Isolation and *X*-ray Structure Determination of the Cluster Dianion $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$, and the Identification of the Cluster Previously reported with this Stoicheiometry as $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$

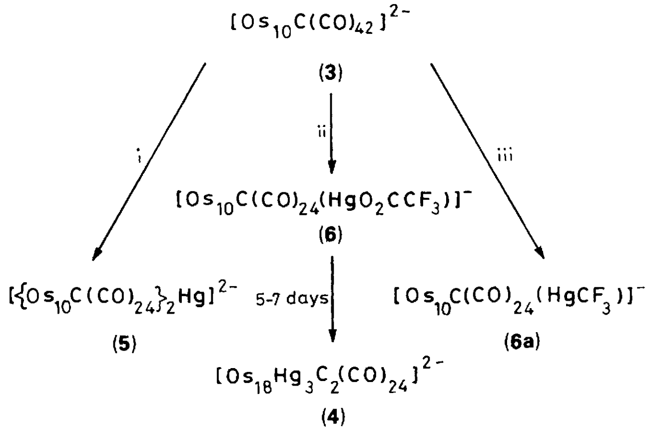
Lutz H. Gade,[a] Brian F. G. Johnson,[a] Jack Lewis,*[a] Mary McPartlin,*[b] and Harold R. Powell[b]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *School of Chemistry, The Polytechnic of North London, N7 8DB, U.K.*

The reaction of $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) with mercuric salts has been reinvestigated and with $Hg(O_2CCF_3)_2$ it gives mixtures of two 21 metal heteronuclear cluster dianions $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**) and $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (**5**) together with an intermediate, $[Os_{10}C(CO)_{24}(HgO_2CCF_3)]$ (**6**) in varying proportions depending on reaction conditions; *X*-ray structure analysis of salts of $[Os_{10}C(CO)_{24}(HgCF_3)]^-$ (**6a**), an analogue of (**6**), and of $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (**5**) are reported, the latter having a previously unobserved metal framework consisting of two $[Os_{10}C(CO)_{24}]$ units linked by a single mercury atom bridge; the previously reported solid state 21 metal framework, believed to be that of $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$, has now been reassigned as that of the cluster dianion $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**).

There is a very close similarity between the 21 metal atom framework of the recently discovered[1] giant cluster dianion $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**1**), obtained from reaction of the tetracapped octahedral[2] decaruthenium dianion $[Ru_{10}C(CO)_{24}]^{2-}$ with mercuric salts, and that we reported earlier[3] for an osmium–mercury dianion (**2**) (Figure 1) from an analogous reaction of $[Os_{10}C(CO)_{24}]^{2-}$ (**3**). This, together with persistent difficulties associated with the formulation of (**2**), has led us to reinvestigate the osmium system.

Solution studies of the dianion (**2**) and its apparent



Scheme 1. Summary of the reactions of (3) with Hg electrophiles. *Reagents and conditions*: i, 0.5—0.7 equiv. $Hg(O_3SCF_3)_2$; ii, 1.5 equiv. $Hg(O_2CCF_3)_2$; iii, 1 equiv. $F_3CHg(O_2CCF_3)$.

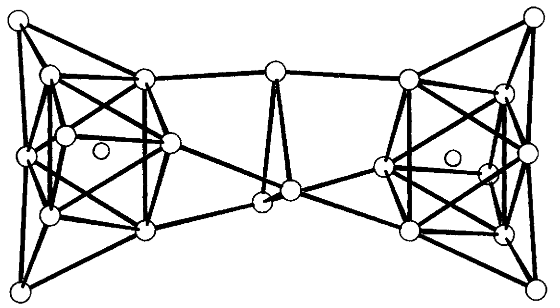


Figure 1. The 21 metal framework structure reported earlier[3] for $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$, which is very similar to that recently discovered for $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**1**),[1] where the central unit is unambiguously shown to be a triangle of mercury atoms.

decomposition to its precursor decaosmium dianion $[Os_{10}C(CO)_{24}]^{2-}$ (**3**), led to the original formulation as $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$.[3] Despite exhaustive studies with later improved *X*-ray data, only 42 carbonyl ligands could be located for the dianion crystallographically (Figure 2), and no evidence of significant electron density due to the missing six carbonyl ligands has been detected. This alone does not preclude their existence as the best refinement was obtained with a 50 : 50 disorder of the metal framework in space group $P\bar{1}$; the virtual C_3 symmetry of the overall observed structure makes the presence of further disorder possible, as mercury and osmium are indistinguishable in *X*-ray work.

The observation that the $[N(PPh_3)_2]^+$ salt of $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**1**) is isomorphous with the reported $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ dianion (**2**) immediately indicated the possibility that the species characterised in the earlier *X*-ray study is the dianion $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**) and that the solid state structure does not correspond to the dianion reported in solution, for which there is strong evidence that the formulation $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ is correct.

