Synthesis and Structural Characterisation of the Heteronuclear Raft Complex $[Os_3(CO)_{11}Hg]_3$

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The heteronuclear clusters $[M_3(CO)_{11}Hg]_3$ (M = Ru, Os) have been prepared by the reaction of $[M_3H(CO)_{11}]^-$ with Hg^I and Hg^{II} salts; $[Os_3(CO)_{11}Hg]_3$ has been characterised by an *X*-ray analysis and shown to contain a raft-like Os_9Hg_3 metal framework.

Reactions of carbonyl clusters of the iron sub-group with triphenylphosphinegold(I) chloride have yielded a variety of mixed-metal cluster complexes exhibiting a range of novel geometries.[1] Similar reactions using mercury(II) or mercury(I) salts might also prove of interest, since species such as $ClHg^+$ are isoelectronic with R_3PAu^+.

In this communication we report the synthesis and characterisation of the heteronuclear cluster compounds $[M_3(CO)_{11}Hg]_3$ (M = Ru, Os), which are obtained by the reaction of $[N(PPh_3)_2][M_3H(CO)_{11}]$ with an equimolar quantity of a mercury(II) or mercury(I) salt, in dry methanol. These compounds are unusual in that they are considered to contain a central M_3Hg_3 planar core, in fact the whole twelve metal atom skeleton may be described as a raft. They represent a hitherto unknown class of heteronuclear cluster.

When salts containing Hg^{II} salts are employed the reaction is simple, leading to the formation of $[M_3(CO)_{11}Hg]_n$ (60% yield) and $[M_3H(CO)_{10}(OH)]$ (30% yield). If Hg^I salts are used the reaction is modified slightly, with Hg_2Cl_2 the reaction is accompanied by the deposition of mercury.

The i.r. spectra of these complexes are relatively simple exhibiting five bands in the carbonyl stretching region. For $[Os_3(CO)_{11}Hg]_3$ the resonances occur at 2109s, 2070vs, 2042vs, 2003m, and 1955m cm^{-1}, in CH_2Cl_2. The simplicity of the spectra reflects the arrangement of the carbonyls in an '$Os_3(CO)_{11}$' unit, all these units apparently being equivalent in the molecule. None of the mass spectra for these complexes gave a clear molecular ion. The ^1H n.m.r. spectra did not indicate the presence of hydride ligands. In order to establish the molecular geometry an *X*-ray analysis of $[Os_3(CO)_{11}Hg]_3$ was undertaken. Orange crystals of the complex were obtained from tetrahydrofuran–CH_2Cl_2 solution.

Crystal data: $C_{33}Hg_3O_{33}Os_9$, $M = 3237.63$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.677(9)$, $b = 15.071(9)$, $c = 15.297(8)$ Å, $\alpha = 71.97(4)$, $\beta = 87.89(5)$, $\gamma = 63.95(4)°$, $U = 2871.1$ Å^3, $Z = 2$, $D_c = 3.74$ g cm^{-3}, $F(000) = 2778$, $\mu(\text{Mo-}K_\alpha) = 278.87$ cm^{-1}. Intensity data ($2\theta_{max} = 45.0°$) were recorded on a Stoe–Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an ω–θ scan technique. The data were corrected for absorption and averaged to give 5356 unique observed reflections [$F > 6\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares (Hg and Os anisotropic) to $R = 0.067$.†

The molecular structure of $[Os_3(CO)_{11}Hg]_3$ is shown in Figure 1 together with some important bond parameters. The metal framework consists of a central, approximately equilateral Hg(1)Hg(2)Hg(3) triangle. Each edge of this triangle is symmetrically bridged by an Os atom [Os(1), Os(4), and Os(7)] of an Os_3 triangular unit to give a planar (maximum deviation 0.27 Å) Hg_3Os_3 core. A second Os atom [Os(2), Os(6), and Os(8)] is terminally co-ordinated to one of the bridged Hg atoms. The third Os atom [Os(3), Os(5), and Os(9)] in each Os_3 triangle is not involved in bonding with Hg atoms, and the twelve metal atom framework may be described as a raft. The three Os_3 triangles are skewed with respect to the central Hg_3 triangle; the dihedral angles between the Hg(1)Hg(2)Hg(3) plane and Os(1)Os(2)Os(3), Os(4)Os(5)Os(6), and Os(7)Os(8)Os(9) planes are 12.2, 19.1, and 23.5°, respectively. All 33 carbonyl groups are terminal. In each Os_3 triangle, the Os atom which bridges two Hg atoms has three carbonyls bonded to it while the other two Os atoms are each bonded to four. The molecule exhibits idealised three-fold symmetry.

