$[Os_5(CO)_{16}]$: *X*-Ray Crystal and Molecular Structure†

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Summary A single crystal *X*-ray diffraction study on $[Os_5(CO)_{16}]$ reveals a trigonal bipyramidal (D_{3h}) metal unit which is slightly distorted towards a capped butterfly arrangement (C_{2v}).

The pink-red pentanuclear cluster $[Os_5(CO)_{16}]$ was first discovered by us as a product of the pyrolysis of $[Os_3(CO)_{12}]$ in small amounts (*ca.* 7%) using extensive t.l.c.[1] The molecular formula $[Os_5(CO)_{16}]$, like those of $[Os_6(CO)_{18}]$ and $[Os_7(CO)_{21}]$,[1,2] was primarily deduced on the basis of mass spectrometry. We report here an *X*-ray structure determination of $[Os_5(CO)_{16}]$ which supports our initial view that the carbonyl groups are in an unusual arrangement around a distorted trigonal bipyramid of metal atoms.

Crystal data: $C_{16}O_{16}Os_5$, *M* 1399·2, trigonal, space group $P3_121$, $a = b = 9{\cdot}204(2)$, $c = 24{\cdot}818(4)$ Å, $Z = 3$, $D_c = 3{\cdot}83$ g cm^{-3}. Data were collected on an automated Stoe two-circle diffractometer using graphite monochromated

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† Reprints not available.

Mo-K_α radiation, and corrected for absorption. The structure was solved by multisolution tangent refinement and difference electron density syntheses. Refinement with anisotropic osmium and isotropic light atoms converged to an R of 0·039 from 809 independent reflections. Constraining the C–O distances to be equal led to a virtually identical final R and molecular parameters, but refinement of the enantiomorphous structure in the space group $P3_221$ led to R *ca.* 0·003 higher.

The molecule possesses a crystallographic two-fold axis with the 8-co-ordinate osmium atom (Os-1) on this axis attached to four terminal carbonyl groups, whilst the remaining osmium atoms are each bonded to three terminal carbonyls. The structure is shown in the Figure. The bonds to Os-1 are appreciably longer than the other Os–Os bonds. The Os–C and C–O bond lengths are all essentially equal with mean values of 1·86(5) and 1·17(5) Å respectively. There is evidence of weak interactions between two of the carbon atoms and non-bonded osmium atoms [C-7 · · · Os-3 2·89(5) and C-8 · · · Os-2 2·68(4) Å, Os-2–C-7–O-7 168(5) and Os-1–C-8–O-8 168(3)°], but the remaining Os–C–O units are linear within experimental error.

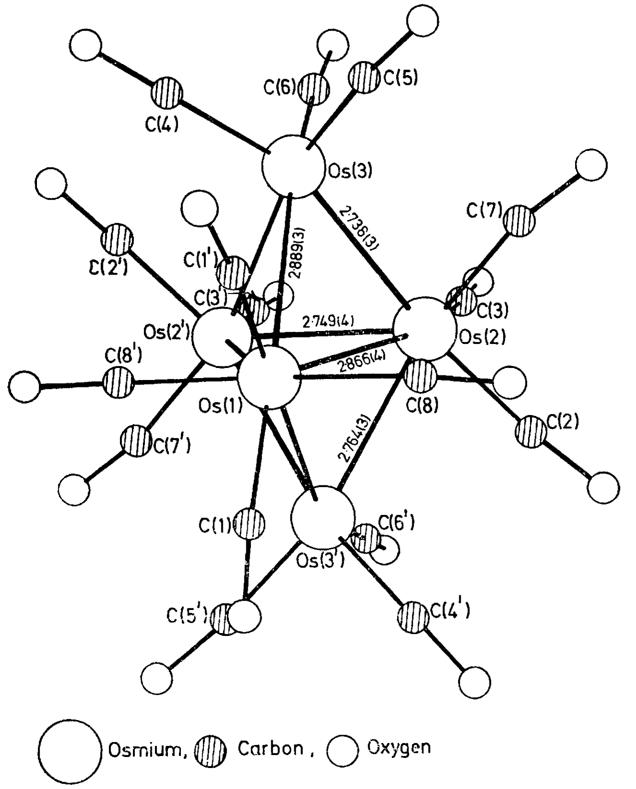

FIGURE. The structure of $[Os_5(CO)_{16}]$.

Five-metal-atom clusters are rare and those characterized include $[M_5(CO)_{15}C]$ (M = Fe, Ru, or Os) (square-based pyramid),[3] $[Ni_5(CO)_{12}]^{2-}$ (distorted trigonal bipyramid),[4] and $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, or W) (distorted trigonal bipyramid).[5] The arrangement of the Os_5 unit according to most theories should be a trigonal bipyramid.[1] The lengthening of the metal bonds associated with Os-1 towards a capped butterfly arrangement of metal atoms may reflect the difference in electron density associated with the $[Os(CO)_4]$ and $[Os(CO)_3]$ groups. Alternatively, $[Os_5(CO)_{16}]$ may be considered in the light of arguments recently proposed[6] which suggest that the polyhedron described by the CO groups is of importance in any discussion of structure. The X-ray structure establishes a close-packed arrangement of the CO groups in one of the standard triangulated polyhedra.[7] Thus the arrangement of CO groups around the five osmium atoms is merely a reflection of the preferred interstitial packing of these five atoms within the 16 CO polyhedron.[7] The more intimate packing of an osmium atom with four rather than three CO groups consequently leads to a lengthening of metal bonds associated with this atom.

A structural transformation[8] occurs on converting $[Os_6(CO)_{18}]$ into $[H_2Os_6(CO)_{18}]$ and according to Wade's theory we predict an analogous change in metal atom arrangement on going from $[Os_5(CO)_{16}]$ to $[H_2Os_5(CO)_{16}]$. A single crystal X-ray diffraction study on this latter cluster is in progress.

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[1] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **37**, C39; *J.C.S. Dalton*, 1975, 2606.
[2] R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.
[3] C. R. Eady, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organometallic Chem.*, 1973, **57**, C82.
[4] G. Longoni, P. Chini, L. D. Lower, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 5034.
[5] J. K. Ruff, R. P. White, Jr., and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 2159.
[6] B. F. G. Johnson, *J.C.S. Chem. Comm.*, 1976, 211.
[7] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 3rd Edn., 1962, p. 1003.
[8] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, accepted for publication.

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