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Decacarbonyl-μ-hydrido-μ-vinyl-*triangulo*-triosmium: A Combined X-ray and Neutron Diffraction Study

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$HOs_3(C_2H_3)(CO)_{10}$ is monoclinic with $a = 9{\cdot}914\,(3)$, $b = 14{\cdot}398\,(5)$, $c = 12{\cdot}416\,(4)$ Å, $\beta = 99{\cdot}77\,(5)^\circ$, space group $P2_1/n$, $Z = 4$. The structure was solved by the heavy-atom method for the X-ray data, and the H atoms were located by a neutron difference synthesis. The X-ray scattering was dominated by the Os contribution, which enabled a single set of atomic positional and thermal parameters to be refined simultaneously by least squares on 1927 X-ray data (with $\sin\theta/\lambda > 0{\cdot}352$ Å^{-1}) and 1197 profile-fitted neutron data. The final R' values were 0·0317 (X-ray) and 0·0287 (neutron). The combined refinement was more precise, and freer from systematic errors, than individual refinements on full X-ray or neutron data alone. The vinyl group and hydride both bridge the $(OC)_3Os{-}Os(CO)_3$ edge of the $Os_3(CO)_{10}$ cluster; all the carbonyls are terminal. The vinyl group and the Os to which it is σ-bonded [C(41)–Os(3) 2·107 (3) Å] are coplanar to within 0·15 Å; the slight lengthening of the C–C double bond and distortions from planarity are consistent with a π interaction with Os(2) [C(41)–Os(2) 2·273 (3), C(42)–Os(2) 2·362 (3) Å]. The hydride bridges the same edge of the Os_3 triangle as the vinyl group, with Os(2)–H(1) 1·813 (4), Os(3)–H(1) 1·857 (4) Å and Os–H–Os 101·6 (2)°; the significantly shorter Os–H bond is made by the vinyl π-bonded Os atom.

Introduction

In single-crystal X-ray diffraction studies of structures containing both light and very heavy elements, the light-atom positions are determined relatively imprecisely, and it may prove impossible to find the H atoms. The light atoms can be found more precisely by neutron diffraction studies, but because neutron-beam fluxes are low such studies require large crystals (which may introduce extinction problems) and are time-consuming. Least-squares refinement of a single set of atomic positional and thermal parameters to fit simultaneously a full X-ray data set and a possibly incomplete neutron data set should provide optimum structural information with efficient use of expensive neutron-beam time. It is customary to refine two independent sets of positional parameters, because electron density (responsible for the X-ray diffraction) does not correspond exactly to spherical atoms centred at the nuclei (found by neutron diffraction). When atoms of high atomic number are present this problem is not serious provided that the low-angle X-ray data (which contain most of the information about bonding electrons) are omitted, because the majority of the X-ray scattering arises from the inner-core electrons of the heavy atoms; for the structure reported here, R is about 9% for Os atoms alone. Refinement of anisotropic thermal parameters tends to absorb systematic errors introduced by inadequate absorption corrections (more important for the X-ray data here) and extinction corrections (affecting mainly the neutron data). Careful corrections are thus necessary for both data sets, but the resulting common set of thermal parameters should be less subject to systematic errors than thermal parameters obtained with only one type of radiation.

The molecular structure reported here for $HOs_3(C_2H_3)(CO)_{10}$ confirms the spectroscopic and chemical conclusions of Jackson, Johnson, Kelland, Lewis & Schorpp (1975) and Deeming, Hasso & Underhill (1975), and is similar to the structure of the μ-but-1-enyl analogue (Guy, Reichert & Sheldrick, 1976). The hydride has been located bridging the same edge of the Os_3 triangle as the vinyl group, as predicted. The uncertainties in the bond lengths involving the C and O atoms are about a factor of 5 smaller for the combined refinement than for refinement on the X-ray data alone, and nearly an order of magnitude smaller than those for the μ-but-1-enyl analogue (which was refined to an R of 0·032, but for a smaller ratio of data to refined parameters).

Experimental

The compound was prepared by the reaction of di-μ-hydrido-decacarbonyl-*triangulo*-triosmium with acetylene (Deeming, Hasso & Underhill, 1975), and recrystallized from *n*-pentane. X-ray intensities were collected at 20 ± 2°C with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), and a crystal which had been ground to an approximate sphere (diameter 0·17 ± 0·03 mm). Data were corrected for absorption by a semi-empirical method in which transmission factors were calculated for a pseudo-ellipsoid, six parameters being refined to minimize the variation in intensity of 15 strong reflexions measured at a variety of azimuthal settings. The merging R for the 424 azimuthal scan data dropped from 0·037 before correction to 0·017 after; for the full 6332 measured reflexions the decrease was from 0·021 (artificially low because of cancellation of absorption errors at similar azimuthal settings) to 0·019. Equivalent corrected data were averaged to give 2679 unique reflexions covering the range $6 < 2\theta < 60°$. Cell dimensions were obtained by a least-squares fit to 2θ values for 1243 reflexions measured as the difference in ω centroids of hkl at $+2\theta$ and $-h-k-l$ at -2θ.