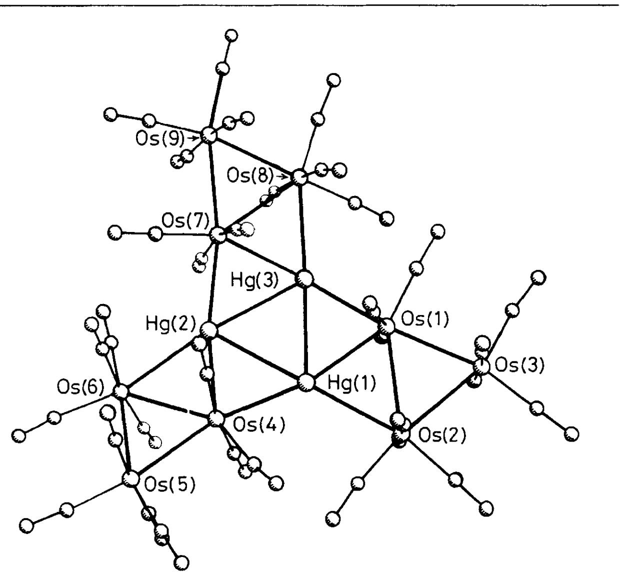

Figure 1. The molecular structure of $[Os_3(CO)_{11}Hg]_3$. Bond lengths: Hg(1)–Hg(2), 3.122(3); Hg(1)–Hg(3), 3.082(3); Hg(2)–Hg(3), 3.097(3); Hg(1)–Os(1), 2.763(3); Hg(1)–Os(2), 2.978(3); Hg(1)–Os(4), 2.730(3); Hg(2)–Os(4), 2.755(3); Hg(2)–Os(6), 2.994(3); Hg(2)–Os(7), 2.717(4); Hg(3)–Os(1), 2.719(3); Hg(3)–Os(7), 2.745(4); Hg(3)–Os(8), 3.044(4); Os(1)–Os(2), 3.015(4); Os(1)–Os(3), 2.860(3); Os(2)–Os(3), 2.915(3); Os(4)–Os(5), 2.859(3); Os(4)–Os(6), 3.022(3); Os(5)–Os(6), 2.928(3); Os(7)–Os(8), 3.004(3); Os(7)–Os(9), 2.863(4); Os(8)–Os(9), 2.908(4) Å.

The structure of the central Hg_3Os_3 core is similar to that observed in the planar hexa-osmium cluster $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$,[2] or in the mixed-metal anion $[Fe_3Pt_3(CO)_{15}]^{2-}$.[3]

Mercury clusters are rare. The only cluster to have been characterised crystallographically which contains triangular arrangements of Hg atoms is $[Hg_6Rh_4(PMe_3)_{12}]$,[4] in which Rh atoms cap four tetrahedrally disposed faces of the Hg_6 octahedron. The average Hg–Hg distance in this cluster is 3.142(3) Å which is slightly longer than the average distance

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† The atomic co-ordinates for this work are available on request from Professor Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

of 3.100(6) Å in $[Os_3(CO)_{11}Hg]_3$. The Hg–Hg distance in the title complex is similar to the value of 3.07 Å for the Hg–Hg separation in the trinuclear complex $[Fe(CO)_4(HgBr)_2]$.[5] In the observed structure of $[Os_3(CO)_{11}Hg]_3$ there must be a bonding interaction between the formally Hg^{II} atoms in order for the molecule to maintain the discrete twelve metal atom framework. This is despite the fact that the Hg–Hg distances are longer than those in the metal (2.99 Å)[6] and in a number of Hg–Hg chain complexes.[7] It is unusual to observe direct bonding between Hg^{II} atoms. In most cases where Hg–Hg bonds have been observed the Hg atoms have been in the 1+ oxidation state[7] and the Hg–Hg distances have been significantly shorter than in the title complex. $[Os_3(CO)_{11}Hg]_3$ is formally a 174 electron system, and may be termed electron-deficient since the bonding within the metal framework cannot adequately be described in terms of two-centre bonds.

Hg^{II} has been polymerised previously to give the cluster $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2Hg]_4$,[8] in which four Hg atoms form a square plane with the substituted Mn atoms bridging the edges. In this complex the Hg–Hg distance is considerably shorter, at 2.888(3) Å, than that observed in $[Os_3(CO)_{11}Hg]_3$.

The distances from the bridging Os atoms to the Hg atoms are significantly shorter [mean 2.74(2) Å] than the distances between the Hg atoms and the non-bridging Os atoms [mean 3.1(1) Å]. The Os–Os bond lengths between the Os atoms involved in bonding to the Hg atoms are long compared to the value observed [2.887(3) Å] in the parent complex $[Os_3(CO)_{12}]$,[9] but similar to the values observed for a number of hydrido bridged Os–Os bonds.[10] The other two Os–Os bond lengths within each triangle are shorter, the distance between the $Os(CO)_3$–$Os(CO)_4$ units being *ca.* 0.06 Å shorter than the distance between the two $Os(CO)_4$ units.

It is of interest to contrast the production of $[Os_3(CO)_{11}Hg]_3$ with the related reaction involving triphenylphosphinegold(I) chloride. The anion $[Os_3H(CO)_{11}]^-$ reacts with Ph_3PAuCl to give $[Os_3H(CO)_{10}(AuPPh_3)]$ in good yield.[11] However, when this cluster is refluxed with a two-fold excess of $[N(PPh_3)_2]Cl$ the dianion $[Os_6Au(CO)_{20}H_2]^{2-}$ is obtained.[12] This dianion contains a central Au atom linking two Os_3 triangles, but there is no evidence for further polymerisation as occurs in the HgOs system.

When $[M_3H(CO)_{11}]^-$ (M = Ru, Os) is treated with Cu^I or Cu^{II} salts, in an analogous manner to the mercury reactions, a complex with the formula $[M_3(CO)_{11}Cu]_n$ (*n* = unknown) is obtained. With Cu^{II} salts the reaction proceeds cleanly to the above product. With Cu^I salts the initial product is a red complex $[M_3(CO)_{11}Cu_2]_n$, which in air undergoes further reaction to give the yellow $[M_3(CO)_{11}Cu]_n$ and Cu metal. Although the mono- and di-copper complexes must have different structures their i.r. spectra are very similar, and similar to that of $[Os_3(CO)_{11}Hg]_3$, and must simply reflect the presence of the '$Os_3(CO)_{11}$' units in all cases.

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