

X-Ray Structures of the Hexanuclear Cluster Complexes [Os₆(CO)₁₈]²⁻, [HOs₆(CO)₁₈]⁻, and [H₂Os₆(CO)₁₈][†]

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Summary X-Ray analyses of three osmium cluster complexes has shown that two, [Os₆(CO)₁₈]²⁻ and [HOs₆(CO)₁₈]⁻, have the approximately regular octahedral structure expected for hexanuclear clusters with 86 valence electrons, but the third, [H₂Os₆(CO)₁₈], has an unusual monocapped square-pyramidal Os₆ arrangement.

WADE'S theory¹ applied to a transition metal M₆ cluster with 86 valence electrons predicts an octahedral metal arrangement with seven skeletal bonding electron pairs. The recently characterised² hexanuclear cluster complexes 2[Ph₃PMe]₂⁺[Os₆(CO)₁₈]²⁻ (I), [(Ph₃P)₂N]⁺[HOs₆(CO)₁₈]⁻ (II), and [H₂Os₆(CO)₁₈] (III) provide a unique opportunity for X-ray structural studies of a series of Os₆ clusters, with 86 valence electrons, which differ only in the charge and the number of H-ligands present.

TABLE. Crystal data for (I), (II), and (III).

Compound	(I)	(II)	(III)·0·5CH ₂ Cl ₂
Crystal class	Trigonal	Triclinic	Monoclinic
Space-group	<i>P</i> 3̄1 <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12·045	9·508	16·607
<i>b</i>	12·045	16·690	15·564
<i>c</i>	24·767	18·170	22·303
α(°)	(90)	97·83	(90)
β	(90)	97·80	90·97
γ	120	90·05	(90)
<i>Z</i>	2	2	8
No. of unique reflections	739	2928	3502
(<i>I</i>)/σ(<i>I</i>) ≥	3·0	3·0	2·5
Anisotropic	Os, P, CO	Os, P	Os
<i>R</i> -value	0·057	0·067	0·059

Data for the crystals are listed in the Table. The intensities were measured with very small crystals [maximum dimensions: (I), 0·08; (II), 0·1; and (III), 0·05 mm] using a Philips PW 1100 four-circle diffractometer and graphite single crystal monochromatised Mo-*K*_α radiation. Full-

matrix least-squares refinement was used, and the phenyl rings were treated as rigid groups (C-C, 1·395 Å).

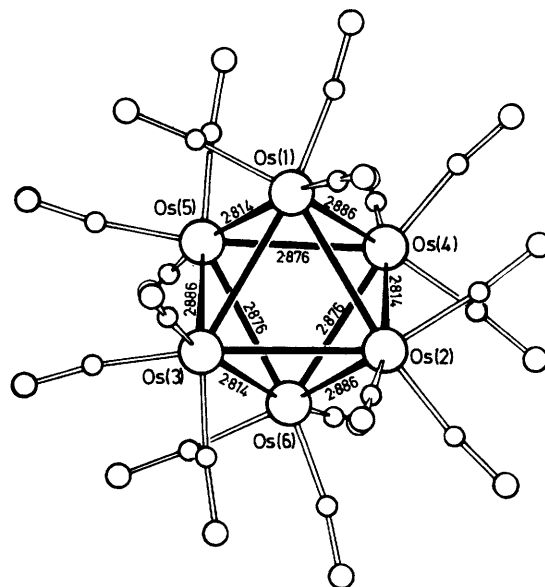


FIGURE 1. The structure of the [Os₆(CO)₁₈]²⁻ anion in (I) showing the Os-Os bond lengths (Å). E.s.d.'s average 0·004 Å. Average Os-C bond length 1·83(5) Å.