The large (volume approximately 40 mm^3) crystal employed for the neutron data collection was obtained by adding a seed crystal to a saturated solution in *n*-pentane, which was allowed to cool very slowly. Data were measured on the Andromache Mark VI four-circle neutron diffractometer at AERE Harwell. The crystal was mounted on a glass rod with the diffractometer φ axis collinear with the [101] crystal zone axis. A squashed Ge monochromator was employed, giving a neutron wavelength of 1·1803 (5) Å. Data were collected at 22 ± 2°C for one quadrant of reciprocal space with $1 < 2\theta < 70°$; the $2\theta/\omega$ scans covered 1° in ω to either side of the computed peak position. One check reflexion was measured every 10 reflexions to monitor crystal stability and neutron-beam fluctuations, but it showed little variation in intensity.

Two procedures for neutron data reduction were investigated: an orthodox (peak-minus-background) approach, and profile fitting. In the latter approach a normalized 'learnt profile', itself a function of 2θ, was derived from the profiles observed for well centred reflexions of intermediate strength. Very strong reflexions were not used to derive the learnt profile because of the possibility of profile distortion caused by extinction. The intensity of each reflexion was then estimated by a least-squares fit of the learnt profile (for the appropriate 2θ) to the observed reflexion profile, the ω offset between the two profiles being chosen to give an optimum fit. The intensities and standard deviations found by both methods were compared for each reflexion, and the intensity with the lowest $\sigma(I)$ was chosen for subsequent calculations. Usually the profile fitting gave the lowest $\sigma(I)$, but some high-intensity reflexions were more satisfactory with the peak-minus-background approach. Where the best fit was not within 7ω steps (0·3°) of the median of the reflexion profile, the peak-minus-background values were used instead; such reflexions invariably proved to be very weak, and were not used for refinement purposes. Data obtained by this procedure proved superior to the data obtained from the pure peak-minus-background approach in the combined X-ray/neutron refinements, and were therefore employed for the final refinements described below.

Numerical absorption corrections based on indexed crystal faces were applied to the neutron data (μ = 0·068 cm^{-1}); the mean path lengths derived in this calculation were retained for use in the subsequent extinction corrections. The transmission factors ranged from 0·988 to 0·974. 1721 neutron data were measured, giving 1472 unique reflexions of which 1203 were observed [$I > 3\sigma(I)$]; six of these with $\sin\theta/\lambda <$ 0·085 Å^{-1} were excluded from the refinements because of asymmetric backgrounds. Only 1014 unique observed reflexions were obtained with the pure peak-minus-background method.

Crystal data

$HOs_3(C_2H_3)(CO)_{10}$, monoclinic, $P2_1/n$, a = 9·914 (3), b = 14·398 (5), c = 12·416 (4) Å, β = 99·77 (5)°, U = 1746·6 Å^3, Z = 4, D_x = 3·34 g cm^{-3}.

Structure solution and refinement

The structure was initially solved and refined with the X-ray data alone. The three unique Os atoms were found by multisolution $\sum_2$ sign expansion, and the C and O atoms by difference syntheses. The structure was refined by blocked-matrix least squares with complex neutral-atom scattering factors, the weighting scheme $w = [\sigma^2(F) + 0·00027F_o^2]^{-1}$ (chosen to give a flat analysis of variance in terms of the magnitude of F_o), and all atoms anisotropic to a final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$ of 0·0288 and a corresponding unweighted R of 0·0320 for 2463 unique reflexions with $I > 2\sigma(I)$. No extinction effects were observed. The major features in a difference synthesis were peaks of height about 1 e Å^{-3} close to the Os atom positions. No attempt was made to locate the H atoms from the X-ray data alone.

