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Preliminary communication

MERCURY-BRIDGED, NITROSYL SUBSTITUTED, TRIRUTHENIUM CARBONYL CLUSTERS: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[Ru_3(NO)(CO)_{10}]_2Hg$

M. PILAR GÓMEZ-SAL, BRIAN F.G. JOHNSON, JACK LEWIS, PAUL R. RAITHBY and S.N. AZMAN B. SYED-MUSTAFFA
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)
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Summary

The neutral mixed-metal cluster $[Ru_3(NO)(CO)_{10}]_2Hg$ has been prepared by the reaction of the $[Ru_3(NO)(CO)_{10}]$,with $HgCl_2$. An X-ray crystal structure shows that the mercury atom links two Ru_3 triangular units by bridging an Ru—Ru edge of each unit. The dihedral angle between the two Ru_2Hg triangles is 27.6°. In each Ru_3 triangle a nitrosyl ligand bridges the same Ru—Ru edge as the bridging Hg atom while the ten carbonyl groups are all terminal.

Transition metals of Groups Ib and IIb have been shown to link transition metal cluster carbonyl fragments, via metal—metal interactions, to give relatively "open" metal frameworks. In the anions $[\{Os_3H(CO)_{10}\}_2M]^-$ (M = Ag [1], Au [2]) the Group Ib element links two Os_3 triangles by bonding to the two formally "unsaturated" Os—Os edges to give a planar Os_2MOs_2 central core. Mercury has been observed to link a variety of cluster units by a number of different modes of coordination, ranging from a Hg atom sitting between two Pt_3 triangles, coordinating to all six of the Pt atoms [3], to a Hg_2 unit which links two mononuclear Co complexes via a σ bond to each [4].

It is interesting to note that under the same reaction conditions as are employed to prepare the anion $[\{Os_3H(CO)_{10}\}_2M]^-$ (M = Ag [1], Au[2]), treatment of $[Os_3H(CO)_{11}]^-$ with mercury(I) and mercury(II) salts affords the raft complex $[Os_3(CO)_{11}Hg]_3$ [5] and not the expected system with a mercury atom linking two Os_3 triangular units. In order to investigate the generality of the reaction of mercury salts with trinuclear cluster anions we are carrying out a series of experiments, and in this communication we report the results of the reaction between $HgCl_2$ and the "saturated" nitrosyl cluster anion $[Ru_3(NO)(CO)_{10}]^-$.

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Reaction of a methanolic solution of $[(Ph_3P)_2N][Ru_3(NO)(CO)_{10}]$ with $HgCl_2$ (2/1 molar ratio) immediately gives a deep red precipitate, which has been characterised as $[Ru_3(NO)(CO)_{10}]_2Hg$; The infrared spectrum of this complex (CH_2Cl_2 solution) shows carbonyl stretching frequencies at 2107vw, 2094m, 2061vs, 2033m, and 2016m cm^{-1}, while a band at 1538m cm^{-1} may be assigned to a nitrosyl stretching mode. The mass spectrum of the cluster shows a molecular ion at m/e 1434 (based on ^{102}Ru) and a series of peaks at 200, 201, 202, and 204 which may be assigned as isotopic mercury fragments.

To confirm that the complex did consist of a mercury atom linking two Ru_3 triangles in a manner analogous to that observed for the Group Ib elements with Os_3 triangular systems [1,2] a single crystal X-ray diffraction study* was undertaken. The structure of $[Ru_3(NO)(CO)_{10}]_2Hg$ is illustrated in Fig. 1, which includes some important bond parameters**. The Hg(1) atom lies on a crystallographic two-fold axis and μ_2-bridges the Ru(1)—Ru(2) and the symmetry related Ru(1')—Ru(2') edges. In contrast to the $[\{Os_3H(CO)_{10}\}_2M]^-$ (M = Ag, Au)

