of such molecules. These studies have elucidated both the geometrical structure of representative examples of these species [*e.g.* $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ (Sutton & Dahl, 1967)] and their reactivities. In addition, the electronic structure of such complexes has been examined by experimental methods [photoelectron spectroscopy (Sherwood & Hall, 1982; DeKock, Wong & Fehlner, 1982, and references therein) and diffraction methods (Leung, Coppens, McMullan & Koetzle, 1981; Leung, Holladay & Coppens, 1981)] and analysed theoretically (Sherwood & Hall, 1982; DeKock, Wong & Fehlner, 1982, and references therein). The interest in such molecules has been stimulated by the possibility that the observed μ_3-C*R* bonding mode may be a good model for the binding of such organic fragments to metal surfaces (*e.g.* Muetterties, Rhodin, Band, Brucker & Pretzer, 1979). We report here X-ray and neutron single-crystal diffraction studies on $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ at 200 and 11 K respectively. The synthesis of this compound by Calvert & Shapley (1977) beautifully illustrates the reasons for the interest in the chemistry of cluster complexes as models for the chemistry of metal surfaces. Thus at various stages C–H, Os–H and Os–C bond formation and cleavage mediated by the cluster were observed, and at least three binding modes for simple C_1 hydrocarbon fragments were identified (*i.e.* μ-CH_3, μ-CH_2 and μ_3-CH). Such processes are key ones in the reactions of hydrocarbons with surface metal atoms. The low temperature at which neutron data were collected has enabled very precise characterization

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of both the nuclear positions and the vibrational motion. The latter information is of considerable utility since it allows the model to be evaluated for internal consistency and the vibrational amplitudes, particularly of the light atoms, can be compared with other sources of information on vibrational motion, *e.g.* from IR spectroscopy.

Data collection

Crystals of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ were grown from pentane solution. A small multi-faceted, approximately spherical crystal was mounted under N_2 in a thin-walled glass capillary for X-ray diffraction measurements, details of which are given in Table 1. X-ray intensity measurements used in the solution and refinement of the structure were made at 200 (2) K.* Nicolet *P*3*m* diffractometer, $\theta/2\theta$ scans of width $2\cdot4° + \Delta_{\alpha_1\alpha_2}$, sampling one hemisphere of reciprocal space. Crystal temperature maintained by use of a slightly modified LT-1 crystal-cooling device. Mo *Kα* X-rays, monochromated by use of a graphite crystal, for all measurements. Intensity data corrected for Lorentz, polarization and absorption effects. Absorption correction applied on the basis of the variation in intensity of 181 azimuthal scan data collected for five independent reflections at room temperature. Standard reflections monitored after every 50 observations showed a monotonic 7% decrease in intensity; an appropriate correction was applied. The room-temperature unit cell, as determined by X-ray diffraction measurements on the same crystal, is $a = 9\cdot476\,(4)$, $b = 11\cdot847\,(5)$, $c = 15\cdot806\,(7)$ Å, $\alpha = 112\cdot77\,(3)$, $\beta = 89\cdot62\,(3)$, $\gamma = 98\cdot26\,(3)°$, $U = 1616\cdot8\,(11)$ Å^3. Neutron diffraction measurements carried out on an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor. The wavelength of the neutron beam [1·1617 (5) Å] was selected by diffraction from the (220) planes of a Ge monochromating crystal and was calibrated against KBr [$a_0 = 6\cdot60000\,(13)$ Å at 298 K].

A crystal of volume *ca* 4 mm^3 of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ was grown from pentane solution by seeding with a small crystal. This crystal was mounted on a hollow Al pin with rubber glue and placed under helium in an Al can inside a closed-cycle refrigerator (Air Products and Chemicals Inc. Displex® model CS-202) for neutron diffraction measurements. Temperature of crystal lowered at ~1 K min^{-1} to 10·5 K and maintained at 11 (1) K during the two-week period of data collection. Scans along axial reciprocal-lattice rows confirmed the periodicity of the triclinic lattice given in Table 1. Intensity measurements made by a $\theta/2\theta$ step-scan method, scan widths between 2·8° for $2\theta < 55°$ and $(1\cdot1 + 3\cdot63 \tan\theta)°$ for $2\theta > 55°$. All reflections, within a unique hemisphere of reciprocal space, were measured for $0 < \sin\theta/\lambda < 0\cdot582$ Å^{-1}; for $0\cdot582 < \sin\theta/\lambda < 0\cdot678$ Å^{-1} measurements were limited to those 405 reflections calculated to be the most intense on the basis of preliminary refinements. Absorption corrections applied based on the indexed faces of the crystal with values of (μ/ρ) for C, O and Os atoms taken from *International Tables for X-ray Crystallography* (1974) and using an empirical value for H of $\mu/\rho = 2\cdot645$ m^2 kg^{-1} (McMullan & Koetzle, 1979). Details of data collection and reduction are given in Table 1.