A difference synthesis computed with the neutron data and the positional and thermal parameters derived from the X-ray data showed four large negative peaks corresponding to the four unique H atoms. A variety of full-matrix refinements, in which a single set of atomic positional and anisotropic thermal parameters for all 29 atoms were fitted simultaneously to X-ray and neutron data, were investigated. The final model included X-ray and neutron scale factors, a neutron extinction parameter, and the Os scattering length for neutrons. The full neutron data (1197 unique observed reflexions) were employed, but X-ray data with $\sin\theta/\lambda <$ 0·352 Å^{-1} were omitted to reduce systematic errors arising from the bonding-electron distribution. The positional parameters refined in this method are thus essentially the nuclear positions. 1927 unique observed X-ray data were employed for refinement. The Os scattering length refined to 1·076 (3) × 10^{-12} cm, close to the value of 1·07 × 10^{-12} cm quoted in *International Tables for X-ray Crystallography* (1974), which was the source of the other neutron scattering lengths. The weighting scheme was $w = [\sigma^2(F) + gF_o^2]^{-1}$, with g set to 0·00027 for X-ray and 0·00025 for neutron data. The refinement converged well, and gave flat analyses of variance. Final residuals were R = 0·0369 (X-ray), 0·0292 (neutron) and R' = 0·0317 (X-ray), 0·0287 (neutron). When a similar number of neutron data from the peak-minus-background instead of the profile-fitted method were employed, the neutron R and R' increased by about 0·017 and 0·007 respectively.

A difference synthesis was computed with positional and thermal parameters from the combined refinement, and full X-ray data were weighted to emphasize the low-angle data. This showed residual electron density at the Os atoms as well as features which could be attributed to the distribution of bonding electrons, *e.g.* positive electron density near the centre of the C—O bonds and around the C—C bond. No quantitative interpretation of these features was attempted.

Final positional and thermal parameters for the combined refinement are presented in Tables 1 and 2, bond lengths and angles in Tables 3 and 4.*

Table 1. *Atom coordinates* (×10^4)

	x	*y*	*z*
Os(1)	−69 (1)	3561 (1)	2311 (1)
Os(2)	−141 (1)	1567 (1)	2710 (1)
Os(3)	1948 (1)	2353 (1)	1683 (1)
H(1)	1709 (3)	1637 (2)	2880 (3)
C(41)	204 (2)	1606 (1)	947 (2)
H(41)	−644 (5)	1898 (3)	393 (4)
C(42)	58 (3)	662 (2)	1158 (2)
H(421)	943 (6)	223 (3)	1457 (4)
H(422)	−864 (6)	295 (3)	824 (4)
C(11)	1269 (2)	3699 (1)	3640 (2)
O(11)	2029 (3)	3809 (2)	4421 (2)
C(12)	−1303 (2)	3340 (1)	937 (2)
O(12)	−2035 (3)	3268 (2)	136 (3)
C(13)	−1560 (2)	3976 (2)	3002 (2)
O(13)	−2429 (3)	4235 (3)	3405 (3)
C(14)	530 (2)	4686 (1)	1736 (2)
O(14)	875 (3)	5358 (2)	1375 (3)
C(21)	−105 (2)	2077 (1)	4132 (2)
O(21)	−74 (2)	2327 (2)	5004 (3)
C(22)	−2106 (2)	1588 (1)	2389 (2)
O(22)	−3255 (3)	1607 (2)	2183 (2)
C(23)	58 (2)	343 (2)	3315 (2)
O(23)	147 (4)	−358 (2)	3727 (3)
C(31)	1994 (2)	3146 (2)	480 (2)
O(31)	1996 (3)	3628 (2)	−251 (3)
C(32)	3481 (2)	2944 (1)	2611 (2)
O(32)	4420 (3)	3250 (2)	3154 (3)
C(33)	3101 (2)	1415 (1)	1251 (2)
O(33)	3795 (3)	871 (2)	964 (2)

