High Nuclearity Pt–Rh Carbonyl Clusters. Synthesis and *X*-Ray Characterization of the $[Pt_2Rh_{11}(\mu\text{-}CO)_{12}(CO)_{12}]^{3-}$ and $[PtRh_{12}(\mu\text{-}CO)_{12}(CO)_{12}]^{4-}$ Anions

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Two new high nuclearity cluster anions, $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ and $[PtRh_{12}(CO)_{24}]^{4-}$ have been obtained by controlled pyrolysis of $[PtRh_5(CO)_{15}]^-$; their structures show the hexagonal close packed metal array found in the isoelectronic series $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$, with a Pt atom inside a 12 metal atom shell, but with a different arrangement of CO ligands.

Many examples of mixed metal clusters are known, but few high nuclearity species have so far been characterized. Since both platinum and rhodium give large metal carbonyl clusters, we undertook studies to establish the existence of high nuclearity Pt–Rh species by thermal treatment of the smaller mixed clusters (5—7 metal atoms) already characterized.[1,2] We report here the first two species obtained, $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ and $[PtRh_{12}(CO)_{24}]^{4-}$, which are the largest mixed-metal cluster anions as yet known.

Pyrolysis of $Na[PtRh_5(CO)_{15}]$,[1] performed in refluxing MeOH in the presence of $NaHCO_3$, gave a mixture of anions which, after removal of the solvent and re-dissolution in water, was subjected to fractional precipitation of the alkali metal salts. The potassium salt of $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ was obtained by addition of KCl up to a concentration of 15—20%, and further addition of CsCl gave $Cs_4[PtRh_{12}(CO)_{24}]$ as a minor component of the reaction mixture.

The trianion $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ was further purified by

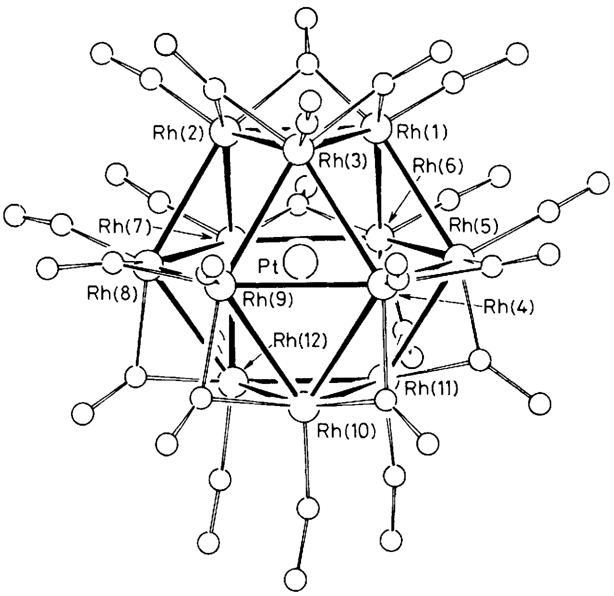

Figure 1. A view of the anion $[PtRh_{12}(\mu\text{-}CO)_{12}(CO)_{12}]^{4-}$.

transformation into the Cs^+ salt by metathesis in water (overall yield *ca.* 15%). Subsequent metathesis in methanol with ten different bulky cations, gave mostly crystalline samples, but only the mixed cation salt, $Cs_2(NEt_3Pr^n)[Pt_2Rh_{11}(CO)_{24}]$, was suitable for *X*-ray data collection.

The tetra-anion was recrystallized directly from MeOH–propan-2-ol as the Cs^+ salt solvated by two MeOH molecules. These crystals were found to be suitable for diffraction studies.