Table 1. *Crystal data and details of data collection and refinement*

	X-ray	Neutron
Temperature (K)	200 (2)	11 (1)
M_r	838·7	838·7
Space group	$P\bar{1}$	$P\bar{1}$
Z	4	4
a (Å)	9·399 (3)	9·295 (2)
b (Å)	11·665 (4)	11·457 (3)
c (Å)	15·651 (7)	15·622 (4)
α (°)	112·32 (3)	111·66 (2)
β (°)	90·11 (3)	90·32 (2)
γ (°)	97·80 (3)	96·93 (2)
U (Å^3)	1570 (1)	1532·6 (7)
D_x (Mg m^{-3})	3·55	3·64
D_m (Mg m^{-3})	Not measured	Not measured
$F(000)$	1455·4e	541·3 fm
Data collection, reduction and refinement		
λ (Å)	0·71069	1·1617 (5)
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0·594	0·678
Crystal shape and size	Sphere, diameter 0·10 ± 0·02 mm	Faces {001}, $(0\bar{1}0)$, {011}, $(01\bar{2})$, $(0\bar{1}3)$, $(\bar{2}10)$, $(1\bar{1}0)$, (101), $(10\bar{1})$, $(1\bar{1}2)$: volume 4·11 mm^3
μ (mm^{-1})	24·27	0·047
Transmission range	0·025–0·010	0·938–0·914
Standard reflections; variation of intensity	$4\bar{2}2$, 362; ±1·5%	071, $45\bar{8}$; ±1·3%
Reflections for unit-cell determination; range	15; $15 < 2\theta < 31°$	32; $44\cdot3 < 2\theta < 62\cdot2°$
Measured reflections	4768	5666
Unique reflections	4456	5373
R(merge)	0·042	0·0094
$n[I > n\sigma(I)]$	2	2
Observed reflections	4121	4962
w	$[\sigma_c^2(F_o) + 0\cdot0008F_o^2]^{-1}$	$[\sigma_c^2(F_o) + 0\cdot00005F_o^2]^{-1}$
$R(F)$	0·044	0·022
$wR(F)$	0·054	0·022
S	1·32	1·50
Extinction correction		
mosaic spread	—	56 (1)″ arc
$(F_c\text{corr.}/F_c)_{min}(hkl)$	—	0·79 (106)

Solution and refinement of the structure

The structure was solved and refined with the 200 K X-ray data, assuming space group $P\bar{1}$. The six unique Os atoms were located by inspection of the Patterson function and all non-hydrogen atoms located from subsequent difference Fourier syntheses; H atoms were not located. Blocked full-matrix refinement of

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* Estimated standard deviations are given in parentheses here, and throughout this paper.

the structure model against the 11 K neutron data was commenced with non-hydrogen positional parameters derived from the X-ray analysis and μ-hydride H atoms at calculated positions (Orpen, 1980). The two methylidyne H atoms were located as the largest negative features on a difference scattering density map. The final refined model incorporated an isotropic secondary-extinction parameter for a type I crystal with a Lorentzian distribution of mosaicity (Becker & Coppens, 1974) in addition to an overall scale factor, positional and anisotropic thermal parameters, and the scattering length of Os [final value 10·66 (2) fm, *cf.* literature value 10·7 fm (Koester, Rauch, Herkens & Schröder, 1981)]. Other neutron scattering lengths from Koester (1977); X-ray atomic scattering factors and anomalous-scattering terms from *International Tables for X-ray Crystallography* (1974). Details of the refinement procedure and results are presented in Table 1. Refinement against the neutron data was terminated when all parameter shifts were less than 0·02σ. Final difference nuclear density maps showed no features greater than 0·7 fm $Å^{-3}$ in magnitude (*cf.* H atoms showed peaks $\sim -10{\cdot}2$ fm $Å^{-3}$). The positional and anisotropic vibrational parameters derived from the neutron analysis are listed in Tables 2 and 3 respectively.* Tables 4 and 5 list the derived internuclear distances and interbond angles. All discussion of the results given below refers to the results of the neutron analysis except where noted to the contrary. No attempt was made to apply rigid-body or riding-motion corrections to bond lengths calculated from the neutron data. Fourier transform IR spectra of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$, as a KBr disc, were measured at room temperature and at liquid-nitrogen temperature on a Nicolet 7199 spectrometer.

