A Monocapped Octahedral Form of Rh_7 [Metal Atom] Cluster in the Tetramethylammonium Salt of Hexadecacarbonylheptarhodate Trianion

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Summary Hexadecacarbonylheptarhodate trianion, $[Rh_7(CO)_{16}]^{3-}$, has been found to be a monocapped octahedron of metal atoms with seven terminal, six double-bridging, and three face-bridging carbonyl groups.

RHODIUM appears to be unique in giving cluster anions with more than six metal atoms. We are reporting elsewhere the molecular structure of the dianion $[Rh_{12}(CO)_{30}]^{2-}$ which consists of two octahedral units connected through a metal–metal bridge.[1]

We report here the results of an *X*-ray structural investigation on the compound $[N(CH_3)_4]_3$ $[Rh_7(CO)_{16}]$ which has been recently prepared by Chini and Martinengo.[2] This salt crystallizes in the orthorombic system with cell constants, from precession photographs and Mo-K_α radiation (λ = 0·7107 Å), a = 24.10(3), b = 13·97(2), c = 12·22(2) Å, and V = 4114 Å^3. The measured density of 2·45(5) g. cm.$^{-3}$ agrees with the value of 2·53 g.cm.$^{-3}$ computed for Z = 4. The space group, chosen on the basis of systematic extinctions and of the Patterson map, is *Pnma* (No. 62); this requires special positions for one cation and for the anion.

Very small crystals were found of sufficiently good quality for diffraction work. The intensities were, accordingly, very low; the set of observed structure factors upon which the present determination is based consists of 550 independent non-zero observations, measured by microdensitometry on precession films.

The structure has been solved by direct methods and refined by block-diagonal least-squares. The metal atoms

were treated anisotropically; because of conspicuous oscillations of oxygen and carbon atoms, constraints[3] were introduced in the cations which were treated as rigid tetrahedra with N–C distances of 1·50 Å, and on the CO distances which were given values of 1·15 Å for terminal groups and 1·19 Å for bridging groups, in agreement with previously found values.[1] R was 0·071.

The trianion is shown in Figure 1; the atoms Rh(2), Rh(4) and Rh(5) lie on the mirror plane and atoms Rh(1) and Rh(3) are reflected into Rh(11) and Rh(33), respectively. Of the 16 carbonyl groups, seven are in terminal positions, one for each metal atom; those bonded to Rh(2), Rh(4), and Rh(5) lie on the mirror. Six groups are bridging on edges (two of them on the mirror) and three more groups are bridged on faces (one on the mirror). There is a formal excess of two electrons with respect to a noble-gas configuration for all the atoms in the cluster; in this respect the present anion does not deviate from the behaviour of the known octahedral clusters of cobalt,[4–6] rhodium,[1,7] and ruthenium.[8,9] With regard to the stereochemistry, there is close similarity between $[Rh_7(CO)_{16}]^{3-}$ and $[Co_6(CO)_{16}]^{2-}$ whose ligand distribution can be obtained from that of the present anion by removing Rh(5) with its terminal CO group and transforming the three double bridges into linearly bonded groups.[4,5]

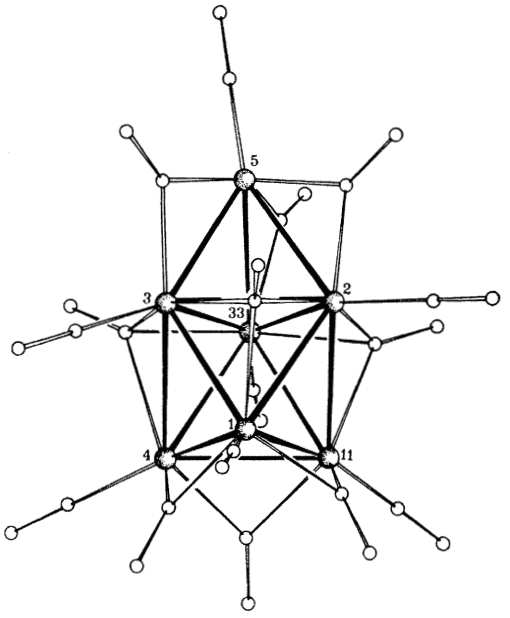

FIGURE 1. *A perspective view of the trianion* $[Rh_7(CO)_{16}]^{3-}$.

The metal atoms form the monocapped octahedron shown in Figure 2; this solid consists of an octahedron and a tetrahedron sharing a face. The *basal* atoms Rh(1), Rh(11) and Rh(4) form a regular triangle, with Rh–Rh distances of 2·72(1) Å, and are eight-fold co-ordinated by four metal atoms and four CO groups. Atoms Rh(2), Rh(3), and Rh(33), nine-fold co-ordinated by five metal atoms and four CO groups, also define a regular triangle with Rh–Rh distances of 2·77(1) Å. The two triangles are parallel, and in projection Rh(5) is at the centre of both. The resulting arrangement may be considered as a fragment of a metallic close packing; its ideal C_{3v} symmetry is destroyed by small displacements of the centres of the two triangles, and of Rh(5), from the C_3 axis, so that there remains only the C_s symmetry dictated by the space group.

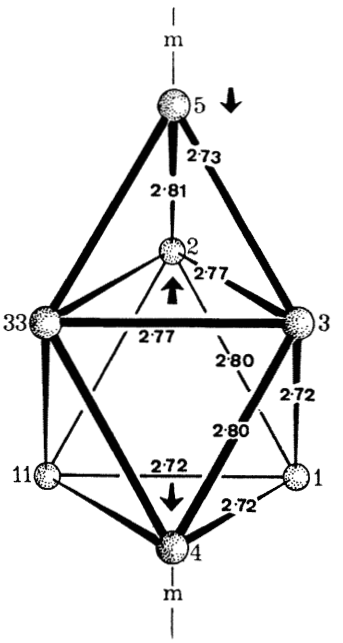

FIGURE 2. *Metal cluster in* $[Rh_7(CO)_{16}]^{3-}$ *with independent* Rh–Rh *distances. Individual e.s.ds are* 0·01 Å. *The arrows indicate the displacements of* Rh(5) *and of the centres of the two triangles from the ideal* C_3 *axis.*

As for the metal–carbon interactions, the following mean distances are found for terminal groups 1·82 Å, for double-bridging groups 1·97 Å, and for face-bridging groups 2·14 Å. Although the constraints assumed in the refinement for the C–O distances make the assignment of e.s.ds to individual and mean Rh–C distances problematical, the present results seem reasonable in the light of previously determined values[1] in $[Rh_{12}(CO)_{30}]^{2-}$.

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