The Structure of $[Os_7(CO)_{21}]$; *X*-Ray and ^{13}C Nuclear Magnetic Resonance Analyses†

By Colin R. Eady, Brian F. G. Johnson, and Jack Lewis*
(*The University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)
and Ronald Mason,* Peter B. Hitchcock, and K. Mark Thomas
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary The heptaosmium carbonyl, $[Os_7(CO)_{21}]$, has been fully characterised in the solid state by single crystal *X*-ray analysis; the structure in solution has also been established by ^{13}C n.m.r. spectroscopy.

The orange-brown binary carbonyl $[Os_7(CO)_{21}]$, which was isolated as one of several products of the pyrolysis of $[Os_3(CO)_{12}]$ in a sealed tube,[1] has now been fully characterised by single-crystal *X*-ray analysis and ^{13}C n.m.r. spectroscopy.‡

The complex $[Os_7(CO)_{21}]$ crystallises from toluene, in the monoclinic space group $P2_1$, with $a = 14{\cdot}301(2)$, $b = 9{\cdot}774(2)$, $c = 11{\cdot}056(2)$ Å, $\beta = 91{\cdot}45(2)°$, $Z = 2$. Of a total of 2661 integrated *X*-ray reflexion intensities measured by automatic diffractometry (Mo-K_α), 1801 reflexions only with $I > 3\sigma(I)$ were used in the structural analysis. The crystal was an irregularly shaped lump and with μ, the linear absorption coefficient, equalling 306 cm^{-1}, much difficulty was experienced in applying an accurate absorption correction and, as a consequence, in locating the carbonyl ligands with fair precision. Osmium atomic positions were located from an unsharpened Patterson synthesis, and the unequivocal positioning of the carbonyl groups was established by repeated difference Fourier analysis; a least-squares refinement with Os–C and C–O bond lengths constrained to 1·89 and 1·15 Å, respectively, and anisotropic (Os) and isotropic (C and O) thermal parameters has converged to $R_1 = 0{\cdot}089$ and $R_2 = 0{\cdot}093$. The diffraction data have remaining systematic errors and the average e.s.d. of 0·006 Å in the Os–Os bond lengths (Figure) is nominal and undoubtedly a serious underestimate.

The osmium atoms are arranged with a fairly regular capped octahedral geometry; Os(1) · · · · Os(6) form an octahedron with a mean osmium–osmium bond length of 2·855 Å. The capping atom, Os(7), forms metal–metal bonds of average length 2·819 Å. At face value, there is a significant difference between these mean distances, as indeed there is between the mean distance (2·902 Å) within the 'non-capped' base of the octahedron [Os(1), Os(2), and Os(3)] and the remainder. However, the experimental uncertainties are too great to develop a detailed bonding scheme.

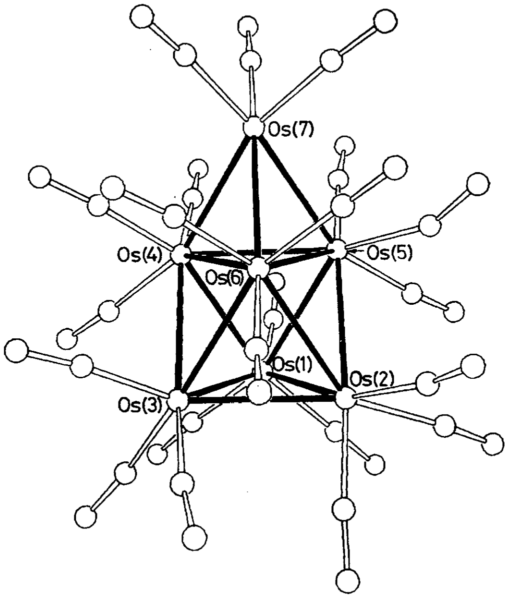

Figure. The molecular structure of $[Os_7(CO)_{21}]$. The bond lengths within the metal polyhedron are: Os(1)–Os(2), 2·880; Os(1)–Os(3), 2·935; Os(1)–Os(4), 2·849; Os(1)–Os(5), 2·849; Os(2)–Os(3), 2·892; Os(2)–Os(5), 2·876; Os(2)–Os(6), 2·876; Os(3)–Os(4), 2·854; Os(3)–Os(6), 2·839; Os(4)–Os(5), 2·834; Os(4)–Os(6), 2·824; Os(4)–Os(7), 2·806; Os(5)–Os(6), 2·848; Os(5)–Os(7), 2·830; Os(6)–Os(7), 2·821; average e.s.d. 0·006 Å.

As in $[Os_6(CO)_{18}]$,[2] the carbonyl ligands are all terminally bonded. Their arrangement, relative to one another within the octahedral fragment, is remarkably similar to that in $[H_2Ru_6(CO)_{18}]$[3] but is in obvious contrast to the ligand polyhedral arrangement in $[Os_6(CO)_{18}]$ where the

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† No reprints available.

‡ 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.

metal polyhedron is of bicapped tetrahedral symmetry. There are simple rules[4] for rationalising the geometries of the metal polyhedra in these cluster complexes but we can also note that ligand–ligand interactions stabilise, by *ca.* 23 kJ mol^{-1}, the observed structure of [$Os_6(CO)_{18}$], *vis à vis* the arrangement in the [$Os_6(CO)_{18}$] fragment of [$Os_7(CO)_{21}$]; equally, a tricapped tetrahedral metal polyhedron for [$Os_7(CO)_{21}$], with terminal carbonyl ligands is destabilised, by ligand–ligand interactions alone, relative to the observed monocapped octahedral arrangement.

^{13}C N.m.r. studies of [^{13}C]-isotopically enriched [$Os_7(CO)_{21}$] (^{13}CO, *ca.* 40%) clearly indicate that the monocapped octahedral arrangement [idealised (C_{3v} symmetry)] observed for the seven osmium atoms in the solid persists in solution. The same spectrum is observed at 90 and 0 °C; three resonances are observed in the intensity ratio 3:3:1 corresponding to the carbonyl groups associated with the three different types of osmium atoms observed in the mono-capped octahedral arrangement. This spectrum is related to that of [$HOs_6(CO)_{18}$]$^-$ [5] at low temperature (−112 °C) which also possesses idealised C_{3v} symmetry and may be viewed as [$Os_7(CO)_{21}$] with the $Os(CO)_3$ cap replaced by the hydrido-ligand. The spectrum of [$Os_7(CO)_{21}$] remains unchanged throughout the temperature range from *ca.* 90 to 0 °C and only at −110 °C do the CO groups associated with the triangular planes Os(1)–Os(2)–Os(3) and Os(4)–Os(5)–Os(6) show evidence of static behaviour. It is noteworthy that [$HOs_6(CO)_{18}$]$^-$ exhibits a similar low barrier to fluxionality.

The complex [$Os_7(CO)_{21}$] possesses the same number of valence electrons as [$Rh_7(CO)_{16}$]$^{3-}$ [6] and the metal polyhedra are similar. These clusters have seven electron pairs according to the Wade description and utilising the previously reported[2b] extension of Wade's theory to account for cases $s = n$ and $s = (n - 1)$, a mono-capped octahedron is the predicted geometry.

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