

Synthesis and X-Ray Crystal Structure Analysis of the Largest Binary Osmium Carbonyl Cluster: $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$

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The largest binary carbonyl cluster dianion so far observed in the iron triad, $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ (**1**), has been obtained from the vacuum pyrolysis of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$.

It has been shown previously that high nuclearity carbonyl clusters of metals in the iron triad can be built up by combination of reactive fragments thermally generated from appropriate low nuclearity precursors;¹⁻³ however, until now the largest structurally characterised cluster isolated from

pyrolyses has been $[\text{Os}_{11}\text{C}(\text{CO})_{27}]^{2-}$ generated in very low yields from $\text{Os}_3(\text{CO})_{12}$ or $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$.⁴

The isolation of new larger osmium clusters has been achieved by a systematic investigation of the high nuclearity fractions generated by vacuum pyrolysis of $\text{Os}_3(\text{CO})_{10}$ -

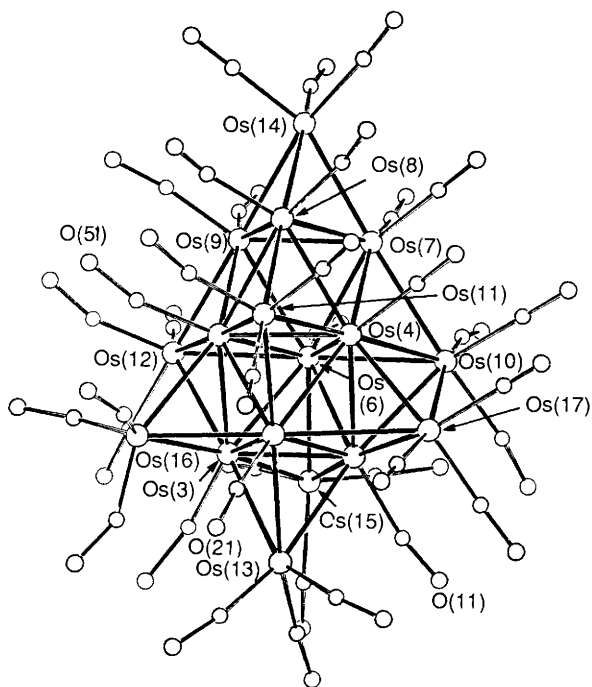


Figure 1. Molecular structure of the dication $[\text{Os}_{17}(\text{CO})_{36}]^{2+}$ (1). Principal bond distances are (Å) (max. e.s.d. 0.006 Å): Os(1)–Os(2) 2.574, Os(1)–Os(3) 2.588, Os(1)–Os(4) 2.740, Os(1)–Os(6) 2.594, Os(1)–Os(10) 2.770, Os(1)–Os(13) 2.764, Os(1)–Os(15) 2.761, Os(1)–Os(17) 2.675, Os(2)–Os(3) 2.601, Os(2)–Os(4) 2.665, Os(2)–Os(5) 2.635, Os(2)–Os(11) 2.788, Os(2)–Os(13) 2.773, Os(2)–Os(16) 2.797, Os(2)–Os(17) 3.154, Os(3)–Os(5) 2.670, Os(3)–Os(6) 2.712, Os(3)–Os(12) 2.762, Os(3)–Os(13) 2.793, Os(3)–Os(15) 2.740, Os(3)–Os(16) 2.720, Os(4)–Os(5) 2.714, Os(4)–Os(6) 2.724, Os(4)–Os(7) 2.735, Os(4)–Os(8) 2.734, Os(4)–Os(10) 2.730, Os(4)–Os(11) 2.757, Os(4)–Os(17) 2.673, Os(5)–Os(6) 2.767, Os(5)–Os(8) 2.767, Os(5)–Os(9) 2.758, Os(5)–Os(11) 2.791, Os(5)–Os(12) 2.797, Os(5)–Os(16) 2.767, Os(6)–Os(7) 2.735, Os(6)–Os(9) 2.780, Os(6)–Os(10) 2.868, Os(6)–Os(12) 2.809, Os(6)–Os(15) 2.772, Os(7)–Os(8) 2.770, Os(7)–Os(9) 2.732, Os(7)–Os(10) 2.849, Os(7)–Os(14) 2.792, Os(8)–Os(9) 2.724, Os(8)–Os(11) 2.799, Os(14)–Os(8) 2.792, Os(9)–Os(12) 2.758, Os(9)–Os(14) 2.791, Os(10)–Os(17) 3.142.

