Synthesis and *X*-Ray Characterization of the High-nuclearity $[Rh_{17}(\mu_3\text{-}CO)_3\text{-}(\mu\text{-}CO)_{15}(CO)_{12}]^{3-}$ Anion containing a Tetracapped Twinned Cuboctahedral Cluster

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Summary The novel anion $[Rh_{17}(CO)_{30}]^{3-}$, which has been obtained by refluxing a mixture of $Rh_4(CO)_{12}$ and NaOH (OH^-: Rh, 1 : 5·5) in propan-2-ol, has been shown by *X*-ray crystallography to contain a cluster which is a fragment of a hexagonal close-packed structure (3 layers: 6/7/4) and is derived from the twinned cuboctahedron present in the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$, with the other four rhodium atoms capping square faces.

THE study of high nuclearity carbonyl cluster compounds has shown that the metal atoms possess a marked tendency to assume arrangements which are fragments of metallic lattices; different geometries are usually related to the presence of interstitial main-group elements, which require large interstitial holes as, for instance, in the recently characterized anion $[Rh_{10}S(CO)_{22}]^{2-}$.[1]

We have already described rhodium compounds containing clusters with closest-packed metal atoms, *e.g.* the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2,[2] 3,[3] 4[4]) and $[Rh_{22}(CO)_{37}]^{4-}$ (ref. 5), and we report here the synthesis and structure of a new example, namely the anion $[Rh_{17}(CO)_{30}]^{3-}$. This novel anion has been isolated from the mixture of anions formed by refluxing under nitrogen for 4—5 h $Rh_4(CO)_{12}$ (1—2 g) with NaOH (OH^-: Rh, 1 : 5·5) in propan-2-ol (30—40 ml). Isolation was performed by fractional precipitation of the sodium salts from water as already described.[5] After separation of the fractions at 2·5 and 10% NaCl concentration, which contain the $[Rh_{14}(CO)_{26}]^{2-}$ (ref. 6) and $[Rh_{22}(CO)_{37}]^{4-}$ (ref. 5) anions, respectively, on addition of NaCl up to 15% concentration dark brown crystals of $Na_3[Rh_{17}(CO)_{30}]\cdot nH_2O$ were obtained in 15—20% yield after 2 days. The corresponding salts with bulky organic cations can be obtained by metathesis in propan-2-ol.

The complex i.r. spectrum in tetrahydrofuran (THF) solution shows bands at 2052mw, 2018vs, 2000vs, and 1955mw, br. cm^{-1} (terminal CO), and 1855m, 1820ms, and 1763w cm^{-1} (bridging CO) in accord with the *X*-ray structure. No hydride signals have been observed in the ^{1}H n.m.r. spectrum from τ −20 to +60 either at room temperature or at −90 °C. ^{13}C and ^{103}Rh N.m.r. spectra are under investigation.

The anion is air-sensitive and reacts with MeCN to give a new species. In the presence of halide ions disproportionation is observed affording $[Rh(CO)_2X_2]^-$ and another new species. Both new species are under investigation. No protonation could be observed with CF_3CO_2H in polar solvents such as THF. The $[Rh_{17}(CO)_{30}]^{3-}$ anion reacts with Bu^{t}OK in MeCN or with KOH in MeOH to give more reduced species which are easily protonated to give a family of compounds in which the Rh_{17} cluster seems to be maintained.[7]

Crystals suitable for *X*-ray analysis were obtained by slow diffusion of a solution of tetra-n-propylammonium bromide in propan-2-ol into an MeOH solution of the sodium salt of the novel anion.†

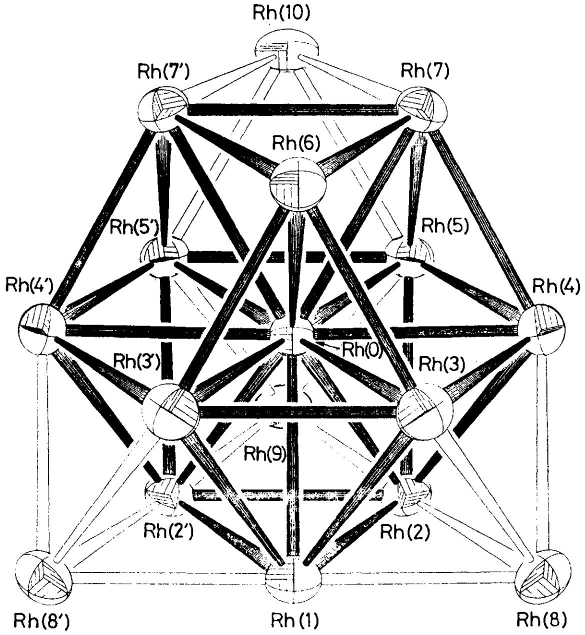

FIGURE 1. A view of the metal-atom cluster of the anion $[Rh_{17}(CO)_{30}]^{3-}$. A crystallographic mirror plane passes through atoms Rh(0), Rh(1), Rh(6), Rh(9), and Rh(10). The twinned cuboctahedral moiety is indicated by black bonds.