Table 2. *Atomic positional parameters*

	x	*y*	*z*
Os(1)	0·07635 (6)	0·28018 (5)	0·05208 (3)
Os(2)	−0·00560 (6)	0·24702 (5)	0·22096 (3)
Os(3)	−0·22655 (6)	0·25300 (5)	0·09238 (3)
C(1)	−0·06036 (9)	0·14042 (8)	0·08080 (6)
C(11)	0·04264 (10)	0·20154 (8)	−0·07877 (6)
O(11)	0·02237 (12)	0·15009 (10)	−0·15657 (7)
C(12)	0·17499 (10)	0·44408 (8)	0·05569 (6)
O(12)	0·23421 (12)	0·53831 (10)	0·05807 (8)
C(13)	0·25040 (9)	0·20481 (8)	0·04263 (6)
O(13)	0·35348 (11)	0·15795 (10)	0·03643 (7)
C(21)	0·03533 (10)	0·38663 (8)	0·34103 (6)
O(21)	0·05687 (12)	0·46769 (10)	0·41066 (7)
C(22)	−0·12337 (10)	0·13906 (8)	0·26810 (6)
O(22)	−0·19398 (12)	0·07229 (10)	0·29474 (7)
C(23)	0·15691 (9)	0·16039 (8)	0·22395 (6)
O(23)	0·25170 (11)	0·10514 (10)	0·22055 (7)
C(31)	−0·29172 (9)	0·18564 (8)	−0·03458 (6)
O(31)	−0·32567 (12)	0·14755 (10)	−0·11127 (7)
C(32)	−0·36415 (10)	0·13663 (8)	0·12134 (6)
O(32)	−0·44014 (12)	0·06347 (10)	0·13876 (7)
C(33)	−0·34528 (10)	0·39194 (8)	0·12414 (6)
O(33)	−0·41880 (12)	0·46933 (10)	0·14136 (8)
Os(4)	0·48828 (6)	0·18336 (5)	0·68463 (3)
Os(5)	0·56726 (6)	0·35709 (5)	0·59261 (3)
Os(6)	0·78856 (6)	0·23562 (5)	0·64586 (3)
C(2)	0·59403 (9)	0·16671 (8)	0·56325 (6)
C(41)	0·42841 (10)	0·24389 (8)	0·81245 (6)
O(41)	0·39214 (12)	0·27744 (10)	0·88640 (7)
C(42)	0·50406 (9)	0·01403 (8)	0·67568 (6)
O(42)	0·51412 (11)	−0·08804 (9)	0·66662 (7)
C(43)	0·29617 (10)	0·13338 (8)	0·62951 (6)
O(43)	0·18210 (11)	0·10505 (10)	0·59447 (7)
C(51)	0·66483 (9)	0·37171 (8)	0·48884 (6)
O(51)	0·72057 (12)	0·37734 (10)	0·42527 (7)
C(52)	0·56042 (10)	0·53818 (8)	0·66179 (6)
O(52)	0·55549 (12)	0·64281 (10)	0·70377 (7)
C(53)	0·38689 (10)	0·32445 (8)	0·52294 (6)
O(53)	0·28156 (11)	0·30486 (10)	0·47929 (7)
C(61)	0·90393 (10)	0·23416 (8)	0·54447 (6)
O(61)	0·96842 (12)	0·23292 (10)	0·48227 (7)
C(62)	0·94123 (10)	0·33287 (8)	0·74130 (6)
O(62)	0·03434 (12)	0·38745 (10)	0·79422 (7)
C(63)	0·84028 (10)	0·07479 (8)	0·63663 (6)
O(63)	0·86965 (12)	−0·02149 (10)	0·63073 (7)
H(12)	0·1032 (3)	0·3566 (2)	0·17791 (13)
H(13)	−0·0866 (3)	0·3616 (2)	0·06833 (14)
H(23)	−0·1566 (3)	0·3318 (2)	0·21323 (13)
H(1)	−0·0682 (3)	0·0382 (2)	0·04628 (13)
H(45)	0·4803 (3)	0·3464 (2)	0·69534 (13)
H(46)	0·6718 (2)	0·2429 (2)	0·74090 (13)
H(56)	0·7370 (3)	0·3909 (2)	0·66247 (14)
H(2)	0·5771 (3)	0·0881 (2)	0·49723 (13)

Discussion

The crystal structure of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ consists of isolated molecules separated by normal van der Waals distances. The shortest intermolecular contacts are between methylidyne H atoms [H(1)···H(1') 1·955 Å, where H(1') is related to H(1) by $-x$, $-y$, $-z$]; other close contacts include O(21)···O(21') 2·855 Å [O(21') is related to O(21) by $-x$, $1-y$, $1-z$] and O(23)···O(42') 2·863 Å [O(42') is related to O(42) by $1-x$, $-y$, $1-z$], other O···O contacts being >2·93 Å. The short H(1)···H(1') contact is appreciably shorter than the sum of the van der Waals radii involved (usually taken as 1·2 Å). A number of factors may be involved: firstly, the temperature of the analysis is unusually low leading to reduced intermolecular contacts relative to higher-temperature studies; secondly, the neutron-determined H positions have longer C–H distances than X-ray determined values and hence H···H intermolecular contacts generally shorter than those to be expected from X-ray studies; thirdly, the C(1)–H(1)···H(1') contact is non-linear [∠C(1)–H(1)···H(1') = 120·8°]; and fourthly, the C(1)–H(1) vector points in to a crevice in the molecule across the inversion centre such that the H(1) lies above the triangle formed by C(1'), C(11') and C(13') allowing efficient packing of pairs of molecules about inversion centres through the crystal [the other methylidyne hydrogen H(2) is involved in similar contacts pairing molecules about different inversion centres].

The two crystallographically independent molecules present in the structure show essentially

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* Lists of structure factors for both data sets, a full list of bond angles derived from the neutron analysis, and all results of the X-ray structure analysis (positional and anisotropic thermal parameters, bond lengths and angles) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39435 (58pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Anisotropic temperature factors* (Å$^2 \times 10^4$)

