Synthesis, Characterisation, and Molecular Structure of the Cluster Anion $[HOs_4(CO)_{13}]^-$

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Summary Reaction of $[HOs_3(CO)_{11}]^-$ with $[Fe_2(CO)_9]$ in refluxing tetrahydrofuran leads to the isolation of $[HOs_4(CO)_{13}]^-$, which has been shown by spectroscopic and *X*-ray crystallographic techniques to contain an Os_4 tetrahedron, one edge of which is bridged by a CO ligand.

The anion $[HFe_4(CO)_{13}]^{-1}$ is of special interest because of the unusual bonding mode shown by one of the thirteen carbonyl groups. This unique CO ligand bonds through both the C and O atoms thereby donating four electrons to the Fe_4 cluster unit and, in effect, spans three Fe atoms. The Fe_4 cluster is also unusual in that it forms a butterfly rather than the anticipated tetrahedral arrangement. The view is held that these two phenomena, one being the result of the other, are a consequence of the steric requirements imposed by the fourteen ligands. We now report the synthesis, and complete characterisation, of the related osmium anion $[HOs_4(CO)_{13}]^-$ which, although possessing a different structure to that of its Fe analogue, exhibits structural characteristics in keeping with our view of steric crowding by CO ligands.

The salt $[PPN][HOs_4(CO)_{13}]$ $[PPN = (Ph_3P)_2N]$ has been prepared as one of the products of pyrolysis of $[PPN][HOs_3(CO)_{11}]$ (refluxing tetrahydrofuran, 18 h; refluxing dioxan, 4 h) and as the major product from the reaction of $[PPN][HOs_3(CO)_{11}]$ with $Fe_2(CO)_9$ in tetrahydrofuran [reaction (1)]. Yields by the latter route (*ca.* 26%) are much better than from the simple pyrolysis reaction (*ca.* < 5%).

$$[PPN][HOs_3(CO)_{11}] \xrightarrow[\text{refluxing THF}]{Fe_2(CO)_9} [PPN][HOs_4(CO)_{13}] + [PPN][HFeOs_3(CO)_{13}] \qquad (1)$$

The salt $[PPN][HOs_4(CO)_{13}]$ was obtained as dark red crystals which are air stable. The i.r. spectrum (CH_2Cl_2) has seven bands in the ν(CO) region, six of which may be assigned to terminally bound CO (2066m, 2026s, 2012s, 1999s, 1966m, and 1933sh cm^{-1}), and the seventh (1799br) to a bridging CO. The single high-field resonance at τ 30·1 in the ^1H n.m.r. spectrum is ascribed to a bridging hydride.

Crystal data: $[C_{36}H_{30}NP_2][C_{13}HO_{13}Os_4]$, $M = 1\,664{\cdot}5$, triclinic, $P\bar{1}$, $a = 9{\cdot}251(3)$, $b = 15{\cdot}392(6)$, $c = 19{\cdot}073(7)$ Å, $\alpha = 107{\cdot}98(3)$, $\beta = 100{\cdot}78(3)$, $\gamma = 93{\cdot}95(3)°$, $U = 2\,514{\cdot}2$ Å^3, $Z = 2$, $D_c = 2{\cdot}20$ g cm^{-3}; μ(Mo-K_α) $= 101{\cdot}78$ cm^{-1}. 4 394 intensities ($3{\cdot}0° < 2\theta < 45{\cdot}0°$) were measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K_α radiation. The data were corrected for absorption and Lorentz polarisation factors, and merged to give 3 483 unique observed intensities $[F > 3\sigma(F)]$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least-squares (Os, P, and N anisotropic); the phenyl rings were refined as rigid groups with H atoms placed in idealised positions (C–H, 1·08 Å, C–C–H, 120·0°), and assigned a common isotropic temperature factor. The residuals are $R = 0{\cdot}045$ and $R' = [\Sigma\omega^{\frac{1}{2}}\Delta/\Sigma\omega^{\frac{1}{2}}|F_0|] = 0{\cdot}048$ †

