Joint *X*-Ray and Neutron Diffraction Refinement of the Crystal and Molecular Structure of Tri-μ-hydrido-μ-iodo-*cyclo*-tetrakis(tricarbonylosmium)(4 *Os–Os*)

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The title compound $[Os_4I(CO)_{12}H_3]$ crystallises in the monoclinic space group *C*2/*c* with *a* = 17.307(8), *b* = 8.040(3), *c* = 17.760(9) Å, β = 119.80(2)°, and *Z* = 4. Simultaneous refinement of a single parameter set to 1 925 *X*-ray [(sin θ)/λ > 0.45] and 607 neutron data has led to *R* 0.034 (*X*-ray) and 0.035 (neutron). The Os atoms adopt a ' butterfly ' configuration, with the iodine sitting on the crystallographic two-fold axis and bridging the two ' wing-tip ' metal atoms. One hydride also lies on the two-fold axis and bridges the Os–Os ' hinge ' bond [Os–H 1.788(4) Å]. The other two hydrides bridge the longer Os(hinge)–Os(wing-tip) bonds and lie closer to the ' wing-tip ' metals [Os–H 1.754(4) (two) and 1.823(5) Å (two)]. Each Os atom is also bonded to three terminal carbonyl groups.

ONLY under fortuitous circumstances do *X*-ray diffraction studies of heavy-metal carbonyl hydrides yield useful information about the hydrogen atoms because the *X*-ray scattering is dominated by the metal-atom contribution. Neutron diffraction offers a better method of locating the light atoms, but since neutron-beam fluxes are low such studies require large crystals and long periods of time for data collection. Consequently there have been few neutron diffraction studies on cluster species. Only five trinuclear clusters having ' edge-bridging ' hydride ligands appear to have been investigated: $[Ru_3(CO)_9(CCBu^t)H]$,[1] $[Os_3(CO)_{10}H_2]$,[2] $[Os_3(CO)_{10}(CH_2)H_2]$,[3] $[Os_3(CO)_{10}(C_2H_3)H]$,[4] and $[Os_3(CO)_9H_2(S)]$.[5] In the two earlier neutron diffraction studies on tetranuclear clusters, $[FeCo_3(CO)_9\{P(OMe)_3\}_3H]$ [6] and $[Ni_4(C_5H_5)_4H_3]$,[7] the hydrides have been found to act as ' face-capping ' groups.

A report of the chemistry and *X*-ray structure of $[Os_4I(CO)_{12}H_3]$ has appeared.[8] The neutron diffraction study was undertaken in order to locate the hydride ligands, to see if these positions could be related to the proposed structure of the parent complex $[Os_4(CO)_{12}H_4]$,[9] and to gain information on the nature of metal–hydride bonding. In this determination we have attempted to optimise the extraction of structural information by fitting a single set of atomic parameters to both *X*-ray and neutron data. Low-angle *X*-ray data were excluded from refinements because they contain information about bonding electrons as well as inner-core electrons (which are assumed to be centred on the nuclear positions).

EXPERIMENTAL

X-Ray Data Collection.—Pale yellow crystals were deposited from cyclohexane. A total of 5 294 intensities were recorded on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation, a θ—2θ scan technique, and a crystal of dimensions *ca.* 0.064 × 0.096 × 0.144 mm. Unit-cell dimensions were determined from the angular measurements of 25 strong reflections with 20 < 2θ < 30°. Weak reflections which gave $I_t - 2^{\frac{1}{2}}I_t < I_b$ on the first scan were omitted, where I_t is the intensity at the top of the peak and I_b the mean background intensity. Data were collected with a constant scan speed of 0.05° s^{-1} and a variable scan width (range of 0.60 + 0.02 tan θ°) and background measurement time proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan. Three standard reflections were measured at 3 h intervals throughout the data collection and showed no significant variation in intensity. The variance of the intensity *I* was calculated as the sum of the variance due to counting statistics and $(0.03I)^2$. An empirical absorption correction based on a pseudo-ellipsoid model was applied; six parameters were refined to minimise the variation in intensity of a large number of reflections and their symmetry equivalents. Equivalent reflections were averaged to give 2 724 unique data with $F > 4\sigma(F)$.