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* Lists of X-ray and neutron structure factors and analyses of variance have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33528 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	33 (1)	33 (1)	35 (1)	1 (1)	1 (1)	2 (1)
Os(2)	34 (1)	33 (1)	28 (1)	0 (1)	7 (1)	−4 (1)
Os(3)	32 (1)	38 (1)	29 (1)	2 (1)	8 (1)	−2 (1)
H(1)	45 (2)	60 (2)	40 (2)	7 (2)	7 (2)	−1 (2)
C(41)	44 (1)	46 (1)	25 (1)	−5 (1)	7 (1)	−8 (1)
H(41)	67 (3)	68 (3)	39 (3)	−1 (2)	4 (2)	−3 (2)
C(42)	56 (2)	44 (2)	41 (2)	−11 (1)	14 (1)	−11 (1)
H(421)	92 (3)	50 (3)	70 (3)	−12 (2)	34 (3)	2 (3)
H(422)	93 (3)	68 (3)	66 (3)	−25 (2)	25 (3)	−35 (3)
C(11)	48 (1)	34 (1)	41 (2)	0 (1)	−5 (1)	3 (1)
O(11)	65 (2)	58 (2)	48 (2)	−3 (1)	−19 (2)	1 (1)
C(12)	43 (1)	50 (1)	41 (2)	9 (1)	−7 (1)	−6 (1)
O(12)	69 (2)	81 (2)	58 (2)	13 (2)	−29 (2)	−12 (1)
C(13)	51 (1)	65 (1)	54 (2)	0 (1)	13 (1)	23 (1)
O(13)	78 (2)	132 (3)	92 (3)	0 (2)	36 (2)	53 (2)
C(14)	66 (1)	41 (1)	48 (2)	7 (1)	1 (1)	−10 (1)
O(14)	117 (2)	54 (2)	81 (2)	24 (2)	5 (2)	−32 (2)
C(21)	42 (1)	42 (1)	33 (2)	−8 (1)	11 (1)	−3 (1)
O(21)	61 (1)	63 (2)	37 (2)	−15 (1)	19 (1)	−6 (1)
C(22)	36 (1)	68 (1)	42 (1)	0 (1)	9 (1)	−11 (1)
O(22)	30 (2)	131 (3)	75 (2)	5 (2)	1 (1)	−13 (1)
C(23)	80 (1)	34 (1)	43 (1)	6 (1)	19 (1)	−1 (1)
O(23)	168 (3)	41 (2)	77 (2)	21 (2)	37 (2)	5 (2)
C(31)	48 (1)	58 (1)	40 (2)	14 (1)	16 (1)	6 (1)
O(31)	83 (2)	93 (2)	57 (2)	43 (2)	31 (2)	21 (2)
C(32)	39 (1)	51 (1)	43 (1)	−1 (1)	3 (1)	−10 (1)
O(32)	57 (2)	96 (2)	69 (2)	−10 (2)	−3 (2)	−27 (2)
C(33)	50 (1)	39 (1)	45 (1)	1 (1)	19 (1)	2 (1)
O(33)	73 (2)	48 (2)	73 (2)	−2 (1)	33 (1)	14 (1)

Table 3. *Bond lengths* (Å)

Os(2)–H(1)	1·813 (4)	Os(3)–H(1)	1·857 (4)
C(41)–H(41)	1·078 (7)	C(42)–H(421)	1·093 (8)
C(42)–H(422)	1·077 (7)	Os(2)–Os(1)	2·917 (2)
Os(3)–Os(1)	2·857 (2)	C(11)–Os(1)	1·944 (3)
C(12)–Os(1)	1·949 (3)	C(13)–Os(1)	1·925 (3)
C(14)–Os(1)	1·905 (3)	Os(3)–Os(2)	2·845 (2)
C(41)–Os(2)	2·273 (3)	C(42)–Os(2)	2·362 (3)
C(21)–Os(2)	1·907 (4)	C(22)–Os(2)	1·921 (3)
C(23)–Os(2)	1·913 (3)	C(41)–Os(3)	2·107 (3)
C(31)–Os(3)	1·887 (4)	C(32)–Os(3)	1·941 (3)
C(33)–Os(3)	1·904 (3)	C(42)–C(41)	1·396 (4)
O(11)–C(11)	1·134 (3)	O(12)–C(12)	1·132 (3)
O(13)–C(13)	1·131 (3)	O(14)–C(14)	1·143 (3)
O(21)–C(21)	1·137 (3)	O(22)–C(22)	1·125 (3)
O(23)–C(23)	1·128 (3)	O(31)–C(31)	1·143 (3)
O(32)–C(32)	1·141 (3)	C(33)–O(33)	1·139 (3)

Table 4. *Bond angles* (°)