The structure of the [Os₆(CO)₁₈]²⁻ anion in (I) is shown in Figure 1. The anion has crystallographic *D*₃ symmetry but for clarity the related bonds and atoms are labelled separately. There are two equivalent parallel faces that are exactly equilateral (Os-Os, 2·876 Å). These are slightly twisted from *O*_h symmetry so that the remaining bonds alternate long (2·886 Å) and short (2·814 Å). Molecular orbital calculations³ using an idealised *O*_h geometry for [Co₆(CO)₁₄]⁴⁻ give a closed shell configuration for the

† No reprints available.

anion; more generally the stability of octahedral structures, for other M_6 clusters with 86 valence electrons, has been related to this.⁴ However, exact O_h symmetry for the metal atoms in such clusters is extremely rare, and $[\text{Os}_6(\text{CO})_{18}]^{2-}$ has D_3 not O_h symmetry of the Os_6 core. Possibly the presence of three terminal carbonyls per osmium atom, which prevents the anion as a whole having higher than D_3 symmetry (D_{3d} is ruled out by impossibly close O-O contacts) gives rise to metal-ligand interactions such that distortion of the Os_6 core from O_h to D_3 symmetry is necessary to produce a closed shell configuration for the ground state of this cluster. It should be noted however that even the $[\text{Co}_6(\text{CO})_{14}]^{4-}$ anion, geometrically capable of exact overall O_h symmetry, is found from X-ray studies to have significant differences in its Co-Co lengths and approximate D_{3d} symmetry.⁵

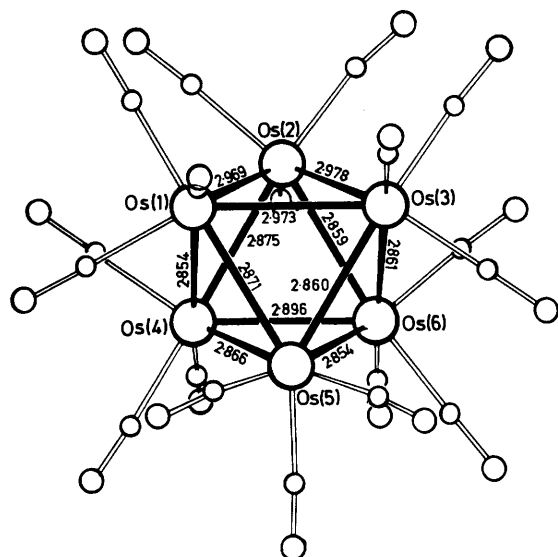


FIGURE 2. The structure of the $[\text{HOs}_6(\text{CO})_{18}]^-$ anion in (II) showing the Os-Os bond lengths (Å). E.s.d.'s average 0.003 Å. Average Os-C bond length 1.90(5) Å. The face-bridging hydrogen is above Os(1), Os(2) and Os(3).

The anion in (II), $[\text{HOs}_6(\text{CO})_{18}]^-$, has the octahedral structure shown in Figure 2. One triangular face, Os(1), Os(2), and Os(3), has significantly longer edges (mean Os-Os 2.973 Å) than any of the other Os-Os bonds (mean 2.863 Å) and the carbonyl ligands appear to be pushed back from this face. This is consistent with a face-bridging hydrogen bonded to Os(1), Os(2), and Os(3), as described previously.² Similar long edges, for two opposite triangular faces, in the octahedral cluster complex $[\text{H}_2\text{Ru}_6(\text{CO})_{18}]$ (IV) were attributed to the two face-bridging hydrogens.⁶

The structure of the neutral dihydride $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$ (III) is shown in Figure 3; the cluster has non-crystallographic C_s symmetry. Its ^1H n.m.r. spectrum (a doublet of doublets) ruled out the possibility of (III) having two symmetrical face-bridging hydrides as in $[\text{H}_2\text{Ru}_6(\text{CO})_{18}]$;⁶ a face and edge bridging hydride were tentatively suggested.²

The ^{13}C n.m.r. spectrum at low temperature is consistent (1:1:1:1:2:2:2:2:2:4, -85°C) with this solid state structure with the 2H ligands lying on the plane of symmetry in, according to the ^1H n.m.r. spectrum, dissimilar

environments. At high temperature, coalescence occurs to produce a spectrum composed of three signals (6:6:6, $+100^\circ\text{C}$), indicating that CO scrambling between Os(1) and Os(6) (or accidental degeneracy) is occurring. The positions of the hydride ligands are open to question. On the basis of ^{13}C - ^1H coupling and Os-Os bond lengths, one hydride ligand may be associated with an edge Os(2)-Os(5) or Os(3)-Os(4) and one with a triangular face Os(1)-Os(3)-Os(4) [edges 0.05 Å greater than the Os(2)-Os(5)-Os(6) face] or a square face Os(2)-Os(3)-Os(4)-Os(5). The distribution of the carbonyl ligands, which are arranged well clear of the base of the pyramid, indicates that the hydrogen ligands may be associated with this square face.

