

Neutron Diffraction Analysis of $\text{H}_2\text{Os}_6(\text{CO})_{18}$

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$\text{H}_2\text{Os}_6(\text{CO})_{18}$ is one of the more intriguing compounds in metal cluster chemistry. A rare example of a non-octahedral hexanuclear cluster, it was first prepared in 1976 from the vacuum pyrolysis of $\text{Os}_3(\text{CO})_{12}$ and subsequent acidification.¹ The structure, reported later that year by McPartlin and co-workers,² consists of a capped square pyramid of osmium atoms (Figure 1) augmented by three terminal carbonyl ligands on each Os atom. The unconventional shape of the cluster contrasts markedly with its isoelectronic analogues, $[\text{Os}_6(\text{CO})_{18}]^{2-}$ and $[\text{HOs}_6(\text{CO})_{18}]^-$, which have the usual octahedral structure.²

In this paper, we report a single-crystal neutron structure determination of $\text{H}_2\text{Os}_6(\text{CO})_{18}$ and the location of the two hydrogen atoms of this molecule, which were not found in the original X-ray study and have been the subject of much speculation. The original authors² postulated that one of the H atoms is located on either the Os(2)–Os(5) edge or the Os(3)–Os(4) edge, and the second H atom is associated with either the Os(1)–Os(3)–Os(4) triangular face or the Os(2)–Os(3)–Os(4)–Os(5) square face. This assignment was based in part on the ^{13}C and ^1H NMR spectra of the compound, which indicated that the two H ligands are associated with the plane of symmetry of the molecule.

This was followed soon thereafter by a suggestion by Pauling,³ in one of his infrequent papers on metal cluster compounds, that the two hydride ligands are terminal, bonded to the atoms Os(3) and Os(4). Finally, in 1976, Orpen introduced a potential energy calculational method for predicting the positions of H atoms in clusters⁴ and applied it to $\text{H}_2\text{Os}_6(\text{CO})_{18}$ to predict that both H atoms should be edge-bridging, located on the Os(2)–Os(5) and Os(3)–Os(4) edges of the cluster. We consequently undertook a single-crystal neutron structure determination of $\text{H}_2\text{Os}_6(\text{CO})_{18}$ to settle this issue.

A sample of the title compound was prepared as reported¹ and recrystallized from CH_2Cl_2 to yield a crystal (volume 0.9 mm^3) used in the single-crystal neutron analysis. Data were collected at 20 K on the Instrument D19 at the Institut Laue-Langevin equipped with a Displex cryostat and a position-sensitive area detector.^{5a} The unit cell parameters (at 20 K) for $\text{H}_2\text{Os}_6(\text{CO})_{18} \cdot 0.5\text{CH}_2\text{Cl}_2$ are $a = 16.3535(6)$ Å, $b = 15.3170(6)$ Å, $c = 22.0871(8)$ Å, $\beta = 90.437(2)^\circ$, space group $P2_1/c$ (monoclinic). A total of 7561 reflections were collected and merged into 4415 independent reflections with positive F^2 values.^{5b} Phasing of the neutron data was carried out using the atomic coordinates of the non-hydrogen atoms obtained from

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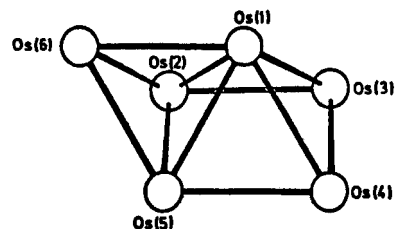


Figure 1. Os_6 skelton of $\text{H}_2\text{Os}_6(\text{CO})_{18}$, as determined from the earlier X-ray analysis (ref 2).