Os(3)–Os(1)–Os(2)	59·0 (1)	Os(3)–Os(2)–Os(1)	59·4 (1)
Os(2)–Os(3)–Os(1)	61·5 (1)	Os(3)–H(1)–Os(2)	101·6 (2)
Os(1)–Os(2)–H(1)	84·9 (1)	Os(3)–Os(2)–H(1)	39·7 (1)
Os(1)–Os(3)–H(1)	85·9 (1)	Os(2)–Os(3)–H(1)	38·6 (1)
Os(3)–C(41)–Os(2)	80·9 (1)	C(41)–Os(2)–Os(1)	78·5 (1)
C(41)–Os(2)–Os(3)	47·0 (1)	C(42)–Os(2)–Os(1)	113·3 (1)
C(42)–Os(2)–Os(3)	71·6 (1)	C(41)–Os(3)–Os(1)	82·4 (1)
C(41)–Os(3)–Os(2)	52·1 (1)	C(41)–Os(2)–H(1)	78·2 (1)
C(42)–Os(2)–H(1)	84·4 (1)	C(41)–Os(3)–H(1)	81·8 (1)
C(42)–Os(2)–C(41)	35·0 (1)	C(42)–C(41)–Os(2)	76·0 (1)
C(42)–C(41)–Os(3)	121·3 (2)	C(41)–C(42)–Os(2)	69·0 (1)
Os(2)–C(41)–H(41)	113·3 (2)	Os(3)–C(41)–H(41)	124·8 (2)
Os(2)–C(42)–H(421)	102·4 (3)	Os(2)–C(42)–H(422)	113·7 (3)
C(42)–C(41)–H(41)	113·9 (3)	H(422)–C(42)–H(421)	115·2 (4)
C(41)–C(42)–H(421)	121·6 (3)	C(41)–C(42)–H(422)	121·0 (4)
C(11)–Os(1)–Os(2)	89·4 (1)	C(11)–Os(1)–Os(3)	83·4 (1)
C(12)–Os(1)–Os(2)	87·6 (1)	C(12)–Os(1)–Os(3)	91·5 (1)
C(13)–Os(1)–Os(2)	100·8 (1)	C(13)–Os(1)–Os(3)	159·4 (1)
C(14)–Os(1)–Os(2)	156·7 (1)	C(14)–Os(1)–Os(3)	98·0 (1)
C(21)–Os(2)–Os(3)	111·2 (1)	C(21)–Os(2)–Os(1)	77·3 (1)
C(22)–Os(2)–Os(1)	90·2 (1)	C(22)–Os(2)–Os(3)	133·7 (1)
C(23)–Os(2)–Os(1)	165·9 (1)	C(23)–Os(2)–Os(3)	120·5 (1)
C(31)–Os(3)–Os(1)	87·7 (1)	C(31)–Os(3)–Os(2)	135·5 (1)
C(32)–Os(3)–Os(1)	94·8 (1)	C(32)–Os(3)–Os(2)	117·7 (1)
C(33)–Os(3)–Os(1)	172·0 (1)	C(33)–Os(3)–Os(2)	111·2 (1)
C(21)–Os(2)–H(1)	90·7 (1)	C(22)–Os(2)–H(1)	173·4 (1)
C(23)–Os(2)–H(1)	88·3 (1)	C(31)–Os(3)–H(1)	173·3 (1)
C(32)–Os(3)–H(1)	87·8 (1)	C(33)–Os(3)–H(1)	89·8 (1)
C(21)–Os(2)–C(41)	154·1 (1)	C(21)–Os(2)–C(42)	167·7 (1)
C(22)–Os(2)–C(41)	96·5 (1)	C(22)–Os(2)–C(42)	93·5 (1)
C(23)–Os(2)–C(41)	112·2 (1)	C(23)–Os(2)–C(42)	78·2 (1)
C(31)–Os(3)–C(41)	95·4 (1)	C(32)–Os(3)–C(41)	169·4 (1)
C(33)–Os(3)–C(41)	90·2 (1)	C(12)–Os(1)–C(11)	174·9 (1)
C(13)–Os(1)–C(11)	93·2 (1)	C(13)–Os(1)–C(12)	91·4 (1)
C(14)–Os(1)–C(11)	91·2 (1)	C(14)–Os(1)–C(12)	90·0 (1)
C(14)–Os(1)–C(13)	102·4 (1)	C(22)–Os(2)–C(21)	92·6 (1)
C(23)–Os(2)–C(21)	90·4 (1)	C(23)–Os(2)–C(22)	97·4 (1)
C(32)–Os(3)–C(31)	94·7 (1)	C(33)–Os(3)–C(31)	96·3 (1)
C(33)–Os(3)–C(32)	91·8 (1)	O(11)–C(11)–Os(1)	177·5 (2)
O(12)–C(12)–Os(1)	175·8 (2)	O(13)–C(13)–Os(1)	178·8 (3)
O(14)–C(14)–Os(1)	178·9 (2)	O(21)–C(21)–Os(2)	175·8 (2)
O(22)–C(22)–Os(2)	178·7 (2)	O(23)–C(23)–Os(2)	175·7 (2)
O(31)–C(31)–Os(3)	178·7 (2)	O(32)–C(32)–Os(3)	176·4 (2)
O(33)–C(33)–Os(3)	177·8 (2)		