From the present reinvestigation of the reaction of $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) with mercuric salts (Scheme 1) we have now clearly demonstrated the existence of two different 21 metal osmium–mercury dianions (**4**) and (**5**) and have characterised them both in solution and in the solid state.

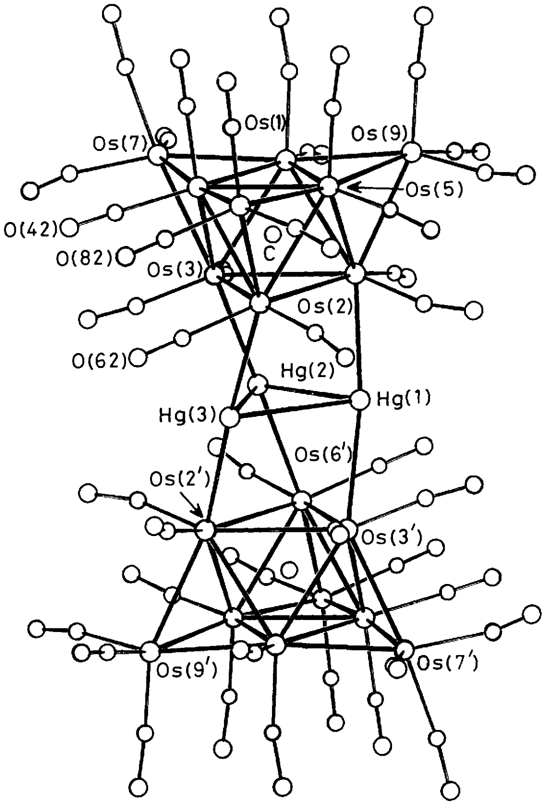


Figure 2. The solid state structure of the dianion originally formulated as $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (ref. 3) now reassigned as $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**).

Reaction of (**3**) with 1.5 equiv. of $Hg(O_2CCF_3)_2$ yields after 5—7 days a heteronuclear osmium–mercury cluster which, based on its ^{13}C NMR spectrum and FAB mass spectrum,† has been unambiguously formulated as $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**), the osmium analogue of (**1**), and identified with the species present in the earlier *X*-ray structure analysis‡ with the overall structure illustrated in Figure 2.[3] Under these reaction

---

† *Spectroscopic data* for the $[N(PPh_3)_2]^+$ salts: $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**); ^{13}C NMR (CD_2Cl_2, 300 K) δ 185.7 (6CO), 184.9 (6CO), 177.7 (12CO), 175.6 (18CO); IR (ν_{CO}/cm^{-1}; CH_2Cl_2) 2072m, 2057s, 2005s; FAB MS most abundant isotopomer for $[Os_{18}Hg_3(C)_2(CO)_{42}]$; *m*/*z* dianion 2615 (simulated 2615), monoanion 5228 (simulated 5230). $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (**5**); IR (ν_{CO}/cm^{-1}); 2083w, 2060vs, 2050msh, 2006s; FAB MS most abundant isotopomer for $[Os_{20}Hg(C)_2(CO)_{48}]$; *m*/*z* dianion 2688 (simulated 2688.5), monoanion *ca.* 5380 (not well resolved, simulated 5377). $[Os_{10}C(CO)_{24}(HgO_2CCF_3)]^-$ (**6**); IR (ν_{CO}/cm^{-1}); CH_2Cl_2: 2092w, 2063vs, 2013s. $[Os_{10}C(CO)_{24}(HgCF_3)]^-$ (**6a**); IR (ν_{CO}/cm^{-1}); CH_2Cl_2: 2092w, 2063vs, 2014s; FAB MS most abundant isotopomer; *m*/*z* 2858.3 (simulated 2857.4).

‡ *Crystal data* for (**5**): $C_{122}H_{60}HgN_2O_{48}Os_{20}P_4$, M = 6448.98, monoclinic, space group $C2/c$, a = 35.526(5), b = 22.517(5), c = 18.288(4) Å, β = 104.76(2)°, U = 14 146.5 Å^3, $F(000)$ = 11 400, μ(Mo-K_α) = 190.46 cm^{-1}, Z = 4, D_c = 3.03 g cm^{-3}. Data were collected in the θ-range 3—25° with a scan width of 0.80; R = 0.0491 for 3837 absorption corrected reflections with $I/\sigma(I)$ >3.0.