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	36 (3)	28 (3)	28 (3)	15 (2)	9 (2)	3 (2)
Os(2)	32 (3)	28 (3)	26 (3)	14 (2)	5 (2)	1 (2)
Os(3)	32 (3)	24 (3)	28 (3)	12 (2)	5 (2)	3 (2)
C(1)	66 (5)	42 (5)	48 (4)	22 (4)	10 (4)	6 (4)
C(11)	82 (5)	67 (4)	53 (5)	20 (4)	4 (4)	13 (4)
O(11)	141 (6)	108 (5)	39 (6)	7 (5)	−6 (4)	16 (5)
C(12)	91 (5)	48 (5)	76 (5)	29 (4)	17 (4)	−7 (4)
O(12)	152 (6)	74 (6)	147 (6)	61 (5)	21 (5)	−26 (5)
C(13)	56 (5)	74 (5)	66 (4)	29 (4)	11 (4)	16 (4)
O(13)	68 (6)	143 (6)	126 (6)	61 (5)	14 (4)	51 (5)
C(21)	76 (5)	65 (4)	44 (5)	11 (4)	10 (4)	−5 (4)
O(21)	130 (6)	84 (5)	62 (5)	−4 (5)	8 (4)	−21 (4)
C(22)	65 (5)	64 (4)	70 (5)	38 (4)	11 (4)	−9 (4)
O(22)	105 (6)	104 (5)	131 (6)	85 (5)	21 (5)	−20 (5)
C(23)	62 (5)	72 (5)	76 (5)	39 (4)	10 (4)	21 (4)
O(23)	75 (5)	110 (5)	126 (6)	57 (5)	16 (4)	48 (5)
C(31)	71 (5)	66 (4)	50 (5)	20 (4)	−7 (4)	2 (4)
O(31)	120 (6)	109 (5)	57 (5)	24 (4)	−14 (4)	10 (5)
C(32)	57 (5)	68 (5)	78 (4)	41 (4)	9 (4)	−4 (4)
O(32)	94 (6)	99 (5)	129 (6)	68 (5)	15 (5)	−25 (5)
C(33)	84 (5)	63 (5)	80 (5)	28 (4)	20 (4)	35 (4)
O(33)	141 (6)	107 (6)	147 (6)	51 (5)	39 (5)	80 (5)
Os(4)	29 (3)	29 (3)	36 (3)	19 (2)	12 (2)	5 (2)
Os(5)	33 (3)	26 (3)	34 (3)	18 (2)	7 (2)	6 (2)
Os(6)	32 (3)	24 (3)	28 (3)	11 (2)	6 (2)	3 (2)
C(2)	57 (4)	41 (4)	42 (5)	12 (4)	2 (4)	8 (4)
C(41)	86 (5)	83 (5)	52 (5)	29 (4)	30 (4)	22 (4)
O(41)	154 (6)	144 (6)	71 (6)	52 (5)	53 (5)	44 (5)
C(42)	64 (5)	45 (5)	69 (4)	33 (4)	6 (4)	8 (4)
O(42)	109 (6)	49 (5)	105 (5)	35 (4)	−3 (4)	15 (4)
C(43)	49 (5)	79 (5)	93 (5)	46 (4)	2 (4)	4 (4)
O(43)	55 (6)	134 (6)	146 (6)	75 (5)	−21 (5)	−12 (5)
C(51)	65 (5)	69 (4)	56 (5)	34 (4)	15 (4)	9 (4)
O(51)	91 (5)	131 (6)	82 (5)	64 (5)	32 (5)	8 (5)
C(52)	79 (5)	41 (5)	82 (5)	21 (4)	10 (4)	8 (4)
O(52)	134 (6)	48 (5)	136 (6)	12 (5)	11 (5)	17 (4)
C(53)	52 (5)	79 (5)	81 (5)	41 (4)	−12 (4)	0 (4)
O(53)	68 (6)	133 (6)	133 (6)	58 (5)	−32 (5)	−1 (5)
C(61)	70 (5)	70 (4)	56 (5)	31 (4)	18 (4)	14 (4)
O(61)	100 (5)	129 (6)	82 (5)	61 (5)	52 (5)	25 (5)
C(62)	68 (5)	59 (4)	70 (5)	20 (4)	−8 (4)	4 (4)
O(62)	101 (6)	91 (5)	103 (6)	11 (5)	−47 (5)	−15 (5)
C(63)	70 (4)	54 (4)	76 (4)	32 (3)	12 (3)	17 (3)
O(63)	122 (5)	61 (5)	128 (5)	51 (4)	27 (4)	39 (4)
H(12)	254 (11)	173 (9)	150 (9)	63 (8)	12 (8)	−33 (8)
H(13)	169 (10)	177 (10)	291 (11)	122 (9)	44 (8)	38 (8)
H(23)	213 (10)	203 (10)	167 (9)	39 (8)	−3 (8)	78 (8)
H(1)	239 (11)	106 (10)	212 (10)	27 (8)	21 (8)	21 (8)
H(45)	272 (11)	155 (9)	186 (10)	80 (8)	81 (8)	57 (8)
H(46)	143 (9)	275 (11)	148 (9)	82 (8)	9 (8)	−4 (8)
H(56)	197 (10)	151 (9)	241 (10)	53 (8)	−37 (8)	21 (8)
H(2)	248 (11)	155 (10)	126 (10)	−8 (8)	−15 (8)	13 (8)

Table 4. *Bond lengths* (Å)

Os(1)–Os(2)	2·894 (1)	Os(1)–Os(3)	2·894 (1)
Os(1)–C(1)	2·104 (1)	Os(1)–C(11)	1·911 (1)
Os(1)–C(12)	1·969 (1)	Os(1)–C(13)	1·905 (1)
Os(1)–H(12)	1·834 (2)	Os(1)–H(13)	1·844 (2)
Os(2)–Os(3)	2·889 (1)	Os(2)–C(1)	2·100 (1)
Os(2)–C(21)	1·963 (1)	Os(2)–C(22)	1·904 (1)
Os(2)–C(23)	1·914 (1)	Os(2)–H(12)	1·838 (2)
Os(2)–H(23)	1·828 (2)	Os(3)–C(1)	2·096 (1)
Os(3)–C(31)	1·908 (1)	Os(3)–C(32)	1·913 (1)
Os(3)–C(33)	1·961 (1)	Os(3)–H(13)	1·827 (2)
Os(3)–H(23)	1·841 (2)	C(1)–H(1)	1·086 (2)
C(11)–O(11)	1·141 (1)	C(12)–O(12)	1·139 (1)
C(13)–O(13)	1·141 (1)	C(21)–O(21)	1·137 (1)
C(22)–O(22)	1·143 (2)	C(23)–O(23)	1·136 (2)
C(31)–O(31)	1·141 (1)	C(32)–O(32)	1·142 (2)
C(33)–O(33)	1·139 (2)	Os(4)–Os(5)	2·888 (1)
Os(4)–Os(6)	2·898 (1)	Os(4)–C(2)	2·097 (1)
Os(4)–C(41)	1·965 (1)	Os(4)–C(42)	1·917 (1)
Os(4)–C(43)	1·905 (1)	Os(4)–H(45)	1·824 (2)
Os(4)–H(46)	1·846 (2)	Os(5)–Os(6)	2·896 (1)
Os(5)–C(2)	2·103 (1)	Os(5)–C(51)	1·913 (1)
Os(5)–C(52)	1·963 (1)	Os(5)–C(53)	1·914 (1)
Os(5)–H(45)	1·838 (2)	Os(5)–G(56)	1·831 (2)
Os(6)–C(2)	2·106 (1)	Os(6)–C(61)	1·914 (1)
Os(6)–C(62)	1·961 (1)	Os(6)–C(63)	1·915 (1)
Os(6)–H(46)	1·827 (2)	Os(6)–H(56)	1·825 (2)
C(2)–H(2)	1·085 (2)	C(41)–O(41)	1·142 (1)
C(42)–O(42)	1·141 (1)	C(43)–O(43)	1·144 (1)
C(51)–O(51)	1·142 (2)	C(52)–O(52)	1·141 (1)
C(53)–O(53)	1·140 (1)	C(61)–O(61)	1·141 (1)
C(62)–O(62)	1·142 (1)	C(63)–O(63)	1·139 (2)