Treatment of neutron extinction

The neutron extinction corrections were based on the method of Becker & Coppens (1974). Since data were collected at a single wavelength, and extinction was not severe, type I secondary extinction with r^* effectively independent of 2θ was assumed. On the further assumption of a Lorentzian distribution for the domain mosaic orientation function, and an effectively spherical crystal but with $\bar{t}$ calculated from the crystal dimensions in the absorption calculation, the expression for the corrected structure factor given by Becker & Coppens is: $F_c^* = k|F_c|[1 + Cx + Ax^2/(1 + Bx)]^{-1/4}$, where $A = 0{\cdot}025 + 0{\cdot}285 \cos 2\theta$, $B = 0{\cdot}15 - 0{\cdot}2 \times (0{\cdot}75 - \cos 2\theta)^2$ if $\cos 2\theta > 0$ or $-0{\cdot}45 \cos 2\theta$ if $\cos 2\theta < 0$, $C = 2$, k is the scale factor, F_c is the calculated structure factor in the absence of extinction, and $x = 10^8 \lambda^2 r^* |F_c|^2 \bar{t}/V^2 \sin 2\theta$. In this expression λ (Å) is the neutron wavelength, $\bar{t}$ (cm) is the mean path length through the crystal, and V (Å^3) is the volume of the unit cell. Studies of extinction as a function of neutron wavelength by Cooper & Rouse (1970) indicate that type I secondary extinction is probable, in which case r^* (in cm in the above expression) may be interpreted as λg, where g (in rad$^{-1} \times 10^8$ if λ is in Å) is the mosaic-spread parameter (Zachariasen, 1967).

In our refinements all derivatives were evaluated analytically, and r^* (multiplied by a constant) was refined as a full-matrix least-squares parameter. In the combined X-ray/neutron refinement described above, r^* refined to 9·0 (3) × 10^{-5} cm – within the range of values found by Cooper & Rouse (1970). The calculated extinction attenuation factors were all in the range 0·7 to 1·0. Plots of F_o/F_c^* against F_o, sin θ and $\bar{t}$ showed little systematic deviation from unity. Fig. 1 shows a plot of observed against calculated attenuation ($F_o/|F_c|$ against $F_c^*/|F_c|$) for the most severely affected reflexions: as predicted the points are scattered about a line of unit slope. Thus for this crystal, the Becker & Coppens (1974) formalism has produced an adequate description of extinction in terms of one refinable parameter (r^*) and the variables F_c, sin θ and $\bar{t}$. The scatter of points about the line in Fig. 1 is significantly greater than would have been expected from the values of $\sigma(F)/F_o$, indicating that extinction is also a function of other systematic variables; a model incorporating anisotropy of mosaic orientation distribution might well have given a significantly better fit. Previous experimental tests of neutron extinction models have often suggested significant anisotropy, even for cubic crystals.

The simultaneous fitting of a single parameter set to both X-ray and neutron data provides a more severe test of the extinction model than single-wavelength neutron data alone, since systematic trends cannot be absorbed by artificial changes in the temperature factors. Similarly, much more care is needed in reducing and then correcting for X-ray absorption than in a pure X-ray study, since systematic errors introduced by inadequacies in the absorption treatment are also traditionally absorbed by the anisotropic temperature factors.

Discussion of the molecular structure

As predicted from solution spectroscopic studies, the vinyl group and the hydride bridge the same edge of an Os_3 triangle (Fig. 2), and all carbonyl groups are terminal. The vinyl group is formally σ-bonded to Os(3) and π-bonded to Os(2); if the vinyl group is considered to donate two electrons in forming the π bond, the Os(3)H(1)Os(2) unit forms a two-electron three-centre bond. Although the Os(2)—Os(3) distance of 2·845 (2) Å is typical for an Os—Os single bond, it may simply be caused by the geometry of the two bridging ligands: it does not necessarily imply a direct Os—Os bond. If no direct bond is drawn between Os(2) and Os(3), and the vinyl π interaction is assumed to occupy one coordination position, then the coordination of each Os atom is close to octahedral, with *trans* H—Os—C angles of 173·3 (1) and 173·4 (1)°. The vinyl group and σ-bonded Os(3) are coplanar to within 0·15 Å, the maximum deviations being shown by H(421) and H(422) which bend away from Os(2) slightly. The interaction with Os(2) should thus be represented as involving the bonding and antibonding π orbitals, rather than as two Os—C σ bonds. The C—C length of 1·396 (3) Å is similar to, but more precise than, the 1·40 (3) Å found in the X-ray diffraction study of the μ-but-1-enyl analogue (Guy, Reichert & Sheldrick, 1976); it is significantly longer than expected for a normal C—C double bond (1·33 Å; Bartell & Bonham, 1960). A relatively weak π interaction would be consistent with the asymmetry of the hydride bridge: Os(2)—H(1) [1·813 (4) Å] is significantly shorter than Os(3)—H(1) [1·857 (4) Å]. The π bond is chemically fairly labile; addition of dimethylphenylphosphine causes it to be replaced by a C(41)—Os(2) σ bond, the P atom being attached to C(42) which is no longer bonded to Os (Churchill, DeBoer, Shapley & Keister, 1976). The bridging hydride was also located in the X-ray analysis of the dimethylphenylphosphine derivative; although the asymmetry of the bridge [Os—H 1·95 (7), 1·80 (8) Å] probably reflects the experimental uncertainties (on chemical grounds a more