Neutron Data Collection.—A large (*ca.* 59 mm^3) block-shaped single crystal was obtained by adding a seed crystal to a saturated solution in cyclohexane and allowing the solution to stand for several weeks. Neutron intensities were measured on the Andromache Mark VI four-circle diffractometer at A.E.R.E. Harwell with a squashed germanium monochromator and neutron wavelength of 1.180 3(5) Å. The crystal was mounted with the diffractometer φ axis collinear with the [010] zone axis; 797 intensities were collected in the range 1 < 2θ < 70° using a 45-step ω scan technique and a step width of 0.04°. One check reflection ($\bar{5}11$) was remeasured every 20 reflections to monitor crystal stability and changes in neutron flux, but no significant variation in intensity was observed. The data were profile fitted to improve the precision of the weaker reflections.[4] Numerical absorption corrections based on indexed crystal faces were applied (μ 0.07 cm^{-1}); the mean pathlengths derived in these calculations were retained for use in the subsequent extinction corrections. Transmission factors ranged from 0.984 9 to 0.977 5. Equivalent reflections were averaged to give 607 unique intensities with $F > 4\sigma(F)$.

RESULTS

Crystal Data.—$C_{12}H_3IO_{12}Os_4$, *M* = 1 226.8, Monoclinic, *a* = 17.307(8), *b* = 8.040(3), *c* = 17.760(9) Å, β = 119.80(2)°, *U* = 2 144.5 $Å^3$, D_c = 3.799 g cm^{-3}, D_m = not measured, $Z = 4$, $F(000) = 2\,111.22$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 251.1 cm^{-1}; neutrons, $\lambda = 1.180\,3(5)$ Å, $\mu = 0.07$ cm^{-1}. Space group $C2/c$ from systematic absences and successful structure refinement.

Structure Solution and Refinement.—The structure was initially solved and refined with the full X-ray data alone.[8] A Fourier-difference synthesis computed with the neutron data and X-ray positional and thermal parameters revealed two large negative peaks corresponding to the two unique hydrogen atoms. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all atoms. A single set of atomic positional and thermal parameters was fitted simultaneously to the full neutron data and the 1 925 X-ray data with $(\sin\theta)/\lambda > 0.45$ (the low-angle X-ray data would have introduced systematic errors arising from the bonding electron distribution). The final model included X-ray and neutron scale factors and a neutron extinction parameter r^* (defined in ref. 4) which refined to 0.044 2(2). The mean-value $\omega\Delta^2$ was relatively independent of the magnitudes of F_o or of $\sin\theta$ with the weighting scheme $w = [\sigma^2(F) + gF_o^2]^{-1}$; g set to 0.000 0 for X-rays and 0.000 6 for neutrons. X-Ray and neutron scattering factors were taken from ref. 10. The final converged residuals were $R = 0.034$ (X-ray), 0.035 (neutron) and $R' = 0.034$ (X-ray), 0.037 (neutron). Table 1 gives the final atomic co-ordinates from the combined refinement. Details of anisotropic thermal parameters, molecular least-squares planes, and observed and calculated structure factors for both X-ray and neutron data sets may be found in Supplementary Publication No. SUP 22772 (15 pp).*

TABLE 1

Atom co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Os(1)	790(1)	4 746(1)	3 726(1)
Os(2)	817(1)	2 587(1)	2 447(1)
I(1)	0	7 208(1)	2 500
C(11)	601(2)	6 097(3)	4 516(2)
O(11)	506(3)	6 814(5)	5 009(3)
C(12)	1 936(2)	5 671(3)	4 041(2)
O(12)	2 593(2)	6 290(4)	4 213(2)
C(13)	1 261(2)	3 008(3)	4 534(2)
O(13)	1 530(2)	1 994(5)	5 050(2)
C(21)	651(2)	1 052(3)	1 543(2)
O(21)	578(2)	94(5)	1 039(2)
C(22)	1 799(2)	3 754(4)	2 502(2)
O(22)	2 382(3)	4 447(6)	2 526(3)
C(23)	1 584(2)	1 101(3)	3 336(2)
O(23)	2 044(3)	168(5)	3 848(2)
H(1)	311(3)	4 171(6)	1 605(3)
H(2)	0	1 309(8)	2 500

After preliminary X-ray data reduction at the Polytechnic of North London and neutron data reduction at A.E.R.E. Harwell, all calculations were carried out on the Cambridge University IBM 370/165 computer with programs written by Professor G. M. Sheldrick.

DISCUSSION

This combined X-ray/neutron study shows that the three hydride ligands bridge three edges of the Os_4 ' butterfly '. One hydride lies on the crystallographic C_2 axis and bridges the Os(2)–Os(2′) bond. The other two hydrides asymmetrically bridge the two long Os(1)–Os(2′) and Os(2)–Os(1′) bonds with the shorter Os–H distances involving the Os ' wing-tip ' atoms. Figures 1 and 2 are views of the cluster showing the positions of the hydrides. The bond lengths and angles associated with the final atomic co-ordinates are listed in Tables 2 and 3, respectively.