For (**6a**): $C_{50}H_{20}F_3HgO_{24}Os_{10}P$, M = 3194.67, triclinic, space group $P\bar{1}$ (no. 2), a = 15.986(3), b = 11.865(2), c = 17.471(4) Å α = 90.12(2), β = 115.81(4), γ = 90.19(2)°, U = 2983.18 Å^3, $F(000)$ = 2788, μ(Mo-K_α) = 238.27 cm^{-1}, Z = 2, D_c = 3.56 g cm^{-3}. Data were collected in the θ-range 3—23° with a scan width of 0.80°; R = 0.0645 for 3451 absorption corrected reflections with $I/\sigma(I)$ >3.0. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

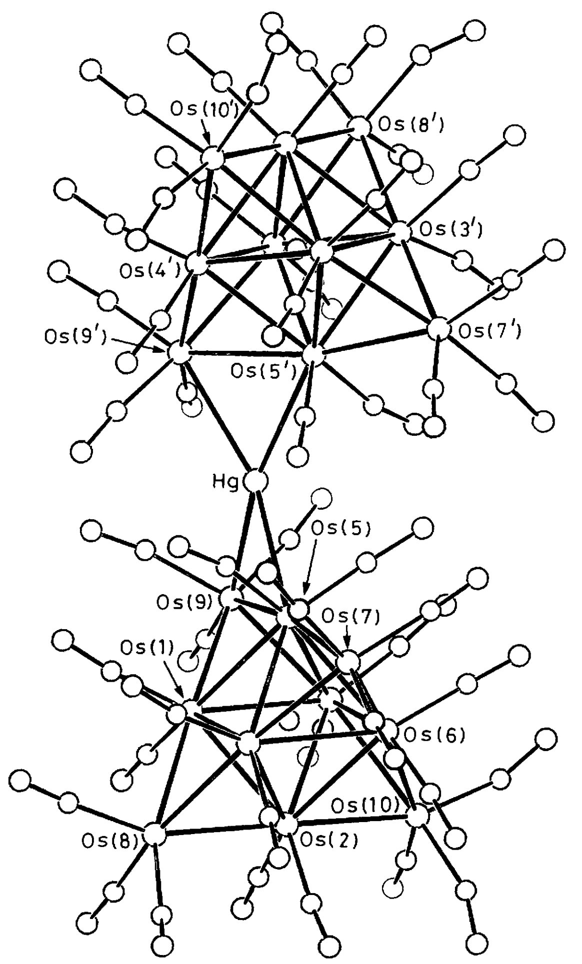


Figure 3. The structure of the dianion $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (**5**) which has crystallographic C_2 symmetry; principal bond distances (Å): Os–Os: (1)–(2) 2.851(2), (1)–(3) 2.869(2), (1)–(4) 2.911(2), (1)–(5) 2.898(2), (1)–(8) 2.800(2), (1)–(9) 2.775(2), (2)–(3) 2.856(2), (2)–(4) 2.886(2), (2)–(6) 2.881(2), (2)–(8) 2.771(2), (2)–(10) 2.744(3), (3)–(5) 2.886(2), (3)–(6) 2.902(2), (3)–(7) 2.750(2), (3)–(8) 2.807(2), (4)–(5) 2.929(2), (4)–(6) 2.835(2), (4)–(9) 2.772(2), (4)–(10) 2.817(2), (5)–(6) 2.916(2), (5)–(7) 2.925(2), (5)–(9) 2.990(2), (6)–(7) 2.764(2), (6)–(10) 2.808(2); Os–Hg: (5)–Hg 2.866(2), (9)–Hg 2.902(2). The dihedral angle between the planes Os(5)–Os(9)–Hg and Os(5')–Os(9')–Hg is 141.57°.

