Preparation and *X*-Ray Structure Determination of the Mixed Cluster $[H_3CoOs_3(CO)_{12}]$

By Sumit Bhaduri, Brian F. G. Johnson, Jack Lewis, Paul R. Raithby, and Douglas J. Watson
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The cluster $[H_3CoOs_3(CO)_{12}]$ was prepared from the reaction of $[H_2Os_3(CO)_{10}]$ with $[Co_4(CO)_{12}]$ in heptane under reflux; a single crystal *X*-ray analysis has revealed a tetrahedral arrangement of the four metal atoms with twelve terminally bound CO ligands.

Studies of the homonuclear clusters $[H_4Ru_4(CO)_{12}]$[1] and $[H_4Os_4(CO)_{12}]$[2] have revealed an extensive and interesting chemistry. Heteronuclear systems of the type $[H_xM_{4-x}M'_x(CO)_{12}]$ (M = Co, Rh, or Ir; M′ = Ru or Os, x = 1—3) will be of interest because of the induced charge distribution between the two dissimilar metal centres. We report the preparation and single crystal *X*-ray analysis of $[H_3CoOs_3(CO)_{12}]$.

The reaction of $[H_2Os_3(CO)_{10}]$ with $[Co_4(CO)_{12}]$ in n-heptane under reflux produces the new trihydrido-cluster $[H_3CoOs_3(CO)_{12}]$. The reaction is best carried out by monitoring the change in i.r. spectrum with time. Optimum yields are obtained if the reaction is stopped as soon as the bridging CO band associated with the $[Co_4(CO)_{12}]$ disappears. After the removal of solvent, followed by separation on silica, the complex $[H_3CoOs_3(CO)_{12}]$ is obtained as pale yellow rhombs. It was characterised initially by mass spectroscopy, supported by ^1H and ^{13}C n.m.r. and i.r. [ν (cyclohexane) 2076vs, 2066ms, 2049w, 2030vs, 2025vs, 2012w, 2005s, 2000sh, and 1982w cm^{-1}] spectroscopic data.

The mixed cluster is extremely air-sensitive and, unlike $[H_4Os_4(CO)_{12}]$, solutions of $[H_3CoOs_3(CO)_{12}]$ rapidly decompose on exposure to air to give $[H_4Os_4(CO)_{12}]$ and $[Os_3(CO)_{12}]$ together with other, as yet uncharacterised, cobalt complexes. In the solid, the complex is stable over a period of several months.

The ^1H n.m.r. spectrum of the complex in CH_2Cl_2 at *ca.* 30 °C exhibits a singlet resonance at −19·1 p.p.m. relative to Me_4Si. This singlet shows no temperature dependence (−85 to 30 °C). The sharpness of this singlet over this temperature range suggests that the hydrido-ligands are associated with the three osmium atoms. Signals arising from hydrido-ligands bound to the cobalt atom might be expected to show line broadening. At higher temperatures, signal broadening is observed and at *ca.* 50 °C, the signal disappears, possibly indicating that some fluxional process is occurring.

^{13}C N.m.r. spectra for *ca.* 60% enriched samples were measured over the temperature range −85 to +25 °C for solutions in CD_2Cl_2. The ^1H-decoupled spectra exhibited two signals at all temperatures; these occurred at 176·0 and 169·0 p.p.m. in the intensity ratio 1 : 2. These are assigned to the CO ligands bound axially and equatorially to the three osmium atoms. In the coupled spectrum, both signals show some fine structure with $J(^{13}C\text{–}H)$ = *ca.* 10 Hz for the signal at 169 p.p.m. assigned to the equatorial CO ligands. No other signals are observed. We assume that because of the large quadrupole moment of ^{59}Co, signal broadening occurs and as a consequence no carbonyl resonance is observed.† The data are consistent with the structure established by single crystal *X*-ray analysis.

Crystal data: $C_{12}H_3CoO_{12}Os_3$, M = 968·7, triclinic, space group $P\bar{1}$, a = 9·191(4), b = 9·889(3), c = 13·555(5) Å, α = 91·03(3), β = 98·47(3), γ = 128·62(3)°, U = 942·4 Å^3, D_c = 3·41 g cm^{-3}, Z = 2, $\mu(\text{Mo-}K_\alpha)$ = 210·76 cm^{-1}. Intensity data (3·0 ⩽ 2θ ⩽ 60·0°) were recorded on a Syntex $P2_1$ four-circle diffractometer, with graphite monochromated Mo-K_α radiation. The 3125 unique observed intensities $[I > 1{\cdot}5\sigma(I)]$ were corrected for absorption, and the structure solved by multisolution Σ_2 sign expansion and Fourier methods. Least-squares refinement, with the Os and Co atoms assigned anisotropic thermal parameters, gave residuals R = 0·038, $R_w = [\Sigma w\Delta^{\frac{1}{2}}/\Sigma w^{\frac{1}{2}}|F_0|]$ = 0·036. The hydride ligands were not located.