(NCMe)₂ at temperatures between 260 and 275 °C and initial pressures of 10^{-3} – 10^{-4} Torr (1 Torr = 133.322 Pa). The first of these species to be structurally characterised is the dark brown dianionic cluster, $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ (1),[†] which is generated under these conditions in up to 10% yield. The compound has similar chromatographic properties to the known decaosmium species $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ (2), but may be separated from the latter by repeated TLC on silica (eluent: acetone/hexane: 60/40; R_f 0.6). The stoichiometry of (1) was initially deduced from FAB MS,[†] and has been confirmed by full X-ray structure analysis of the $[\text{Ph}_4\text{As}]^+$ -salt.[‡]

[†] Spectroscopic data for (1): IR (CH₂Cl₂) 2086 (vw), 2060 (s), 2044 (vs), 2040 (vs), 2028 (m), 2000 (m), 1987 (m), 1969 (w); negative ion FAB mass spectrum, most abundant isotopomer for $[\text{Os}_{17}(\text{CO})_{36}]^{2-}$ dianion 2121 amu (simulated: 2122), m/z monoanion: 4243 amu (simulated: 4244); ¹H NMR (CD₂Cl₂) δ 7.9–7.5 (m, Ph₄As⁺); ¹³C NMR (CD₂Cl₂) δ 196.8 (6 CO), 195.1 (3 CO), 192.6 (3 CO), 187.2 (9 CO), 179.9 (9 CO), 173.4 (3 CO), 166.5 (3 CO).

[‡] Crystal data for $[\text{Os}_{17}(\text{CO})_{36}][\text{AsPh}_4]_2(0.5\text{CH}_2\text{Cl}_2)$ (1): $[(\text{C}_{84}\text{H}_{40}\text{As}_2\text{O}_{36}\text{Os}_{17})(0.5\text{CH}_2\text{Cl}_2)]$, triclinic, space group *P*1 (No. 2), $a = 14.836(3)$, $b = 27.636(6)$, $c = 12.468(2)$ Å, $\alpha = 97.49(2)$, $\beta = 96.51(2)$, $\gamma = 100.11(2)^\circ$, $M = 5050.93$, $U = 4940.80$ Å³, $Z = 2$, $D_c = 3.395$ g cm⁻³, $F(000) = 4422$, $R = 0.0831$ for 6303 reflections with $I/\sigma(I) > 3.0$ corrected for absorption [$\mu(\text{Mo-K}\alpha) = 225.6$ cm⁻¹]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