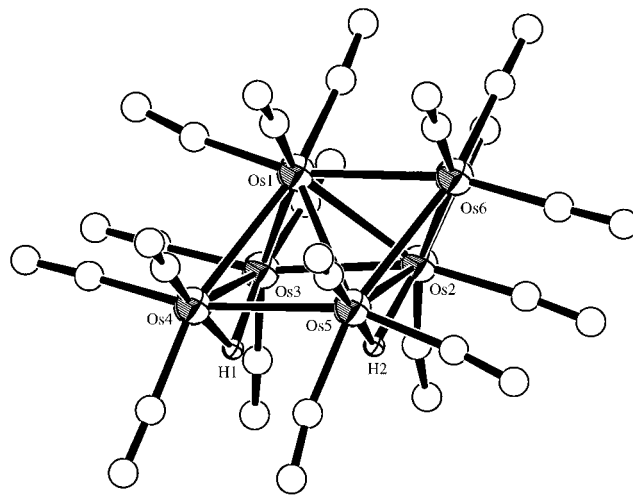


Figure 2. Molecular structure of $\text{H}_2\text{Os}_6(\text{CO})_{18}$, as determined by neutron diffraction.

Table 1. Selected Distances (Å) and Angles (deg) in $\text{H}_2\text{Os}_6(\text{CO})_{18}$

	molecule 1	molecule 2
Os(3)–H(1)	1.820(8)	1.796(8)
Os(4)–H(1)	1.798(8)	1.798(8)
Os(2)–H(2)	1.811(8)	1.816(8)
Os(5)–H(2)	1.803(8)	1.812(7)
Os(1)–Os(2)	2.797(3)	2.828(3)
Os(1)–Os(3)	2.881(3)	2.852(3)
Os(1)–Os(4)	2.841(3)	2.841(3)
Os(1)–Os(5)	2.830(3)	2.827(3)
Os(1)–Os(6)	2.882(3)	2.845(3)
Os(2)–Os(3)	2.869(3)	2.860(3)
Os(2)–Os(5)	2.901(3)	2.893(3)
Os(2)–Os(6)	2.801(3)	2.805(3)
Os(3)–Os(4)	2.970(3)	2.962(3)
Os(4)–Os(5)	2.859(3)	2.875(3)
Os(5)–Os(6)	2.781(3)	2.813(3)
Os(3)–H(1)–Os(4)	110.4(4)	111.0(4)
Os(2)–H(2)–Os(5)	106.7(4)	105.7(4)

the earlier X-ray analysis.² Exhaustive least-squares refinement of all the atomic coordinates resulted in final agreement factors of $R(F) = 4.5\%$ for the 4008 reflections with $F > 4\sigma(F)$, and $R(F) = 5.3\%$ for all 4415 reflections.

The structure of $\text{H}_2\text{Os}_6(\text{CO})_{18}$ is shown in Figure 2, and selected distances and angles are listed in Table 1. There are two independent molecules in the unit cell, which have essentially the same geometry, and one dichloromethane solvent molecule. The most significant result is that both H atoms are in edge-bridging positions, bridging the Os(2)–Os(5) and Os(3)–Os(4) edges, as predicted by Orpen.⁴ The average Os–H distance [1.807(4) Å] and the average Os–H–Os angle [108.4(4)°] are very close to standard values found in other neutron diffraction analyses of edge-bridging hydride ligands.⁶

An alternative view of the cluster is given in Figure 3, which shows that atom H(2) is coplanar with Os(2), Os(5), and four

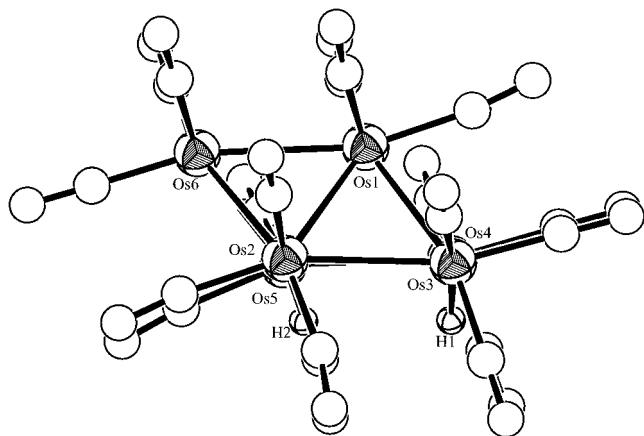


Figure 3. Alternative view of $\text{H}_2\text{Os}_6(\text{CO})_{18}$.

