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References


SHORT STRUCTURAL PAPERS


Dodecacarbonyltetra-μ-hydrido-tetrahedro-tetraosmium

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Abstract. [Os4(CO)12H4], triclinic, P1, a = 9·811 (3), b = 9·893 (3), c = 10·240 (4) Å, α = 85·56 (2), β = 82·71 (2), γ = 88·71 (2)°, U = 982·82 Å3, Z = 2, Dc = 3·72 Mg m-3, μ(Mo Kα) = 25·83 mm-1. The structure refined to R = 0·043 for 1815 unique diffractometer data. The Os atoms define a distorted tetrahedron with approximate D2h symmetry, there being four long and two short metal—metal bonds. Each Os atom is coordinated to three terminal carbonyls. The arrangement of these groups indicates that the four hydrides edge-bridge the four long Os—Os bonds. The molecules pack in a disordered manner about a molecular centre of symmetry in a ratio of 19 : 1.

Introduction. A knowledge of the molecular geometry of the hydrido-carbonyl clusters of the type 

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$M_4(\text{CO})_6 \text{H}_4$ ($M = \text{Re, Ru, Os}$) is of importance because these compounds are the starting materials for many of the reactions which are currently being investigated to establish the role of metal clusters in catalysis (Muetterties, 1977; Muetterties, Rhodin, Band, Brucker & Pretzer, 1979). These structures are also of interest from a theoretical viewpoint since $M_4(\text{CO})_6 \text{H}_4$ compounds ($M = \text{Ru, Os}$) have the correct number of electrons to form six two-centre two-electron bonds, but $\text{Re}_4(\text{CO})_6 \text{H}_4$ is formally unsaturated, and the location of the hydrides is different in the two types of complex (Hoffmann, Schilling, Bau, Kaesz & Mingos, 1978). IR spectral studies have shown that $\text{Ru}_4(\text{CO})_6 \text{H}_4$ and $\text{Os}_4(\text{CO})_6 \text{H}_4$ have the same symmetry (Knox, Koepeke, Andrews & Kaesz, 1975) while the symmetry of $\text{Re}_4(\text{CO})_6 \text{H}_4$ is higher. The structural differences between $\text{Re}_4(\text{CO})_6 \text{H}_4$ and $\text{Ru}_4(\text{CO})_6 \text{H}_4$ have been confirmed by single-crystal X-ray analyses. In $\text{Re}_4(\text{CO})_6 \text{H}_4$ (Wilson & Bau, 1976) the metal atoms define a regular tetrahedron and the 12 carboxyl ligands are eclipsed with respect to the $\text{Re}$--$\text{Re}$ edges; this suggests that the four hydrides cap the four faces of the tetrahedron. In $\text{Ru}_4(\text{CO})_6 \text{H}_4$ (Wilson, Wu, Love & Bau, 1978) the $\text{Ru}_4$ tetrahedron is distorted to $D_{3d}$ symmetry, with four long and two short $\text{Ru}$--$\text{Ru}$ bonds, and the carboxyl groups are staggered with respect to the metal--metal bonds which suggests that the hydrides may bridge the four long tetrahedral edges. There have been many attempts to grow suitable single crystals of $\text{Os}_4(\text{CO})_6 \text{H}_4$ so that the similarity between the Os and Ru analogues could be confirmed, and the bond parameters for the parent cluster hydride established. However, because of disorder problems suitable crystals have proved elusive until recently. Single crystals have now been grown and this X-ray analysis was undertaken.

Crystals of $\text{Os}_4(\text{CO})_6 \text{H}_4$ were obtained as pale yellow, elongated rectangular blocks by slow evaporation (1 month) from chloroform. 1945 intensities were measured (for $3.0 < 2\theta < 50.0^\circ$) on a Philips PW 1100 four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation, an $\omega$--$2\theta$ scan technique, and a crystal $0.096 \times 0.088 \times 0.128$ mm. Lp corrections and semi-empirical absorption corrections (based on a pseudo-ellipsoid model and 440 azimuthal scan data from 20 independent reflections which gave transmission coefficients ranging from 0.378 to 0.995 for the full data set) were applied. Equivalent reflections were averaged to give 1815 unique observed reflections [$F > 3\sigma(F)$]. Cell constants were derived from angular measurements of 25 strong reflections in the range $15 < 2\theta < 25^\circ$.