The i.r. spectra of the two anions, in MeCN, show bands in the CO stretching region at 1992s, 1960sh, and 1808ms cm^{-1} for $Cs_2(NEt_3Pr^n)[Pt_2Rh_{11}(CO)_{24}]$, and at 1968s, 1935mw, 1809mw, and 1783ms cm^{-1} for $Cs_4[PtRh_{12}(CO)_{24}]$. Hydride signals were not observed in the ^1H n.m.r. spectra, from τ −10 to 50, at room temperature, for either anion or from τ 0 to 60 at −79 °C for the trianion. No e.s.r. paramagnetic resonance was detected from a crystalline sample of the trianion at −160 °C. Atomic absorption analyses of both compounds gave Pt/Rh internal ratios which were in good agreement with the proposed formulations.

The structure of the anion $[PtRh_{12}(CO)_{24}]^{4-}$ is illustrated in Figure 1.[†][‡] The metal atom cluster, of D_{3h} idealized symmetry, consists of a 'twinned' cuboctahedral array of rhodium atoms with a central platinum atom. The hexagonal close packed arrangement of metal atoms is the same as previously observed within the isoelectronic family $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2,3,4).[3–5] The anion $[Pt_2Rh_{11}(CO)_{24}]^{3-}$ contains the same cluster (see Figure 2)[§][‡] with one Pt atom at the centre and the second Pt atom disordered on the surface. The carbonyl stereochemistry of the two novel mixed-metal anions is the same, resulting in overall idealized C_{3v} symmetry, which is different from the idealized C_s symmetry present in the Rh_{13} anions. In both the Pt_nRh_{13-n} (n = 1, 2) and Rh_{13} families the CO geometries imply that each surface metal atom bears one terminal ligand and is connected to two edge-bridging ligands; the two different types of bridging CO ligands are however interconvertible by a concerted shift of three ligands [*e.g.*, (numbering of Figure 1) those bridging the edges 1–2, 5–11, and 8–12 in the Pt_nRh_{13-n} clusters and 1–5, 11–12, and 2–8 in the Rh_{13} series]. These different stereochemistries can be tentatively explained by taking into account the absence, in the mixed-metal anions, of hydrides close to the cluster surface. The hydrides may influence the preferred CO arrangement through non-bonding contacts.[4,5] It is noteworthy that the novel anions contain a $M_3(\mu\text{-}CO)_3(CO)_3$ moiety which is connected to the remainder through metal–metal bonds only. A rotation of this moiety by 60° about the three-fold axis would generate a cuboctahedral cluster, but this more sym-

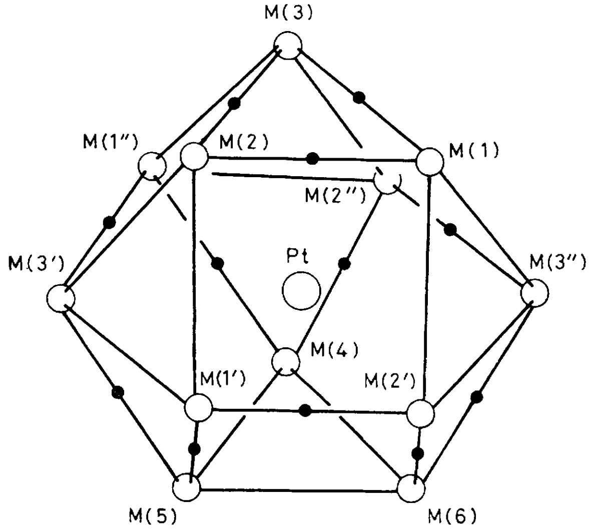

Figure 2. A view of one of the four possible arrangements of the metal cluster in the anion $[Pt_2Rh_{11}(\mu\text{-}CO)_{12}(CO)_{12}]^{3-}$ looking approximately down the tetragonal c axis. The central Pt atom lies on a $\bar{4}$ position, so that the resulting anion is disordered. The surface M atoms are assumed to be (11/12 Rh + 1/12 Pt). The Pt–M and M–M bond distances are in the range 2.629(7)—2·846(3) and 2·580(8)—2·869(4) Å, respectively. The small black circles indicate bridged edges.