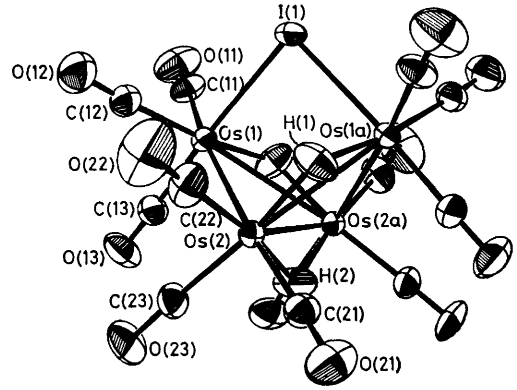

FIGURE 1 ORTEP plot of $[Os_4I(CO)_{12}H_3]$, showing 50% probability thermal ellipsoids

The geometry of the heavier atom fragment of the molecule obtained by the combined refinement differs little from that obtained from the X-ray data alone. However, the estimated standard deviations on the Os–C and C–O bond lengths are almost a factor of 10 lower in this combined refinement. This allows a clearer investigation of the bonding in this complex. If, for the moment, Os–Os bonds where the edge is bridged by a hydride are neglected, each metal atom has a slightly distorted octahedral geometry. Then the bonding may be discussed in terms of the *trans* effect. The shortest Os–C distance, Os(1)–C(13), is *trans* to the bridging iodine atom, which must act as a three-electron donor. A long C(13)–O(13) distance is also associated with this carbonyl ligand. This indicates that although the iodine is a good σ donor it is a poor π acceptor and offers little competition to the carbonyl which withdraws electron density from the metal into π-bonding orbitals. The three next shortest Os–C (carbonyl) distances are *trans* to the bridging hydrides.

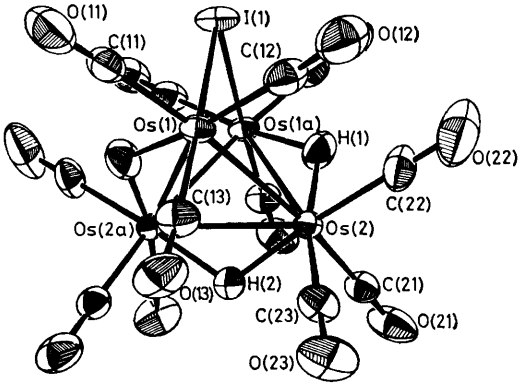

FIGURE 2 View of $[Os_4I(CO)_{12}H_3]$ showing the distribution of the hydride ligands

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

These ligands can have no suitable orbitals available for competition with the carbonyls for back donation from the metals. The longest of these three Os–C distances, Os(1)–C(12), is associated with the shortest Os(1)–H(1′) distance, and the shortest Os–C bond length, Os(2)–C(23), with the longest Os(2)–H(1) distance. The two remaining longer Os–C distances are equivalent and are both *trans* to Os–Os bonds. This indicates that there is some donation of π-electron density from one metal to another. Similar trends in bond lengths have been observed in $[Os_3(CO)_9H_2(S)]$.[5]

TABLE 2

Bond lengths (Å)

Os(2)–Os(1)	2.877(1)	Os(2)–Os(2a)	2.927(2)
Os(2)–Os(1a)	3.055(1)	H(1)–Os(1a)	1.754(4)
I(1)–Os(1)	2.751(2)	H(2)–Os(2)	1.788(4)
H(1)–Os(2)	1.823(5)	O(11)–C(11)	1.125(4)
C(11)–Os(1)	1.927(3)	O(12)–C(12)	1.135(3)
C(12)–Os(1)	1.923(3)	O(13)–C(13)	1.139(3)
C(13)–Os(1)	1.875(3)	O(21)–C(21)	1.139(3)
C(21)–Os(2)	1.930(3)	O(22)–C(22)	1.135(4)
C(22)–Os(2)	1.901(3)	O(23)–C(23)	1.141(4)
C(23)–Os(2)	1.897(3)		

Key to symmetry operation (a) relating designated atoms to reference atoms at (x, y, z): $-x, y, \frac{1}{2} - z$.