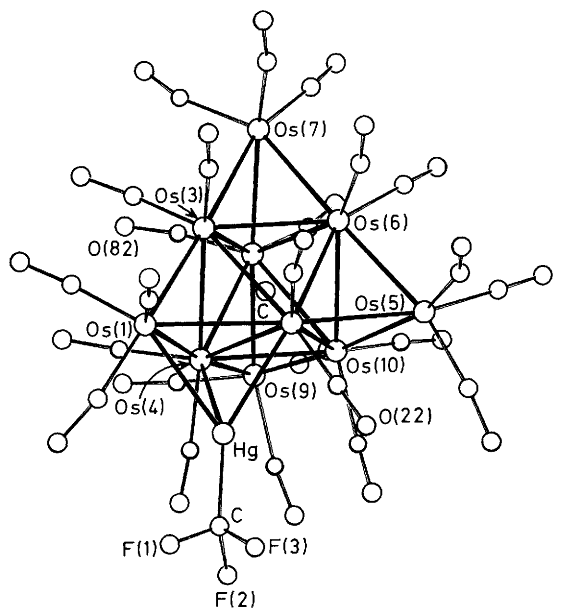


Figure 4. The molecular structure of $[Os_{10}C(CO)_{24}HgCF_3]^-$ (**6a**), an analogue of the intermediate monoanion (**6**); principal bond distances (Å): Os–Os: (1)–(2) 3.054(4), (1)–(3) 2.732(4), (1)–(4) 2.811(4), (2)–(3) 2.926(4), (2)–(4) 3.054(4), (2)–(5) 2.892(4), (2)–(6) 2.865(4), (2)–(10) 2.927(4), (3)–(4) 2.927(4), (3)–(6) 2.831(4), (3)–(7) 2.847(4), (3)–(8) 2.821(4), (4)–(8) 2.874(4), (4)–(9) 2.838(4), (4)–(10) 2.874(4), (5)–(6) 2.739(4), (5)–(10) 2.754(4), (6)–(7) 2.776(4), (6)–(8) 2.841(4), (6)–(10) 2.895(4), (7)–(8) 2.763(4), (8)–(9) 2.728(4), (8)–(10) 2.877(4), (9)–(10) 2.789(4); Os–Hg: (1)–Hg 2.786(4), (2)–Hg 2.733(4), (4)–Hg 3.111(5).

conditions, the decaosmium dianion (**3**) has been decapped and two $Os_9(CO)_{21}$ fragments have been linked by a triangle of mercury atoms.

In contrast, when (**3**) is exposed to only 1 equiv. of $Hg(O_2CCF_3)_2$ a mercury-capped monoanion $[Os_{10}C(CO)_{24}(HgO_2CCF_3)]^-$ (**6**) is initially formed† and slowly converts to a mixture of (**3**), (**4**), and (**6**), together with an additional component (**5**) which, on the basis of its FAB mass spectrum† has the stoicheiometry $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$. Significantly, *X*-ray studies of the dianion (**5**) show it to have a structure quite unlike that observed in the crystals of (**2**) studied earlier[2] {now assigned to $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**)}, but instead to consist of two intact $Os_{10}C(CO)_{24}$ units bridged by a single mercury atom in a type of 21 metal framework not previously observed (Figure 3); the linking Hg atom in (**5**) is four co-ordinate with a geometry intermediate between tetrahedral and square planar similar to that first reported for $[Hg\{Ru_3(CO)_9(C_2Bu^t)\}_2]$.[4] In these reaction conditions it can be concluded that the equilibrium mixture contains the two 21 metal heteronuclear clusters (**4**) and (**5**); the dianion (**5**) is there in moderate concentration and the hitherto unidentified species $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**4**) is there as a minor component (approximate yields less than 20% based on the IR spectra). The dianion $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$ (**5**) may be obtained as the sole major product if $Hg(O_3SCF_3)_2$ (0.5—0.7 equiv.) is used instead of the trifluoroacetate, in which case no mercury capped intermediate analogous to (**6**) is observed and (**5**) is generated immediately. If more than 0.7 equiv. of $Hg(O_3SCF_3)$ are added to a solution of (**3**), no decapping occurs [*i.e.* no (**4**) is observed], but a material of low solubility in most solvents is produced which has not been characterised so far. This may prove to be a mixture of Hg linked oligomers of (**3**), because on addition of an excess of $P(Et)_3$ to this mixture, as on addition to a solution of (**5**), the decaosmium dianion (**3**) is regenerated immediately.

It did not prove possible to isolate the intermediate $[Os_{10}C(CO)_{24}(HgO_2CCF_3)]^-$ (**6**) as crystals, but by use of $F_3CHg(O_2CCF_3)$, a more stable monoanion $[Os_{10}C(CO)_{24}(HgCF_3)]^-$ (**6a**) was isolated and *X*-ray structure analysis‡ of its $[PPh_4]^+$ salt showed that the mercury fragment adopts an asymmetric face capping position (Figure 4). From the almost identical IR spectra of (**6**)† and (**6a**)† a similar Hg-capped structure may be envisaged for the intermediate (**6**).

We are currently reinvestigating the reactions of $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) with gold(I) salts, as there is an obvious possibility that the metal framework we observed in the solid state is $[Os_{18}Au_3(C)_2(CO)_{42}]^{2-}$, not $[Os_{20}Au(C)_2(CO)_{48}]^{2-}$,[3] as the $[N(PPh_3)_2]^+$ salt is also isomorphous with that of $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$.[1]

We thank the S.E.R.C. for a Fellowship to H. R. P. and the British Council for a Scholarship to L. H. G.

Received, 31st August 1989; Com. 9/03694F

References

1 P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin, and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1989, 1513.

2 T. Chihara, R. Komoto, K. Kobayashi, H. Yamazaki, and Y. Matsuura, *Inorg. Chem.*, 1989, **28**, 964; P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin, and H. R. Powell, *J. Organometal. Chem.*, 1989, C17, 377.

3 S. R. Drake, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin, and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1986, 928.

4 S. Ermer, K. King, K. L. Hardcastle, E. Rosenberg, A. M. M. Lanfredi, A. Tiripicchio, and M. T. Camellini, *Inorg. Chem.*, 1983, **22**, 1339.