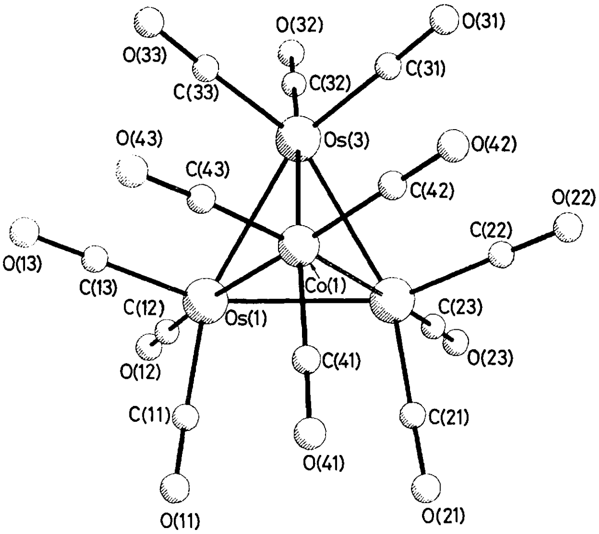

Figure. The molecular structure of $[H_3CoOs_3(CO)_{12}]$. Bond lengths: Os(1)–Os(2), 2·909(1); Os(1)–Os(3), 2·893(1); Os(2)–Os(3), 2·901(1); Os(1)–Co(1), 2·695(2); Os(2)–Co(1), 2·698(1); and Os(3)–Co(1), 2·690(1) Å; bond angles: Os(2)–Os(1)–Os(3), 60·0(1); Os(1)–Os(2)–Os(3), 59·7(1); Os(1)–Os(3)–Os(2), 60·3(1); Os(1)–Co(1)–Os(2), 65·3(1); Os (1)–Co(1)–Os(3), 65·0(1); and Os(2)–Co(1)–Os(3), 65·2(1)°.

The molecular geometry is shown in the Figure, which includes some important bond parameters. The Os_3Co core defines a distorted tetrahedron, and has approximate C_{3v} symmetry. Each metal atom is bonded to three terminal carbonyl ligands. The $M(CO)_3$ units adopt an eclipsed conformation, similar to that found in $[Ir_4(CO)_{12}]$.[3] The

---

† This explanation is perhaps unsatisfying in view of studies on $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ at low temperatures which reveal ^{13}CO resonances. An alternative explanation for the non-observance of $Co\text{-}O^{13}C$ signals in $[H_3CoOs_3(CO)_{12}]$ might be found in the non-incorporation of ^{13}CO at cobalt on labelling.

Os–Os distances [mean 2·901(3) Å] are longer than in $[Os_3(CO)_{12}]$ [mean 2·877(3) Å],[4] while the Co–Os values [mean 2·694(3) Å] are shorter than might be predicted from the sum of the covalent radii, 2·78 Å {using half the Co–Co distance in $[Co_4(CO)_{12}]$,[5] and half the unbridged Os–Os distance in $[H_3Os_4(CO)_{12}I]$,[6] as the covalent radii}. The Os–Os–C(carbonyl) bond angles [mean 114·8(18)°], where the carbonyl group is *trans* to the Co atom, are significantly wider than the other Os–Os–C angles [mean 97·1(18)°] or the Os–Co–C angles [mean 96·3(21)°]. The C(carbonyl)–Os–C(carbonyl) angles are narrower [mean 93·8(10)°] than the corresponding C–Co–C bond angles [mean 98·3(4)°]. There is no such distortion of the carbonyl ligands in the $[Ir_4(CO)_{12}]$[3] and $[Co_4(CO)_{12}]$[5] clusters, but angular deviations of this order, together with an increase in metal–metal bond lengths, have been observed in the $[H_6Re_4(CO)_{12}]^{2-}$ complex,[7] [mean ∠Re–Re–C(carbonyl), 103°; mean ∠C–Re–C, 91°]. These results have been interpreted in terms of the hydride ligands edge-bridging the Re–Re bonds of the tetrahedron. This suggests that a similar effect is occurring in the region of the osmium atoms in the mixed cluster, and that the three hydrogen atoms edge-bridge the Os–Os bonds, lying on the other side of the Os_3 triangle to the $Co(CO)_3$ unit.

The addition of M–M systems to the Os=Os bond in the $[H_2Os_3(CO)_{10}]$ provides an easy route to mixed metal clusters involving an Os_3 nucleus and further work is in progress.

We thank the S.R.C. for financial support and Johnson Matthey and Co. Ltd. for the loan of OsO_4.

(*Received, 5th December* 1977; *Com.* 1237.)

[1] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.
[2] S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.
[3] G. R. Wilkes, Ph.D. Dissertation, University of Wisconsin, 1965.
[4] M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
[5] F. H. Carre, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, 1976, **15**, 380.
[6] B. F. G. Johnson, J. Lewis, M. McPartlin, P. R. Raithby, G. M. Sheldrick, and K. Wong, unpublished results.
[7] G. Ciani, A. Sironi, and V. G. Allbano, *J. Organometallic Chem.*, 1977, **136**, 339.