The $[Rh_{17}(CO)_{30}]^{3-}$ anion contains a compact closest-packed metal-atom cluster of C_s symmetry, illustrated in Figure 1. A crystallographic mirror plane passes through atoms Rh(0), Rh(1), Rh(6), Rh(9), and Rh(10). The cluster is formed by superimposition of three fragments of compact layers (6/7/4), with a sequence *aba*, resulting in a hexagonal close-packed arrangement. It can also be described as a centred twinned cuboctahedron, like that present in the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2,[2] 3,[3] 4[4]), capped by four Rh atoms on four of the six square faces, three on one side and the fourth on the opposite side of the central 7-metal-atom layer. This cluster can be considered as an intermediate between that of the Rh_{13} anions and that present in the large anion $[Rh_{22}(CO)_{37}]^{4-}$.[5]‡

The Rh atoms show metal–metal connectivities ranging from 12 to 4. The array contains 8 tetrahedral, 4 octahedral, and 2 semi-octahedral cavities. The 29 independent Rh–Rh bond lengths range from 2·719(4) to 2·897(3) Å, with an overall mean value of 2·782 Å.

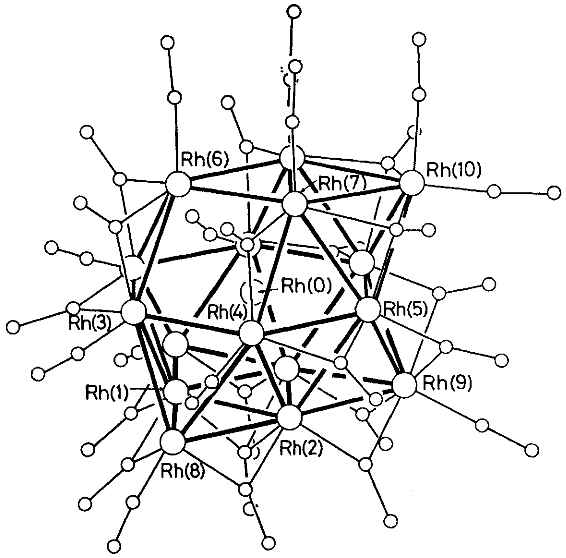

FIGURE 2. A schematic view of the anion $[Rh_{17}(CO)_{30}]^{3-}$.

The 30 carbonyl ligands (Figure 2) are bound as follows: 12 are terminally bound so that 10 surface-metal atoms bear one CO and the capping atom Rh(10) bears two such groups; 5 metal atoms (1, 2, 2′, 5, and 5′) do not possess terminal groups. The mean values of the Rh–C and C–O bond distances for these ligands are 1·81 and 1·20 Å, respectively. 15 carbonyl ligands are edge-bridging: 6 on the edges of the 6-metal-atom triangular layer, 3 on alternate edges of the central 7-metal-atom hexagonal layer, and the remaining 6 on interlayer edges. Two of these groups [on the edges Rh(5)–Rh(9) and Rh(5′)–Rh(9)] are markedly asymmetric [Rh(5, 5′)–C and Rh(9)–C 1·80(4) and 2·26(4) Å, respectively]. The mean values of the Rh–C and C–O bond lengths for the 13 symmetric edge-bridging groups are 1·92 and 1·26 Å, respectively. Three CO groups are face-bridging, on faces (1, 2, 2′), (5, 7, 10), and (5′, 7′, 10), with mean

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† *Crystal data:* $C_{66}H_{84}N_3O_{30}Rh_{17}$, M = 3148·8, orthorhombic, space group $Cmc2_1$ (No. 26), a = 21·550(6), b = 23·962(8), c = 17·761(5) Å, Z = 4. The structure was solved by conventional Patterson and Fourier methods, and refined by block-matrix least-squares, on the basis of 2075 independent significant counter data, up to a current R value of 0·059. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Another Rh_{17} cluster is present in the anion $[Rh_{17}S_2(CO)_{32}]^{3-}$ (J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, 1978, **17**, 2574) which shows a quite different and less compact geometry owing to the interstitial sulphur atoms.

Rh–C and C–O bond lengths of 2·10 and 1·26 Å, respectively.

The anion possesses 216 valence electrons, corresponding to 108 cluster valence molecular orbitals, only one less than the number of $6N_{\text{metal}} + 7$ suggested for compact close-packed high nuclearity carbonyl cluster compounds on the basis of extended Hückel M.O. calculations performed on a number of bare clusters of this type.[8]

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