An $E$ map, calculated using multisolution $\Sigma_2$ sign-expansion techniques, showed four strong peaks which defined a tetrahedron; these were considered to be the Os atoms. A subsequent difference synthesis revealed the positions of the carbonyl groups, but also showed four peaks of height $ca$ 7.8 e $\text{Å}^{-3}$ over the four faces of the Os tetrahedron related to the Os atom positions by an approximate centre of symmetry. These peaks had too high an electron density to be hydride ligands, and there were chemically unreasonable contact distances to the carbonyl groups. An examination of the bond parameters suggested that these peaks represented another orientation of the Os tetrahedron occurring in a small fraction of the sites. The structure was refined by full-matrix least squares. The Os atoms in the two orientations were assigned occupancies $k$ and $1 - k$ respectively; $k$ refined to 0.954 (3). The high-occupancy Os atoms were assigned anisotropic thermal parameters, while the low-occupancy Os atoms, and the C and O atoms (occupancies set to unity) were refined isotropically. A weak constraint was placed on the low-occupancy Os--Os distances, so that the four long and two short bonds in the tetrahedron were each equal; the Os--Os distances refined to values of 2.90 (2) and 2.84 (2) Å. Complex neutral-atom scattering factors (International Tables for X-ray Crystallography, 1974), and a weighting scheme $w = 1.551/[\sigma^2(F) + 0.00021F^2]$ were employed. The refinement converged to $R = 0.043$ and $R_I = \sum w^{1/2}(F_o - F_c)^2/\sum w^{1/2}F^2_c = 0.044$. Final atomic coordinates and isotropic or equivalent isotropic temperature factors are given in Table 1, while the corresponding bond lengths and angles are listed in Tables 2 and 3 respectively.*

**Discussion.** This X-ray analysis confirms that $\text{Os}_4(\text{CO})_6 \text{H}_4$ is isostructural with its Ru analogue (Wilson et al., 1978). The four Os atoms define a distorted tetrahedron with four long [mean 2.964 (2) Å] and two short [mean 2.817 (2) Å] metal–metal bonds. The short bond lengths and angles are listed in Tables 2 and 3 respectively.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36066 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
Table 1. Atom coordinates (×10^4) and equivalent isotropic or isotropic temperature factors (Å² × 10^3)

<table>
<thead>
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<th>Atom</th>
<th>x</th>
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<th>U</th>
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<td>32</td>
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The D_4d symmetry of the tetrahedral core is retained in many of the derivatives of M_4(CO)_{12}H_4 (M = Ru, Os). In Os_4(CO)_{12}H_4, the unbridged edges are significantly shorter [mean of two 2.934 (4) Å] to those in Os_4(CO)_{11}H_4(CNCH_3), but the two bridged edges are similar in length [mean of four 2.798 (9) Å]. This difference is probably due to delocalization of the additional negative charge over the cluster framework, since there is better agreement between the Os-Os bond lengths in Os_4(CO)_{12}H_4 and the neutral derivative Os_4(CO)_{12}H_4(CNCH_3) [mean bridged Os-Os bond lengths of 2.891 (2) Å].
2.963 (2) Å, unbridged 2.822 (1) Å] (Churchill & Hollander, 1980).

The presence of edge-bridging hydrides in Os₄(CO)₁₂H₄ is as expected from simple electron-counting considerations. This complex is an ‘electron precise’ 60 electron system with the correct number of electrons to form two two-centre two-electron Os–Os bonds and four three-centre two-electron Os–H–Os bonds. Re₄(CO)₁₂H₄ has only 56 electrons, and it appears to be more favourable to form four four-centre Re–H bonds; hence the difference in structure between Re₄(CO)₁₂H₄ and Os₄(CO)₁₂H₄.

We thank the Science Research Council for financial support, and Dr M. McPartlin of the Polytechnic of North London for the use of the Philips diffractometer. We are grateful to the Universidad Metropolitania, Venezuela, for a grant (to CZ). Calculations were performed on the Cambridge University IBM 370/165 computer with SHELX 76 (Sheldrick, 1976); the figure was drawn with PLUTO written by Dr W. D. S. Motherwell.