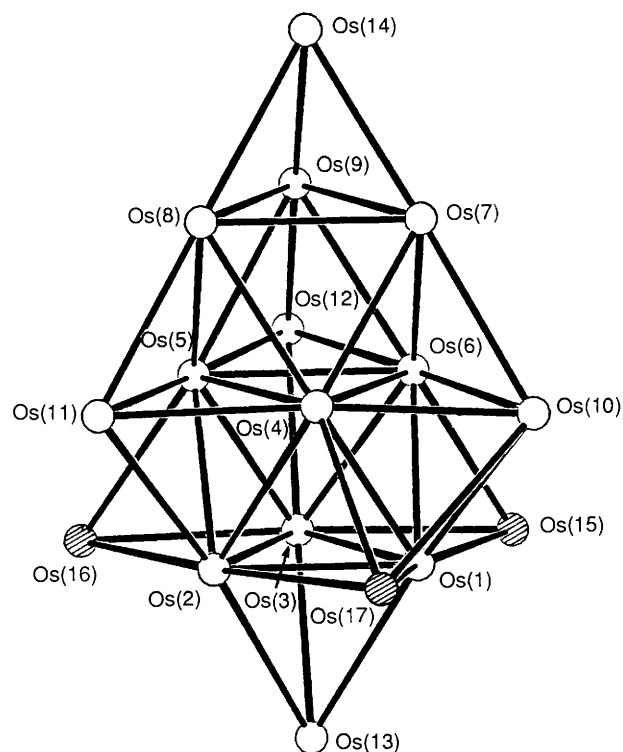


Figure 2. The tricapped trigonal bipyramidal Os_{17} framework in (1). The third cap, Os(17), is asymmetric and bonds to four metal atoms.

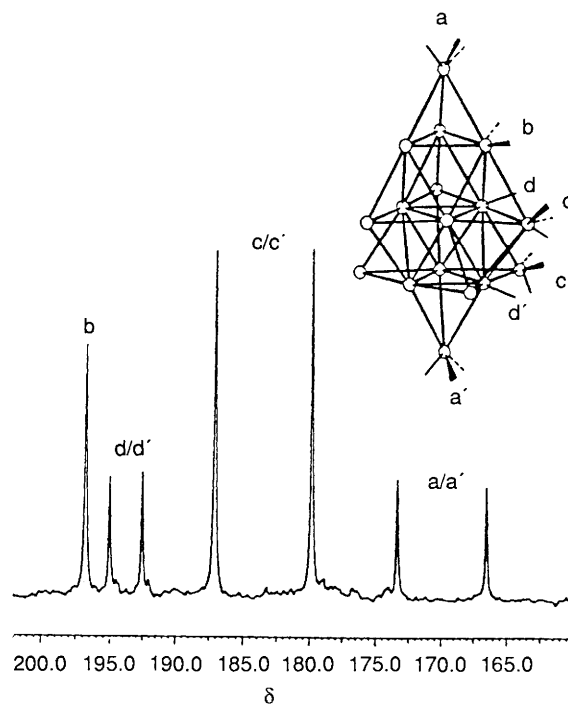


Figure 3. ¹³C NMR spectrum of $[\text{Ph}_4\text{As}]_2[\text{Os}_{17}(\text{CO})_{36}]$ (CD₂Cl₂, 300 K). The partial assignment of the signals is based on their relative intensities and the observation that for high nuclearity Os-clusters the resonances of vertex $\text{Os}(\text{CO})_3$ -carbonyls appear high field relative to those attached to Os-atoms with a higher metal–metal connectivity.

The structure of the cluster (Figures 1 and 2) contains a close packed metal core of 16 Os-atoms and a slightly displaced seventeenth metal atom which breaks the otherwise three-fold symmetry of the system. The stacking sequences of

both cubic and hexagonal close packed metal lattices are combined to give an overall ABCBA-stacking, in contrast to the hexagonal close packed bulk metal. The structure may be described as two face sharing tetrahedra (a trigonal bipyramid) of fourteen Os-atoms with three metal atoms capping the central Os₃-triangles of the faces of one tetrahedron. One cap is distorted to form an extra bond to one of the vertices of the giant trigonal bipyramid. This results in two extremely long Os–Os bonds [Os(17)–Os(2) 3.156(6) and Os(17)–Os(10) 3.142(4) Å].

In contrast to the asymmetry of the solid state structure the ¹³C NMR spectrum of the cluster (50% ¹³C-enriched) recorded at 300 K displays full C_{3v} symmetry (Figure 3). This implies that on the NMR time scale there is no unique distorted cap in the species in solution.

That the metal core does not contain interstitial atoms (as established by ¹H and ¹³C NMR spectroscopy) is unexpected since they are present in all other high nuclearity clusters of this triad and appeared to play an important role in reducing surface ligand overcrowding.⁵ If one assumes an electron count of 122 for the two face sharing octahedra at the centre of the metal core and takes the additional metal–metal bond of the distorted cap into account, the overall electron count of

210 is in agreement with the polyhedral skeletal electron pair theory for condensed polyhedra.⁶

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