identical geometry, each having C_{3v} molecular symmetry within experimental error. This geometry, the atomic labelling scheme and the atomic vibrational tensors are illustrated in Figs. 1 and 2. Each molecule contains a near-equilateral triangle of Os atoms each carrying three terminal, linear carbonyl ligands [mean Os–C–O angle 178·0 (3)°]. The triangle is capped symmetrically by the methylidyne ligand and each of its edges is symmetrically bridged by a hydride ligand.

The average Os–Os distance [2·893 (2) Å] is in the range associated with Os–Os single bonds [*e.g.* 2·877 (1) Å in $Os_3(CO)_{12}$ (Churchill & DeBoer 1977)]. It has been pointed out that there is probably very little direct metal–metal bonding in metal–metal

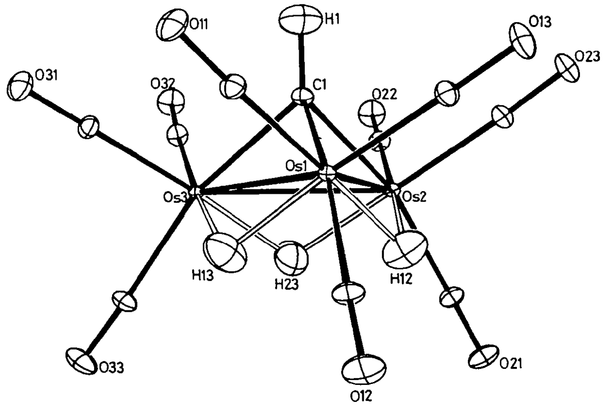


Fig. 1. Molecular geometry of molecule (1) of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ at 11 (1) K: ellipsoids are drawn to enclose 70% probability density.

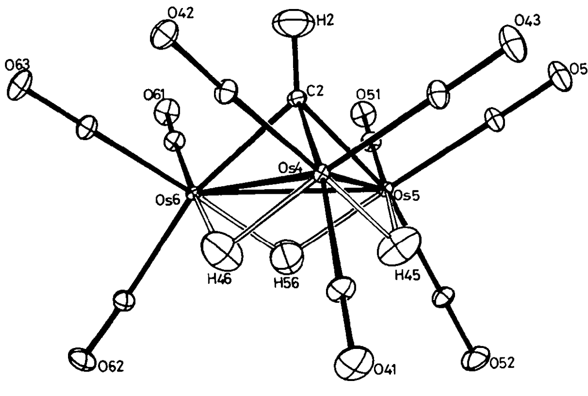


Fig. 2. Molecular geometry of molecule (2) of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ at 11 (1) K: ellipsoids are drawn to enclose 70% probability density.

Table 5. *Bond angles* (°)