The three Os–H–Os bridges are best described as three-centre two-electron bonds. Whether these bonds are ‘ open ’ with no overlap of metal orbitals or ‘ closed ’ with direct metal–metal interaction is less clear. In the case of the two asymmetric bridges this asymmetry makes an accurate assessment difficult, even though the C–Os–H–Os–C units are essentially planar, but the length of the Os–Os vector suggests that there is little direct metal–metal interaction. The C(22)Os(2)H(2)-Os(2′)C(22′) fragment is also approximately planar, and the C(22)–Os(2)–H(2) angle of 172.5(1)° shows that extensions of the *trans* carbonyls would intersect at a point close to the hydride, so that no appreciable Os–Os interaction should be present. In $[W_2H(CO)_9(NO)]$ and $[W_2H(CO)_8(NO)\{P(OMe)_3\}]$,[11] where the W–H–W bonds are considered to be ‘ closed ’ there is a decrease in the H–W–C (carbonyl) angles to 163.8 and 166.2°.

TABLE 3

Bond angles (°)

Os(2)–Os(1)–Os(2a)	59.0(1)	Os(1)–Os(2)–Os(1a)	80.2(1)
Os(1)–Os(2)–Os(1a)	63.5(1)	Os(1a)–H(1)–Os(2)	117.3(3)
I(1)–Os(1)–Os(2)	90.3(1)	C(11)–Os(1)–I(1)	88.5(1)
C(11)–Os(1)–Os(2)	172.0(1)	C(12)–Os(1)–I(1)	89.3(1)
C(12)–Os(1)–Os(2)	92.5(1)	C(13)–Os(1)–I(1)	176.6(1)
C(13)–Os(1)–Os(2)	89.0(1)	C(12)–Os(1)–C(11)	95.4(1)
Os(1)–I(1)–Os(1a)	88.0(1)	C(13)–Os(1)–C(11)	91.7(1)
C(21)–Os(2)–Os(1)	171.2(1)	C(13)–Os(1)–C(12)	94.1(1)
C(22)–Os(2)–Os(1)	91.5(1)	C(22)–Os(2)–C(21)	96.8(1)
C(23)–Os(2)–Os(1)	90.1(1)	C(23)–Os(2)–C(21)	92.5(1)
H(1)–Os(2)–Os(1)	92.1(2)	C(23)–Os(2)–C(22)	91.8(1)
H(2)–Os(2)–Os(1)	88.9(1)	H(1)–Os(2)–C(21)	87.3(2)
H(2)–Os(2)–C(21)	83.2(1)	H(1)–Os(2)–C(22)	75.5(2)
H(2)–Os(2)–C(22)	172.5(1)	H(1)–Os(2)–C(23)	167.1(2)
H(2)–Os(2)–C(23)	80.7(1)	Os(2)–H(2)–Os(2a)	109.8(3)
H(2)–Os(2)–H(1)	112.0(2)	O(21)–C(21)–Os(2)	176.8(3)
O(11)–C(11)–Os(1)	176.2(3)	O(22)–C(22)–Os(2)	179.3(3)
O(12)–C(12)–Os(1)	176.6(3)	O(23)–C(23)–Os(2)	177.5(3)
O(13)–C(13)–Os(1)	176.3(3)		

The symmetric Os(2)–H(2) distance is close to the mean of the asymmetric Os–H bond lengths (1.789 Å), and these distances are slightly shorter than the Os–(μ_2-H) bond values reported in neutron studies in several Os_3 clusters.[3-5] The reason for the asymmetry of the two Os(hinge)–H–Os(wing-tip) is not clear but is probably associated with the small electron inbalance involving the iodine atom co-ordinated to the ‘ wing-tip ’ Os atom. A marked asymmetry of the μ-H has been observed in the structure of $[Os_3(CO)_{10}(C_2H_3)H]$[4] [Os–H 1.813(4) and 1.857(4) Å]. The asymmetry of the hydride bridges is also reflected in the non-bonded interactions of H(1) and H(2), with H(1) · · · Os(1) 3.462 (5), H(1) · · · Os(2a) 3.396 (5), H(1) · · · I(1) 3.102 (8), and H(2) · · · Os(1) 3.360 (5) Å.

The carbonyl groups are all approximately linear, and as has been used as evidence for the positions of hydrides in many *X*-ray structure determinations, they bend away from the hydride bridged Os–Os edges. The Os–Os-*cis* C angles for carbonyls adjacent to the bridged metal–metal bonds have an average value of 108.3° compared to an average of 90.6° for those adjacent to the unbridged edges.

The structure of $[Os_4I(CO)_{12}H_3]$ is related to that of $[Os_4(CO)_{12}H_4]$, which has D_{2d} symmetry, where the four hydrides bridge the four ‘ long ’ edges (2.964 Å) of the Os_4 tetrahedron,[9] by the breaking of one of the hydride bridged Os–Os edges. The hydrogen atom is replaced by the iodine atom and the Os_4 tetrahedron swings open to give the observed ‘ butterfly ’ structure.

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