[†] *Crystal data:* $C_{26}H_8Cs_4O_{26}PtRh_{12}$, M = 2697.9, orthorhombic, space group $P2_1cn$ [non-standard setting of $Pna2_1$ (No. 33)], a = 11.889(5), b = 12.379(5), c = 34.567(11) Å, Z = 4. Intensity data were collected on an Enraf–Nonius CAD4 automated diffractometer with Mo-K_α radiation (λ = 0.71073 Å), by the ω-scan method, within the limits $3° < \theta < 24°$.

The structure solution was based on Patterson and Fourier methods. The refinements were carried out by full-matrix least-squares, on the basis of 1922 significant [$I > 2\sigma(I)$] reflections, up to a current R value of 0.065. One of the Cs^+ cations is disordered, occupying statistically two close positions.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[§] *Crystal data:* $C_{33}H_{22}Cs_2NO_{24}Pt_2Rh_{11}$, M = 2604.5, tetragonal, space group $I4_1/acd$ (No. 142), a = b = 17.271(5), c = 35.326(11) Å, Z = 8. The structure was solved by Patterson and Fourier methods and refined by least-squares methods, on the basis of 664 significant [$I > 2\sigma(I)$] counter data, up to a current R value of 0.055. Both anion and cations lie on special positions: the anion on a $\bar{4}$ position (a in Wyckoff notation), the Cs^+ on a 2-fold axis (e in Wyckoff notation), and $(NEt_3Pr^n)^+$ on a 222 position (b in Wyckoff notation). The anion (Figure 2) exhibits disorder of the surface metal atoms, resulting in four differently oriented arrangements; three of these metals [M(1), M(2), M(3), occupancy 0.75 each] are correctly reproduced three times by the $\bar{4}$ axis, but their fourth equivalent would give rise to a cuboctahedron instead of the found 'twinned' cuboctahedron, which is completed by three further metals of occupancy 0.25 [M(4), M(5), M(6)]. No evidence of a preferred location for the surface Pt atom was found. The same type of disorder applies to the terminal CO groups, while the bridging carbonyls are not disordered, conforming correctly to the local symmetry.

metric geometry does not appear to be favoured in M_{13} arrangements.

The following bond parameters are for the tetra-anion, those of the trianion being of poorer quality owing to disorder. The Pt–Rh bonds are in the range 2.743(4)—2.812(6) Å, with a mean value of 2.776 Å, comparable with the corresponding mean value in $[PtRh_5(CO)_{15}]^-$ of 2.790 Å.[1] The 24 Rh–Rh bonds [range 2.713(8)—2.849(7) Å] have a mean value of 2.778 Å. Both the centre-to-surface and the surface M–M mean bond lengths are in full agreement with the trend found in the family $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$, which shows a progressive decrease in these bond lengths with decreasing number of hydrides (see Table 3 in ref. 5). However, the Rh–Rh bonds belong to six different classes: i, upper edge-bridged triangle, mean 2.732 Å; ii, upper unbridged interlayer bonds, mean 2.767 Å; iii, bridged edges of the central hexagon, mean 2.746 Å; iv, unbridged edges of the same hexagon, mean 2.800 Å; v, lower bridged interlayer bonds, mean 2.827 Å; and vi, lower unbridged triangle, mean 2.755 Å.

The mean values of the Rh–C and C–O bond lengths for the terminal and edge-bridging carbonyls are 1.83 and 1.20, and 1.99 and 1.20 Å, respectively.

Finally, mixed Pt–Rh clusters with a low Pt/Rh ratio, show a tendency to assume metal arrangements similar to those of the isoelectronic homonuclear rhodium cluster compounds, as confirmed by studies on other related species,[6] with the platinum atoms preferably occupying the sites of the cluster with the highest M–M connectivity, as previously found in the nitride $[PtRh_{10}N(CO)_{21}]^{3-}$.[7]

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