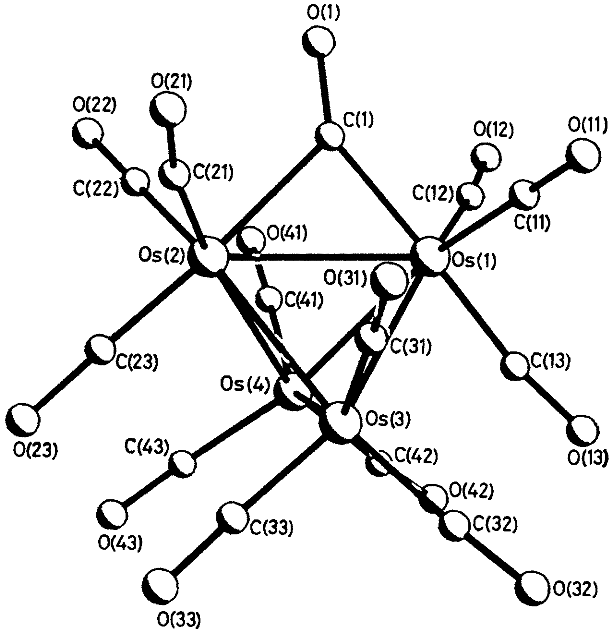

FIGURE 1. The molecular structure of the $[HOs_4(CO)_{13}]^-$ anion, including the atom numbering scheme. Bond lengths Os(1)–Os(2), 2·852(2), Os(1)–Os(3) 2·817(2), Os(1)–Os(4), 2·807(2), Os(2)–Os(3), 2·773(2), Os(2)–Os(4), 2·774(2), Os(3)–Os(4), 2·952(2), Os(1)–C(1), 2·00(3), Os(2)–C(1), 2·22(3) Å, bond angle Os(1)–C(1)–Os(2), 84·8(11)°.

It seems, from a comparison of the structure of $[HOs_4(CO)_{13}]^-$ with that of $[HFe_4(CO)_{13}]^-$,[1] that the increase in metal–metal bond length of *ca.* 0·2 Å, together with that of the metal–carbon bonds of *ca.* 0·09 Å, in going from Fe to Os, sufficiently reduces the steric crowding of fourteen ligands around the metal core to negate the need for the cluster to open to accommodate them (Figure 2). In $[HOs_4(CO)_{13}]^-$ there is enough space for the thirteenth CO group to sit over the Os(1)–Os(2) edge and bridge it in a conventional μ_2-mode. It is of interest, with regard to the bridging carbonyl, that there is only one previous example of a crystallographically characterised μ_2-CO in osmium clusters containing more than three metal atoms, $[Os_8(CO)_{22}]^{2-}$.[2]

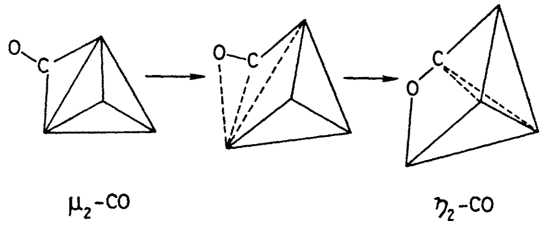

FIGURE 2. Transformation of the $[HOs_4(CO)_{13}]^-$ geometry into that of $[HFe_4(CO)_{13}]^-$ by stretching the carbonyl bridged metal–metal bond.

The chemistry of $[HOs_4(CO)_{13}]^-$ is under investigation. Unlike $[HFe_4(CO)_{13}]^-$, which reacts with $[Me_3O][BF_4]$ to produce $[HFe_4(CO)_{12}COMe]$ by electrophilic attack of Me^+ at the oxygen of the four-electron-donating carbonyl group,[3] no reaction is observed with the osmium anion under the same conditions. This emphasises the different chemical behaviour of the η_2- and μ_2-carbonyl links.

The related heteronuclear systems $[HFeOs_3(CO)_{13}]^-$ and $[HFeRu_3(CO)_{13}]^-$ are also under investigation.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1976, 919.
[2] P. F. Jackson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 60.
[3] P. A. Dawson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 781.