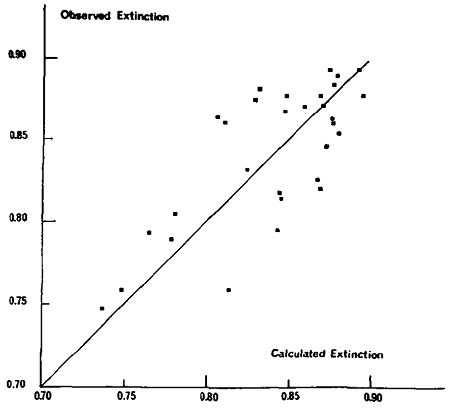

Fig. 1. Plot of observed against calculated neutron extinction attenuation factors ($F_o/|F_c|$ against $F_c^*/|F_c|$) for the most severely affected reflexions.

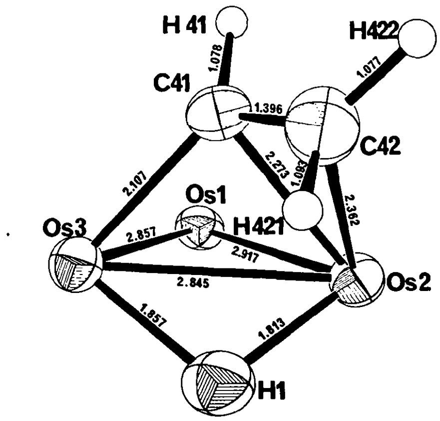

Fig. 2. Bridging-ligand geometry for decacarbonyl-μ-hydrido-μ-vinyl-*triangulo*-triosmium, with 50% probability ellipsoids for some atoms.

symmetrical bridge would have been expected than in the structure reported here, because the bridging C atom makes two σ bonds rather than $\sigma + \pi$), the mean Os—H distance of 1·88 (11) Å is reasonable in the light of the values reported here. A similar bridging situation arises in nonacarbonyl(*tert*-butylethynyl)-μ-hydrido-*triangulo*-triruthenium, where a neutron study by Catti, Gervasio & Mason (1977) found Ru—H 1·789 (5) and 1·796 (5) Å, and Ru—H—Ru 102·3 (3)°, *i.e.* symmetrical within experimental error. However, the Ru—H—Ru plane makes an angle of 115·0° with the Ru_3 cluster plane, in contrast to the angle of 57·6° between the Os—H—Os plane and the Os_3 plane here. The elevation of the H atom with respect to the plane of the heavy-metal triangle is presumably primarily determined by non-bonded interactions with the other ligands, especially those bridging the same bond. In the Ru compound there are two bridging C atoms rather than one, which pushes the H atom further out of the plane.

The mean axial Os—C(O) distance (1·946 Å) and the mean Os—C distance for carbonyls *trans* to Os atoms (1·912 Å) are the same as those found by Churchill & DeBoer (1977) in $Os_3(CO)_{12}$ [1·946 (6) and 1·912 (7) Å]; the remaining four Os—C(O) bonds exhibit consistent *trans* effects: a short Os—C bond [1·887 (4) Å] is *trans* to the long Os—H bond, and *vice versa* [Os—C 1·921 (3) Å], and the Os—C bond *trans* to the vinyl π bond [1·907 (3) Å] is shorter than that *trans* to the vinyl σ bond [1·941 (3) Å]. The C—O bonds are more internally consistent and also significantly longer [mean 1·135 (2) compared with 1·117 (6) Å] than in the refinement on X-ray data alone, reflecting a build-up of electron density between the O and C atoms of the carbonyls. However, it is clear from the anisotropy of thermal motion of the carbonyls (Fig. 3) that significant librational corrections should be added to the Os—C and C—O lengths; it is not clear that a riding model which ignored bending at C would be adequate. A similar comment applies to most room-temperature X-ray and neutron studies of metal carbonyls, so possibly it is better to compare the uncorrected bond lengths.