of their carbonyl ligands, while atom H(1) is also coplanar (but somewhat less so) with the two $\text{Os}(\text{CO})_2$ groups around Os(3) and Os(4). The pattern of basal Os–Os distances (Table 1) shows subtle but reproducible differences: of the two H-bridged edges, Os(3)–Os(4) [av 2.966(3) Å] is slightly longer than Os(2)–Os(5) [av 2.897(3) Å], while both are significantly longer than the unbridged edges Os(2)–Os(3) and Os(4)–Os(5) [av 2.866(3) Å]. The fact that Os(3)–Os(4) is longer than Os(2)–Os(5) may be due to the fact that the latter is further bridged by the face-capping Os(6) atom. Consequently, the Os(2)–H(2)–Os(5) angle [av 106.2(4)°] is correspondingly more acute than the Os(3)–H(1)–Os(4) angle [av 110.7(4)°].

An intriguing question to ask at this point is why the main square pyramidal cavity of the cluster is empty. There is certainly enough space there. A hypothetical H atom at the center of the Os(2)–Os(3)–Os(4)–Os(5) square would make an average Os–H distance of 2.05 Å with the four basal atoms, and an Os–H distance of 1.96 Å with the apical atom Os(1). Those are longer than the expected values of 1.814 Å for edge-bridging ($\mu^2\text{-H}$) and 1.889 Å for face-bridging ($\mu^3\text{-H}$) Os–H distances⁶ but are very close to the interstitial M–H distances found in clusters of the larger transition metals: H–Rh = 1.95(2) Å in $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$,⁷ and H–Ru = 2.037(4) Å in $[\text{HRu}_6(\text{CO})_{18}]^-$.⁸ [In contrast, the other interstitial site, in the center of the Os(1)–Os(2)–Os(5)–Os(6) cavity (a tetra-

hedral hole) is too small: a H atom located in that 4-coordinate site would make an Os–H bond length of 1.74 Å, too short a distance for an interstitial hydride.]

Empty octahedral cavities in osmium cluster hydrides are structural features that have been noticed before. Neutron diffraction studies on the isoelectronic but not isostructural $[\text{HOs}_6(\text{CO})_{18}]^-$ showed the lone H atom to be on the surface of the octahedron, in a face-bridging position.⁹ The structure of another osmium cluster, $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$, also analyzed by neutron diffraction,¹⁰ showed all four hydrogen atoms to be on the surface of the metal cluster (at edge-bridging and face-bridging sites), despite the fact that a central octahedral cavity was vacant in the middle of that decanuclear cluster.

We can think of two reasons why the square pyramidal cavity in $\text{H}_2\text{Os}_6(\text{CO})_{18}$ is vacant. One explanation is electronic: even though it is spatially feasible, perhaps it is electronically (energetically) unfavorable to place H atoms in the square pyramidal cavity of $\text{H}_2\text{Os}_6(\text{CO})_{18}$ or in the octahedral cavities of the other osmium clusters. But that does not explain why the H atom in $[\text{HRu}_6(\text{CO})_{18}]^-$ is interstitial,⁸ while that in the isoelectronic $[\text{HOs}_6(\text{CO})_{18}]^-$ is not.⁹ The second rationalization is steric: perhaps it is feasible for the first H atom in $\text{H}_2\text{Os}_6(\text{CO})_{18}$ to enter the square pyramidal cavity, but that would not leave enough space for the second hydrogen, which then presumably forces both H atoms to adopt edge-bridging positions. In that case, one can speculate that perhaps an *isomer* of $[\text{HOs}_6(\text{CO})_{18}]^-$ could exist: one that has the square pyramidal skeleton shown here, but with an interstitial H atom.

Thus, it appears that the factors that govern the filling of interstitial sites by hydrogen are not yet fully understood. Just because a cavity is empty does not necessarily mean that a H atom will automatically fill it.

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Supporting Information Available: Text describing the details of the neutron structural analysis and tables giving crystal data, atomic coordinates, and bond lengths and angles (9 pages). See any current masthead page for ordering and Internet access instructions.

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