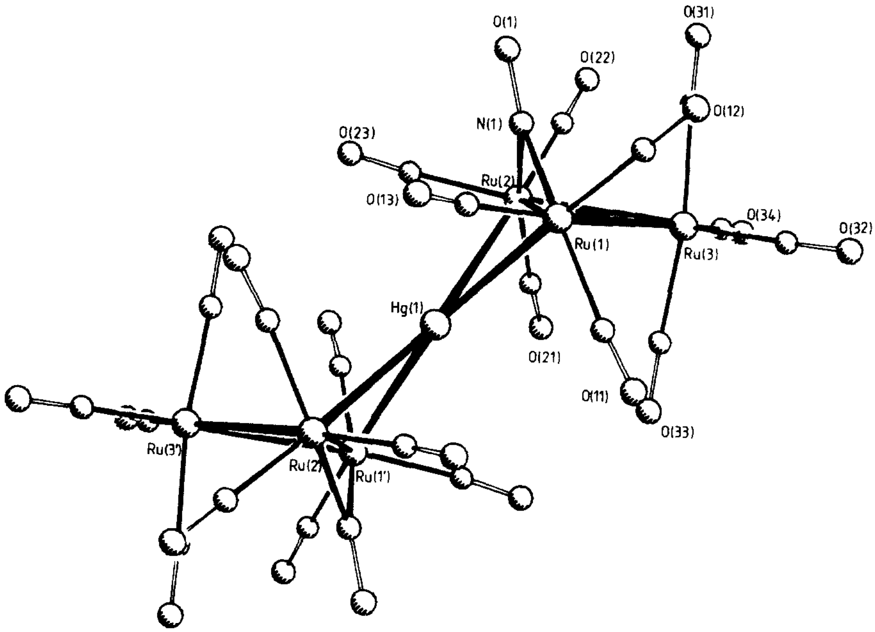

Fig. 1. The molecular structure of $Ru_3(NO)(CO)_{10}$ $_2$Hg. Bond lengths: Hg(1)—Ru(1), 2.868(1); Hg(1)—Ru(2), 2.855(1); Ru(1)—Ru(2), 2.861(1); Ru(1)—Ru(3), 2.835(1); Ru(2)—Ru(3), 2.832(1); Ru(1)—N(1), 1.992(4); Ru(2)—N(1), 1.998(4); N(1)—O(1), 1.209(6) Å. Bond angles: Ru(1)—Hg(1)—Ru(2), 60.0(1); Ru(1)—Hg(1)—Ru(1'), 122.5(1); Ru(2)—Hg(1)—Ru(2'), 121.3(1); Hg(1)—Ru(1)—Ru(2), 59.8(1); Hg(1)—Ru(2)—Ru(1), 60.2(1); Ru(2)—Ru(1)—Ru(3), 59.6(1); Ru(1)—Ru(2)—Ru(3), 59.7(1); Ru(1)—Ru(3)—Ru(2), 60.6(1); Ru(1)—N(1)—Ru(2), 91.6(2)°.

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*Crystal data: $C_{20}HgN_2O_{22}Ru_6$, M = 1427.2. Monoclinic, space group $C2/c$, a 15.746(7), b 9.016(4), c 23.911(11) Å, β 95.11(4)°, U 3381.0 Å^3, D_c 2.79 g cm^{-3}, Z = 4, $F(000)$ 2616, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) = 71.40 cm^{-1}. 3312 reflections measured on a Stoe four-circle diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least squares to R = 0.028 and R_w = 0.031 for 2773 observed reflections [$F > 4\sigma(F)$].

**The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

anions, where the presence of a crystallographic centre of symmetry requires the central Os_2MOs_2 core to be planar [1,2], there is no such constraint in $[Ru_3(NO)(CO)_{10}]_2Hg$, and the dihedral angle between the two Ru_2Hg triangles is 27.6°. However, the "*trans*" orientation of the two triangles observed in the OsAg [1] and OsAu [2] systems is retained, with Ru(3) and Ru(3′) on opposite sides of the Ru_2HgRu_2 core. The dihedral angle between the Ru_2Hg and the Ru_3 planes is 123.3°, which is ca. 9° wider than the average dihedral angles between the Os_2M and Os_3 triangles in $[\{Os_3H(CO)_{10}\}_2M]^-$ (115° for M = Ag [1] and 113° for M = Au [2]). This difference may be at least partly attributed to the presence of the symmetrically μ_2 bridging nitrosyl ligand, which occupies approximately the same position as the hydrides in the OsAg [1] and OsAu [2] anions. The Ru(1)Ru(2)N(1)O(1) plane makes angles of 52.3° and 109.6° with the Ru(1)Ru(2)Hg(1) and Ru(1)Ru(2)Ru(3) planes, respectively. The ten carbonyl groups are essentially linear, and the Ru—C(carbonyl) distances follow the expected trends for carbonyl ligands in competition with *trans* groups for back donation from filled metal orbitals. The longest Ru—C bonds are associated with the carbonyl groups pseudo *trans* to the bridging nitrosyl and with the two axial CO groups on Ru(3). There is no significant difference in Ru—C distances *trans* to Os—Os or Os—Hg vectors.