Os(3)–Os(1)–Os(2)	59·9 (1)	H(12)–Os(1)–C(1)	84·4 (1)
H(12)–Os(1)–C(11)	178·3 (1)	H(12)–Os(1)–C(12)	83·0 (1)
H(12)–Os(1)–C(13)	92·1 (1)	H(13)–Os(1)–C(1)	84·1 (1)
H(13)–Os(1)–C(11)	93·9 (1)	H(13)–Os(1)–C(12)	83·4 (1)
H(13)–Os(1)–C(13)	176·2 (1)	H(13)–Os(1)–H(12)	84·5 (1)
Os(3)–Os(2)–Os(1)	60·0 (1)	H(12)–Os(2)–C(1)	84·5 (1)
H(12)–Os(2)–C(21)	83·7 (1)	H(12)–Os(2)–C(22)	177·5 (1)
H(12)–Os(2)–C(23)	92·0 (1)	H(23)–Os(2)–C(1)	84·6 (1)
H(23)–Os(2)–C(21)	83·1 (1)	H(23)–Os(2)–C(22)	92·5 (1)
H(23)–Os(2)–C(23)	177·0 (1)	H(23)–Os(2)–H(12)	85·4 (1)
Os(2)–Os(3)–Os(1)	60·1 (1)	H(13)–Os(3)–C(1)	84·7 (1)
H(13)–Os(3)–C(31)	89·6 (1)	H(13)–Os(3)–C(32)	176·6 (1)
H(13)–Os(3)–C(33)	85·8 (1)	H(23)–Os(3)–C(1)	84·4 (1)
H(23)–Os(3)–C(31)	174·6 (1)	H(23)–Os(3)–C(32)	92·4 (1)
H(23)–Os(3)–C(33)	83·8 (1)	H(23)–Os(3)–H(13)	85·5 (1)
Os(2)–C(1)–Os(1)	87·0 (1)	Os(3)–C(1)–Os(1)	87·1 (1)
Os(3)–C(1)–Os(2)	87·0 (1)	H(1)–C(1)–Os(1)	127·9 (1)
H(1)–C(1)–Os(2)	127·0 (1)	H(1)–C(1)–Os(3)	127·0 (1)
O(11)–C(11)–Os(1)	177·3 (1)	O(12)–C(12)–Os(1)	178·8 (1)
O(13)–C(13)–Os(1)	179·0 (1)	O(21)–C(21)–Os(2)	179·0 (1)
O(22)–C(22)–Os(2)	178·6 (1)	O(23)–C(23)–Os(2)	176·1 (1)
O(31)–C(31)–Os(3)	177·3 (1)	O(32)–C(32)–Os(3)	176·2 (1)
O(33)–C(33)–Os(3)	177·4 (1)	Os(2)–H(12)–Os(1)	104·0 (1)
Os(3)–H(13)–Os(1)	104·0 (1)	Os(3)–H(23)–Os(2)	103·9 (1)
Os(6)–Os(4)–Os(5)	60·1 (1)	H(45)–Os(4)–C(2)	84·8 (1)
H(45)–Os(4)–C(41)	83·8 (1)	H(45)–Os(4)–C(42)	177·8 (1)
H(45)–Os(4)–C(43)	90·9 (1)	H(46)–Os(4)–C(2)	84·2 (1)
H(46)–Os(4)–C(41)	83·1 (1)	H(46)–Os(4)–C(42)	92·3 (1)
H(46)–Os(4)–C(43)	176·2 (1)	H(46)–Os(4)–H(45)	85·5 (1)
Os(6)–Os(5)–Os(4)	60·1 (1)	H(45)–Os(5)–C(2)	84·3 (1)
H(45)–Os(5)–C(51)	177·6 (1)	H(45)–Os(5)–C(52)	81·1 (1)
H(45)–Os(5)–C(53)	93·7 (1)	H(56)–Os(5)–C(2)	84·1 (1)
H(56)–Os(5)–C(51)	92·8 (1)	H(56)–Os(5)–C(52)	82·1 (1)
H(56)–Os(5)–C(53)	178·2 (1)	H(56)–Os(5)–H(45)	84·9 (1)
Os(5)–Os(6)–Os(4)	59·8 (1)	H(46)–Os(6)–C(2)	84·4 (1)
H(46)–Os(6)–C(61)	176·7 (1)	H(46)–Os(6)–C(62)	86·2 (1)
H(46)–Os(6)–C(63)	92·1 (1)	H(56)–Os(6)–C(2)	84·2 (1)
H(56)–Os(6)–C(61)	92·4 (1)	H(56)–Os(6)–C(62)	84·1 (1)
H(56)–Os(6)–C(63)	176·3 (1)	H(56)–Os(6)–H(46)	84·6 (1)
Os(5)–C(2)–Os(4)	86·8 (1)	Os(6)–C(2)–Os(4)	87·2 (1)
Os(6)–C(2)–Os(5)	86·9 (1)	H(2)–C(2)–Os(4)	127·2 (1)
H(2)–C(2)–Os(5)	127·9 (1)	H(2)–C(2)–Os(6)	127·0 (1)
O(41)–C(41)–Os(4)	179·0 (1)	O(42)–C(42)–Os(4)	177·2 (1)
O(43)–C(43)–Os(4)	177·9 (1)	O(51)–C(51)–Os(5)	178·0 (1)
O(52)–C(52)–Os(5)	178·4 (1)	O(53)–C(53)–Os(5)	178·1 (1)
O(61)–C(61)–Os(6)	177·6 (1)	O(62)–C(62)–Os(6)	177·1 (1)
O(63)–C(63)–Os(6)	179·3 (1)	Os(5)–H(45)–Os(4)	104·1 (1)
Os(6)–H(46)–Os(4)	104·2 (1)	Os(6)–H(56)–Os(5)	104·8 (1)

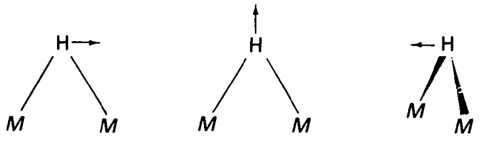
'bonds' with a single hydride bridge (see, *e.g.*, Sherwood & Hall, 1982). The mean Os–H distance is 1·834 (3) Å, similar to such distances reported from neutron diffraction for μ-H ligands in other Os_3 cluster complexes [mean Os–H 1·845 (3) Å in $Os_3(\mu\text{-}H)_2(CO)_{10}$ (Broach & Williams, 1979; Orpen, Rivera, Bryan, Pippard, Sheldrick & Rouse, 1978), Os–H 1·813 (4), 1·857 (4) Å in $Os_3(\mu\text{-}H)(\mu\text{-}CHCH_2)(CO)_{10}$ (Orpen, Pippard, Sheldrick & Rouse, 1978)]. The average Os–methylidyne C distance is 2·101 (2) Å, slightly shorter than that reported for the μ_3-C in $Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9$ [2·15 (2) Å (Shapley, Cree-Uchiyama, St. George, Churchill & Bueno, 1983)]. The Os–C(H) distances here fall in the range of values observed for an asymmetrically bridging (μ_3-CH) ligand in $Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}$ (Shapley, Strickland, St. George, Churchill & Bueno, 1983; with Os–C 2·003 (11), 2·011 (12) and 2·353 (10) Å]. The mean C–H bond length is 1·086 (2) Å, very close to that reported for $Co_3(\mu_3\text{-}CH)(CO)_9$ by Leung, Coppens *et al.* (1981) [1·084 (1) Å by neutron diffraction at 102 K]. The C–H vector is essentially perpendicular to the Os_3 plane [the mean angle between this vector and the plane is 89·4 (2)°]. The Os–C(O) distances fall into two distinct sets: one set of carbonyl ligands lie *trans* to the hydride ligands (see Figs. 1 and 2) and show a mean Os–C distance of 1·911 (2) Å, while the second set lie approximately *trans* to the methylidyne C and show a mean Os–C distance of 1·964 (2) Å. This difference in bond length is a consequence of the powerful π-acid character of the CH ligand which competes with the CO ligands for metal electron density. Similar variation in metal–C(O) bond lengths has been noted by several authors (Zhu, Lecomte, Coppens & Keister, 1982, and references therein; Wong, Haller, Dutta, Chipman & Fehlner, 1982), in related homonuclear trimetal alkylidyne cluster complexes. The C–O bond lengths show no perceptible variations and average 1·141 (1) Å. The molecular geometry at 200 K, as determined by X-ray diffraction, shows no important differences from the neutron result at 11 K; average X-ray bond lengths are Os–Os 2·890 (2), Os–C(H) 2·102 (8), Os–CO(*trans* to H) 1·917 (5), Os–CO(*trans* to CH) 1·960 (8), and C–O 1·126 (4) Å.

