Synthesis and Molecular Structure of $[(Ph_3P)_2N]_2[Os_8(CO)_{22}]$

By Peter F. Jackson, Brian F. G. Johnson, Jack Lewis,* and Paul R. Raithby
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary Reaction of iodide with $[Os_8(CO)_{23}]$ in tetrahydrofuran yields a dark red solid which has been shown by a crystal structure analysis to be $[(Ph_3P)_2N]_2[Os_8(CO)_{22}]$, with the Os atoms in the dianion defining a bicapped octahedron.

The formation of larger metallic carbonyl clusters from smaller units has excited interest both theoretically[1] and with regard to catalytic activity.[2] Carbonyl clusters containing up to 17 rhodium atoms are known,[3] and in the larger units the arrangement of metal atoms is similar to that in the bulk metal.[4] In the case of osmium the largest cluster characterised crystallographically is $[Os_7(CO)_{21}]$,[5] although $[Os_8(CO)_{23}]$ and $[Os_8(CO)_{21}C]$ have been identified by spectroscopic techniques as products of the pyrolysis of $[Os_3(CO)_{12}]$.[6] We report here the synthesis and the first *X*-ray characterisation of an Os_8 cluster anion, $[Os_8(CO)_{22}]^-$.

The reaction of iodide in methanol with $[Os_8(CO)_{23}]$ in tetrahydrofuran yields a dark red crystalline solid which exhibits i.r. vibrational frequencies at 2070w, 2036s, 2014s, 2006vs, 1980s, 1968sh, 1943w, 1763vw, and 1720w. To establish the detailed molecular geometry of the complex, a single-crystal *X*-ray analysis was undertaken. Upon addition of $[(Ph_3P)_2N]Cl$ to the solution dark red, elongated rectangular blocks were obtained by recrystallisation from CH_2Cl_2–MeOH.

Crystal data: $[C_{36}H_{30}NP_2]_2[C_{22}O_{22}Os_8]$, $M = 3214{\cdot}9$, monoclinic, $a = 11{\cdot}477(2)$, $b = 25{\cdot}359(5)$, $c = 33{\cdot}826(6)$ Å, $\beta = 106{\cdot}94(1)°$, $U = 9417{\cdot}7$ Å^3, $Z = 4$, $D_c = 2{\cdot}27$ g cm^{-3}; $\mu(\text{Mo-}K_\alpha) = 108{\cdot}64$ cm^{-1}, space group $C2/c$. 9 877 intensities ($3{\cdot}0 < 2\theta < 45{\cdot}0°$) were recorded on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromated Mo-K_α radiation and the ω–2θ scan technique. The data were corrected for absorption and Lorentz polarisation factors, and averaged to give 5 483 unique observed intensities $[F > 5\sigma(F)]$. The five unique Os atoms were located by multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms from subsequent electron density difference syntheses. The structure was refined by blocked cascade least-squares. The Os and P atoms were assigned anisotropic thermal parameters; the phenyl rings were refined as rigid groups with hydrogens placed in idealised positions (C–H, 1·08 Å; C–C–H, 120·0°), and assigned a common isotropic temperature factor. The weighting scheme $w = [\sigma^2(F) + 0{\cdot}00016\,F^2]^{-1}$ was employed. The current residuals are $R = 0{\cdot}053$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0{\cdot}050$.†

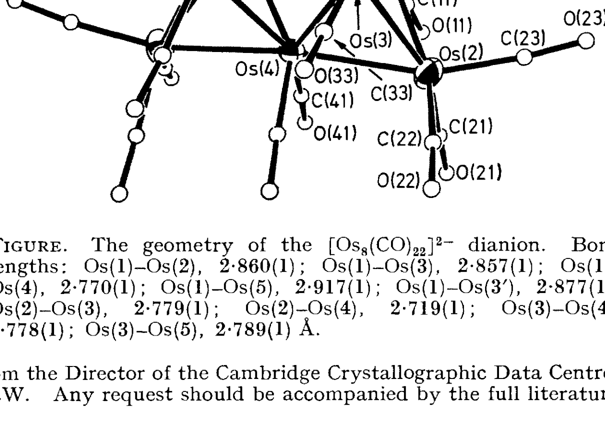

Figure. The geometry of the $[Os_8(CO)_{22}]^{2-}$ dianion. Bond lengths: Os(1)–Os(2), 2·860(1); Os(1)–Os(3), 2·857(1); Os(1)–Os(4), 2·770(1); Os(1)–Os(5), 2·917(1); Os(1)–Os(3′), 2·877(1); Os(2)–Os(3), 2·779(1); Os(2)–Os(4), 2·719(1); Os(3)–Os(4), 2·778(1); Os(3)–Os(5), 2·789(1) Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecular structure of the dianion is shown in the Figure which includes some important bond parameters. The eight Os atoms define a bicapped octahedron with a crystallographic C_2 axis passing through Os(4) and Os(5). The capping metal atoms both lie in the same half of the octahedron but over opposite faces. Two carbonyls symmetrically bridge opposite Os–Os edges of the other half of the octahedron to that bridged by the capping $Os(CO)_3$ units. A bridging carbonyl group has not been previously observed in the structures of higher osmium clusters. The remaining carbonyl ligands are linear and terminal.

The six metal atoms in the octahedron are eight co-ordinate and the capping Os atoms are six co-ordinate. The 'formal oxidation state' of atom Os(1) is $+1$, that of Os(3), Os(4), and Os(5) is **0**, and that of Os(2) is -1. In terms of overall electron counting $[Os_8(CO)_{22}]^{2-}$ is a 110-electron system, and the observed structure is in agreement with that proposed by Wade's skeletal electron counting scheme when extended to include clusters which have *n* metal atoms and *n* or $(n - 1)$ skeletal electron pairs.[6] In this case the number of skeletal electron pairs, *S*, is given by equation (1). This gives a regular octahedral

$$S = \tfrac{1}{2}\{110(\text{total valence electrons}) - |12 \times 8(\text{number of metal atoms})|\} = 7 \quad (1)$$

geometry, but with $(n - 1)$ electron pairs the polyhedron is bicapped.

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