The Hg(1) atom in $[Ru_3(NO)(CO)_{10}]_2Hg$ is considered to be in the 2+ oxidation state, and so would be expected to adopt a linear, two coordinate geometry, as observed in a number of mercury(II) containing mixed-metal complexes [6]. In $[\{Os_3H(CO)_{10}\}_2M]^-$ (M = Ag [1], Au [2]) it has been suggested that the central M atom is in the 1+ oxidation state and the lobes of the *sp* hybridized orbital point at the mid-points of the bridged Os—Os edges to form two, three-centre delocalised bonds. A similar bonding mode may be present in $[Ru_3(NO)(CO)_{10}]_2$-Hg. The Ru—Hg distances show slight asymmetry and are marginally longer than the range of Ru—Hg lengths (2.808(6)—2.840(6) Å) for the Hg atom which links two Ru_3 triangular units by bridging Ru—Ru bonds, in $[Ru_3(CO)_9(C_2\text{-t-Bu})]_2Hg$ [7], in a manner similar to that in $[Ru_3(NO)(CO)_{10}]_2Hg$.

The dihedral angle between the Ru_2Hg and the Ru_3 planes in $[Ru_3(CO)_9$-$(C_2\text{-t-Bu})]_2Hg$ [7] is 45° which is significantly larger than the twist found in $[Ru_3(NO)(CO)_{10}]_2Hg$ but quite similar to the value of 42° for the angle between the Ru_2Au and the Ru_3 planes in the related nitrosyl anion $[\{Ru_3(NO)(CO)_{10}\}_2$-$Au]^-$ [8]. Although there is a variation in dihedral angles between these three complexes it is perhaps more important to note that unlike the $[\{Os_3H$-$(CO)_{10}\}_2M]^-$ (M = Ag [1], Au [2]) anions the central core is not planar. The Ru_3 units in these clusters are formally saturated 48 electron systems while the "$[Os_3H(CO)_{10}]$" units are unsaturated with only 46 electrons associated with them, and the difference in geometry may reflect the difference in electron count. A planar system may favour a greater delocalisation of the "unsaturation" over the metal framework, or a planar geometry could stabilise the "unsaturated" cluster by giving a symmetrically arranged shield of carbonyl groups around the central Ag or Au atom.

The Ru(1)—Ru(2) distance in $[Ru_3(NO)(CO)_{10}]_2Hg$ is consistent with a saturated "$[Ru_3(NO)(CO)_{10}]^-$" unit and is ca. 0.026 Å longer than the average Ru—Ru distance of 2.834(2) Å for the other two edges. By way of contrast the bridged Os—Os edge in $[\{Os_3H(CO)_{10}\}_2Ag]^-$ [1] is ca. 0.15 Å shorter than the other two Os—Os edges and the unsaturation is thought to be localised in this fragment. The bridged Ru(1)—Ru(2) distance in $[Ru_3(NO)(CO)_{10}]_2Hg$ is similar in length to the Ru—Ru "single" bonds in $Ru_3(CO)_{12}$ [9] where the average value is 2.854(1) Å. In the neutral nitrosyl cluster $Ru_3H(NO)(CO)_7[P(OMe)_3]_3$ [10] the bridged Ru—Ru distance (2.816(2) Å) is shorter than the two unbridged Ru—Ru edges (2.843(2) and 2.856(2) Å), and this trend is a common feature in a variety of $M_3H(CO)_{10}X$ clusters [11]. The answer as to why the reverse is true for the Ru_3 triangles in $[Ru_3(NO)(CO)_{10}]_2Hg$ may hinge on steric rather than electronic arguments. The nitrosyl groups in $[Ru_3(NO)(CO)_{10}]_2Hg$ and $Ru_3H(NO)(CO)_7\{P(OMe)_3\}_3$ each act as three electron donors while the Hg atom and the hydride may be considered to donate one electron, so that the electronic configuration in the "$Ru_2(NO)X$" (X = H or Hg) fragments would be similar. The difference in the bridged Ru—Ru distance may be attributed to the larger size of the Hg atom. Churchill has shown that the presence of a large bridgehead atom lengthens the bridged metal—metal distance [12].

The Ru—N(nitrosyl) distances in $[Ru_3(NO)(CO)_{10}]_2Hg$ are similar to the average value of 1.98(1) Å for the equivalent bonds in $Ru_3H(NO)(CO)_7$-$\{P(OMe)_3\}_3$ [10]. The N—O distance is also similar to that in a number of nitrosyl bridged clusters [10,13].

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