The mean Os–H–Os angle is 104·2 (2)° and is close to that obtained from X-ray diffraction analyses of $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CCl)(CO)_9$ [104 (1) and 107 (2)°] by Zhu *et al.* (1982) and $Fe_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)(CO)_9$ [105·5 (4·0)°] by Wong *et al.* (1982). Geometric criteria developed by Bau, Koetzle & co-workers have been used to classify *M*–H–*M* systems as 'open' or 'closed' (Olsen, Koetzle, Kirtley, Andrews, Tipton & Bau, 1974). Those here are 'open' since the angle between the extensions of the C(O)–Os vectors for the carbonyls *trans* to (μ-H) intersect at an average angle of 104·2 (7)°, identical to the mean Os–H–Os angle. Theoretical and experimental studies of the bonding in the congeneric cluster $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ (Sherwood & Hall, 1982) are in agreement with this geometric analysis in concluding that there is little direct metal–metal bonding in these molecules. The angles between C(O)–Os vectors *trans* to the μ_3-CH ligand show the binding of this moiety to be even more 'open' [mean angle = 61·8 (8), mean Os–C–Os 87·0 (1)°]. This geometric feature is in accord with the conclusion of the bonding studies noted above (De Kock *et al.*, 1982; Sherwood & Hall, 1982) that the methylidyne C is best described as *sp* hybridized *with substantial metal–C overlap involving the C* $2p\pi$ orbitals, which overlap would be geometrically 'open'.

The precise low-temperature neutron analysis provides an opportunity for analysis of the vibrational motion of this molecule in the solid state. This analysis is considerably aided by the relatively high (C_{3v}) effective molecular symmetry and the presence of two independent molecules in the crystal. At 11 K it is clear that for the light atoms (especially H atoms) the external, or rigid-body, contribution to mean-square amplitudes is small. Thus mean-square amplitudes of vibration for Os atoms are $<0{\cdot}003$ Å^2, $\sim0{\cdot}006$ Å^2 for C, $\sim0{\cdot}011$ Å^2 for O and $\sim0{\cdot}020$ Å^2 for H atoms. The dominant contribution to atomic motion of the lighter atoms is thus due to zero-point internal modes of vibration. Nevertheless, the 'rigid-bond' postulate (Hirshfeld, 1976) can be invoked to test the vibrational parameters of pairs of atoms of approximately equal mass for internal consistency. The r.m.s. difference in mean-square amplitudes of bonded pairs of Os atoms is $3{\cdot}4\times10^{-4}$ Å^2, which is close to the least-squares estimated standard deviations (e.s.d.'s) in individual Os U_{ii} values ($\sim3\times10^{-4}$ Å^2), while the corresponding value for pairs of C and O atoms is $\sim7\times10^{-4}$ Å^2 with e.s.d.'s $\sim6\times10^{-4}$ Å^2 so that the vibrational parameters do appear satisfactory by this criterion.

In order to assess the vibrational information available from the neutron analysis the IR spectrum of a KBr disc of powdered $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ was measured at liquid-nitrogen temperature (Fig. 3). The interpretation of this spectrum, especially with regard to the hydrogenic vibrations, was greatly facilitated by the work of Andrews, Kettle, Powell & Sheppard (1982) and Oxton (1982*a*, *b*) on related Os and Ru trinuclear clusters. Thus the spectrum shows bands at 3031 and 3019 cm^{-1} due to the C–H stretching mode, four bands between 910 and 870 cm^{-1} due to the C–H bending mode (for strict C_{3v} symmetry these bands would be degenerate, but they are not, the actual solid-state symmetry being C_1), a complex of bands between 1400 and 1330 cm^{-1} due to the in-Os_2H-plane vibrations of the hydride H atoms. There are a variety of bands between 750 and 600 cm^{-1} which includes those due to the totally symmetric Os–(μ_3-C) stretching mode, and the out-of-plane Os–H–Os hydride H mode (see below).

As discussed previously (Orpen & McMullan, 1983; Howard, Jayasooriya, Kettle, Powell & Sheppard, 1979), the internal hydrogenic modes of vibration of the bent *M*–H–*M* system can be described to a good approximation in terms of three independent motions of the H atom. These are illustrated schematically below.