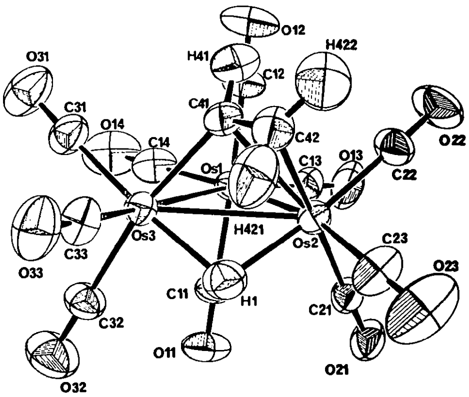

Fig. 3. *ORTEP* plot (Johnson, 1965) of decacarbonyl-μ-hydrido-μ-vinyl-*triangulo*-triosmium showing 50% probability ellipsoids for all atoms.

Discussion of refinement strategy

In a combined refinement on both X-ray and neutron data, the single set of anisotropic temperature factors should be less able to compensate for errors in the neutron extinction and X-ray absorption corrections than refinements based on only one type of radiation. Examination of Fig. 3 provides good qualitative evidence that the refined thermal parameters are physically reasonable: the Os and bridging atoms are relatively isotropic and show less thermal motion than the other atoms; the carbonyl thermal ellipsoids in general have the smallest principal axis close to the Os···O direction; the O atoms show greater thermal motion perpendicular to this direction than do the corresponding C atoms, and the amplitudes along the Os···O directions are similar for O, C and Os [which should apply if the force constants for Os—C and C—O bond stretching are much larger than those for angle deformations, as discussed by Hirshfeld (1976)].

Double-atom procedures for simultaneous refinement of X-ray and neutron data have been proposed (see, for example, Duckworth, Willis & Pawley, 1969), and the refinement of nuclear positions on the basis of high-angle X-ray data alone is also sometimes employed, but a single-atom refinement employing both neutron and higher-angle X-ray data appears to be novel. The advantages are improved least-squares convergence resulting from reduced correlations and the use of more data, and an ability to isolate and hence minimize errors arising from neutron extinction and X-ray absorption. The basic assumption is that the higher-angle X-ray scattering is dominated by the contribution from inner-core electrons which are accurately centred at the nuclear positions; this assumption should be especially justified when heavy atoms dominate the X-ray scattering, as in the structure reported here. The major experimental improvement in the procedure adopted here would be to determine both sets of data at the same low temperature; this would reduce thermal diffuse scattering (which probably affects both sets, thereby introducing a systematic error affecting the thermal parameters) and also minimize the librational shortening of the metal—C and C—O lengths.

The refinement procedure described here should prove effective in obtaining optimum molecular-geometry information for structures containing both light and heavy atoms in cases where only incomplete neutron data are available, *e.g.* because of the limited resources available or the difficulty of growing large enough crystals.

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9-Methylisoguanine Hydrochloride Dihydrate: Crystal Structure and Charge Densities

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Isoguanine is a naturally occurring nucleobase. In order to investigate its tautomeric properties, 9-methylisoguanine(I).HCl.2H$_2$O, $C_6H_8N_5O.HCl.2H_2O$, was crystallized; space group $P2_1/c$, $a = 5{\cdot}189$ (3), $b = 24{\cdot}869$ (8), $c = 8{\cdot}218$ (4) Å, $\beta = 101{\cdot}70$ (6)°. The structure was determined by direct methods and refined to $R = 6{\cdot}6\%$ based on 1527 X-ray structure amplitudes. 9-Methylisoguanine is protonated at N(3), in agreement with charge densities computed with CNDO/2. Two inversion-related molecules are linked by four hydrogen bonds N(1)H$\cdots$O(2) and O(2)$\cdots$H$_2$O$\cdots$H—N(6) and the base pairs are stacked at a distance of 3·26 Å with the N(6) amino groups overlapping the imidazole rings of adjacent molecules.

Isoguanosine, originally isolated from croton seeds and referred to as crotonoside (Cherbuliez & Bernhard, 1952), was subsequently synthesized by Davoll (1951), and characterized as an isomer of guanosine and an analogue of adenosine, adenosin-2-one. The free base, isoguanine, is a constituent of butterfly wings (Purrmann, 1940), and apparently of a cytokinin isolated from corn (Letham, 1973). Isoguanine has hitherto not been found in natural nucleic acids. Isoguanosine (Ravindranathan & Miles, 1965) and some methylated isoguanines (Kazimierczuk & Shugar, 1974) possess, in common with guanosine and its nucleotides, the property of forming aqueous gels which exhibit secondary structure *via* base-pair hydrogen bonding similar to that found in helical polynucleotides. A synthetic polynucleotide, polyisoguanylate, has been prepared and characterized as a multi-stranded helix (Golas, Fikus, Kazimierczuk & Shugar, 1976).

Characterization of the structures of isoguanosine gels, and of polyisoguanylate, requires information regarding the tautomerism of 9-substituted isoguanines.