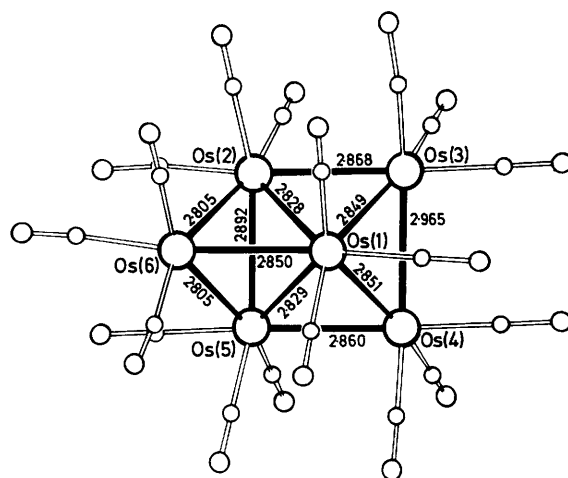


FIGURE 3. The mono-capped square-pyramidal structure of $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$ (III) showing the Os-Os bond lengths (Å). E.s.d.'s average 0.004 Å. Average Os-C bond length 1.89(6) Å.

Although, as for (I) and (II), an octahedral Os_6 arrangement was expected for this cluster, the observed mono-capped square-pyramidal structure may also be rationalised in terms of Wade's theory. All transition metal carbonyl cluster compounds with 86 valence electrons are assumed to have seven skeletal electron pairs. For hexanuclear clusters these may be exactly accommodated in a *closo*-octahedral metal arrangement, as in (I) and (II), whereas in M_7 clusters seven skeletal electron pairs are accommodated

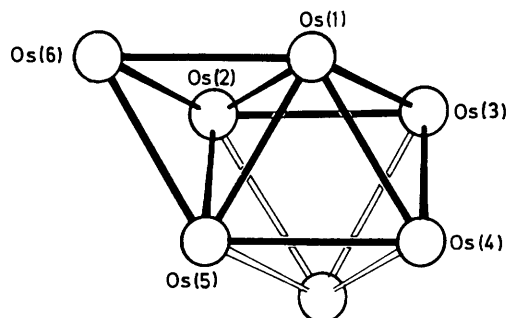


FIGURE 4. The mono-capped square-pyramidal metal arrangement in $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$ (dark bonds) related to the mono-capped octahedral structure of M_7 clusters (cf. ref. 1).

in a mono-capped octahedral arrangement.¹ It is fundamental to Wade's theory that *closo*- and *nido*-versions of the same polygon will accommodate the same number of

skeletal electron pairs. Therefore the mono-capped *nido*-octahedral (mono-capped square-pyramidal) structure of $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$ (Figure 4) is an alternative for the accommodation of seven skeletal electron pairs in an M_6 cluster. The mono-capped square-pyramidal arrangement rather than the octahedral may occur because of a preference of bridging hydrides for sites of lowest co-ordination as observed in borohydride chemistry.⁷

Clearly, this work shows that the structure of a cluster depends not only on the number of skeletal electron pairs available but also on the number and type of ligands present, *e.g.* $[\text{Os}_6(\text{CO})_{18}]^{2-}$, $[\text{HOs}_6(\text{CO})_{18}]^-$, and $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$. Furthermore, it demonstrates that the metal must play a critical role in determining the stereochemistry, as the ruthenium and osmium clusters, $[\text{H}_2M_6(\text{CO})_{18}]$, possess

different geometries; this relates to similar observations on the structures of the 86 valence electron complexes, $[\text{M}_3(\text{CO})_6]_2^{2-}$ ($M = \text{Ni}$ or Pt).⁸

It is interesting to note that the two alternative structures, *e.g.* as with $[\text{Os}_6(\text{CO})_{18}]^{2-}$ and $[\text{H}_2\text{Os}_6(\text{CO})_{18}]$, may be derived from $[\text{Os}_6(\text{CO})_{18}]$ by breaking and where appropriate reforming suitable Os–Os bonds within the bicapped tetrahedral structure.

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