(I) (II) (III)

(I) and (II) are in-plane stretching vibrations (asymmetric and symmetric respectively) and (III) is a deformation mode that changes the orientation of the plane containing the three atoms. It has been shown (Knox, Koepke, Andrews & Kaesz, 1975; Howard *et al.*, 1979) that in transition-metal cluster complexes the stretching modes are essentially independent vibrations showing $1/\sqrt{2}$ H/D isotope effects. For a quantum harmonic oscillator a simple expression relates mean-square amplitude (m.s.a.) of vibration to the frequency (see *e.g.* Cyvin, 1968):

$$\langle x^2\rangle=\frac{h}{8\pi^2c\nu\mu}\left\{\coth\left(\frac{hc\nu}{2kT}\right)\right\},$$

where $\langle x^2\rangle$ is the mean-square amplitude of motion, h Planck's constant, k Boltzmann's constant, T the temperature (K), c the velocity of light, ν the frequency in cm^{-1} and μ the reduced mass of the oscillator. For H atoms, particularly when attached to very massive atoms or groups, $\mu\simeq m_H$, the mass of an H atom. At the very low temperature of this analysis the hyperbolic cotangent term does not differ significantly from unity (*i.e.* only the ground-state vibrational level is populated), thus giving a reciprocal relationship between frequency and $\langle x^2\rangle$. Clearly the m.s.a.'s of individual atoms must be corrected for the motion of atoms to which they are attached before the above relationship can be used to extract frequencies of vibration from the results of a structure analysis. In the present case, the simplest option was taken for this correction, namely to subtract from the m.s.a. of the atom in question the m.s.a. of the (heavy) atom(s) to which it is attached. Thus the value of $\langle x^2\rangle$ appropriate to hydride mode (I) for each H was derived by subtracting the average of the m.s.a.'s for each attached Os atom from the m.s.a. of the H atom, the m.s.a.'s being taken parallel to the Os–Os vector. A similar approach led to reasonable results for the vibration of the H atom in the short, intramolecular hydrogen bond in 2,3-pyridinedicarboxylic acid (Kvick, Koetzle, Thomas & Takusagawa, 1974).

The mean values of $\langle x^2\rangle$ derived in this way for the hydrogenic modes (I), (II), and (III) are 0·0124 (5), 0·0118 (3), 0·0264 (3) Å^2 where the standard errors in parentheses are estimated from the scatter of individual $\langle x^2\rangle$ values. These values correspond to frequencies of 1332 (45), 1395 (30) and 625 (5) cm^{-1},

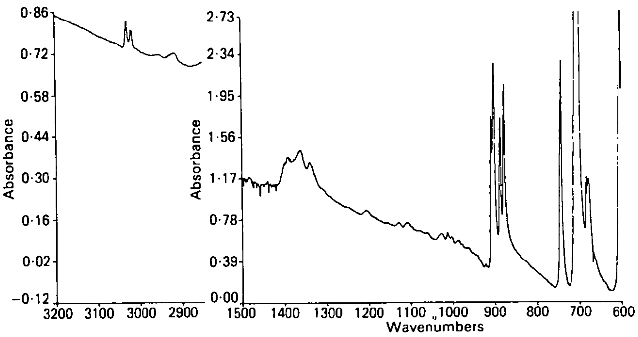


Fig. 3. IR spectrum of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ in KBr disc at 78 K; absorbance *vs* wavenumber.

respectively, for the asymmetric stretch, symmetric stretch and deformation modes (I), (II), and (III). Our previous vibrational analysis of $Ru_4(\mu\text{-}H)_4(CO)_8[P(OMe)_3]_4$ (Orpen & McMullan, 1983) was somewhat less precise and was limited in that anisotropic vibrational parameters were not determined for all atoms. For $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ they are, and there is good agreement between the IR observed values for modes (I) and (II) (*i.e.* 1400–1330 cm^{-1}) and the values calculated from the diffraction data, as was also true for the Ru_4 cluster. In addition the calculated Os–H–Os deformation-mode frequency comes in the expected region [700–600 cm^{-1} (Andrews *et al.*, 1982; Oxton, 1982*a*)] and in a range where there are several IR bands (Fig. 3). The other hydrogenic modes of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ are associated with the methylidyne moiety. Following the same approach we derive mean values of $\langle x^2\rangle = 0{\cdot}0058\,(3)$ and $0{\cdot}0191\,(5)$ Å^2 for the ν_{C-H} symmetric stretch (a_1 in C_{3v}) and δ_{C-H} bend (e in C_{3v}) modes respectively. These values correspond to frequencies of 2870 (150) and 867 (20) cm^{-1} in good agreement with the observed mean values of 3020 and 887 cm^{-1} (the use of $\mu = m_H$ is undoubtedly a worse approximation here than for the Os-bonded H atoms). The magnitudes of the relative errors in the vibrational tensors make estimates of non-hydrogenic m.s.a.'s of vibration much less reliable. The corrected values of $\langle x^2\rangle$ for Os–C(O) stretching and Os–C(O) deformation (*i.e.* for motion $\parallel$ and $\perp$ to the Os–C vector respectively) are $0{\cdot}0016\,(1)$ and $0{\cdot}0048\,(2)$ Å^2 respectively. These last values are presumably due to several, possibly coupled, modes of vibration.

In summary, we have elucidated the detailed structure of $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$ by X-ray and neutron diffraction. In addition we have extracted useful information on the relatively high-energy internal modes of vibration from the diffraction data (*cf.* Trueblood & Dunitz, 1983, and references therein for low-energy internal modes). Although such information is readily accessible from other sources (*e.g.* IR and Raman spectroscopy) the comparison between vibrational data derived from diffraction and spectroscopic experiments allows partial testing of theories explaining internal molecular vibrational behaviour, as well as of the quality of the crystal structure analysis.

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