Synthesis and *X*-Ray Characterization of the Novel $[Rh_{10}S(CO)_{10}(\mu\text{-}CO)_{12}]^{2-}$ Anion; a Bicapped Square-antiprismatic Cluster Containing an Interstitial Sulphur Atom

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Summary The anion $[Rh_{10}S(CO)_{22}]^{2-}$, obtained by slow decomposition of $[Rh_6(CO)_{14}(SCN)_2]^{2-}$ in tetrahydrofuran, has been investigated by *X*-ray diffraction; it contains a bicapped square-antiprismatic metal atom cluster, with an interstitial sulphur atom.

High-nuclearity carbonyl cluster complexes of rhodium exhibit a variety of metal atom geometries. They contain in many cases fragments of metallic lattices, as in the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (h.c.p. cluster),[1] $[Rh_{14}(CO)_{25}]^{4-}$ (b.c.c. cluster),[2] and $[Rh_{22}(CO)_{37}]^{4-}$ (mixed h.c.p.–c.c.p. cluster) (h.c.p. = hexagonal close-packed; b.c.c. = body-centred cubic; c.c.p. = cubic close-packed).[3] The presence of a main-group element in an interstitial hole can stabilize different arrangements of the metal atoms, however. In particular, polyhedra with larger cavities can be found as the ratio of the covalent radii of the interstitial to the lattice metal atoms increases.

With rhodium, interstitial C and N atoms occupy octahedral[4] or trigonal-prismatic[5,6] holes, while P and S atoms stabilize square-antiprismatic cavities,[7,8] and even larger cavities, such as icosahedral or cubo-octahedral, can be expected with interstitial atoms of increased dimensions.

In this paper we report the synthesis and structure of the anion $[Rh_{10}S(CO)_{22}]^{2-}$, the first example of a bicapped square-antiprismatic cluster compound, containing an interstitial sulphur atom. So far only one example of a cluster complex with encapsulated sulphur atoms has been reported, namely the $[Rh_{17}S_2(CO)_{32}]^{3-}$ anion.[8]

We were studying the di-substitution derivatives of $Rh_6(CO)_{16}$ with anionic ligands in order to get products which would be more suitable than the previously reported $[Rh_6(CO)_{14}(CN)_2]^{2-}$ anion[9] for an *X*-ray study of the stereochemistry of the ligands, when we observed that the di-thiocyanato-derivative[10] $[Rh_6(CO)_{14}(SCN)_2]^{2-}$ in tetrahydrofuran (THF) solution decomposes slowly to give a mixture of compounds among which the new anionic complex $[Rh_{10}S(CO)_{22}]^{2-}$ has been isolated and structurally characterized. E.s.r. measurements show that the dianion is diamagnetic.

In a typical experiment $Rh_6(CO)_{16}$ (1·8 g) was stirred under nitrogen for 24 h at room temperature in THF (50 ml) with KSCN (1·2 g) to give a brown solution from which the $[Rh_6(CO)_{14}(SCN)_2]^{2-}$ anion (i.r. bands at 2100 w, 2070 w, 2040 vs, 2010 m, 1775 m, and 1740 w cm^{-1})[10] was precipitated as the bistriphenylphosphineiminium $[(Ph_3P)_2N^+$: $PPN^+]$ salt by addition of aqueous (PPN)Cl. Crystallization of this salt from THF–propan-2-ol by the slow diffusion technique gave directly a first fraction containing crystals of $(PPN)_2[Rh_{10}S(CO)_{22}]$, together with by-products, while the mother liquor, on evaporation to dryness *in vacuo* and subsequent crystallization as above gave a second crop of the sulphur derivative in a pure state. The i.r. spectrum of the PPN^+ salt in THF solution showed bands at 2040 vw, 2010 vs, and 1830 ms cm^{-1}. Crystals of this salt have been investigated by *X*-ray diffraction.†

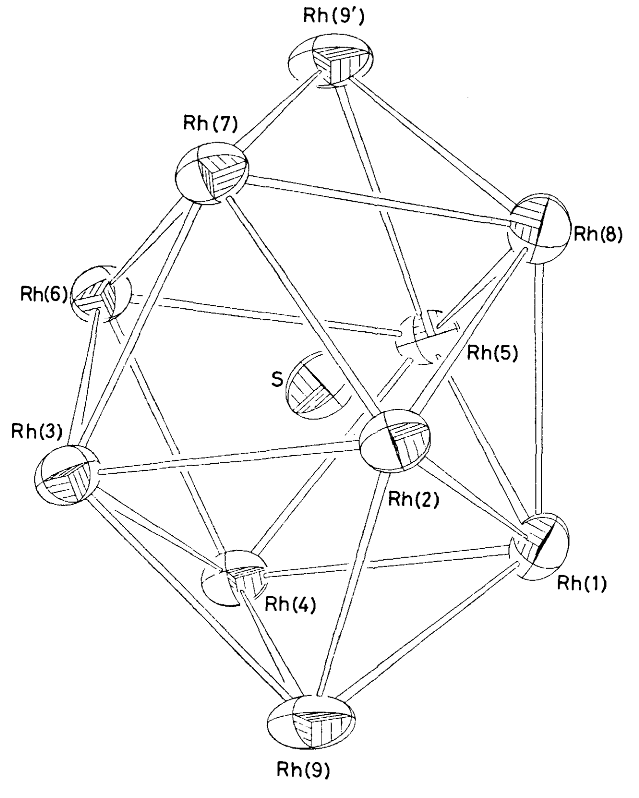

FIGURE 1. A view of the metal atom cluster in $[Rh_{10}S(CO)_{22}]^{2-}$ (one component of the disordered structure).

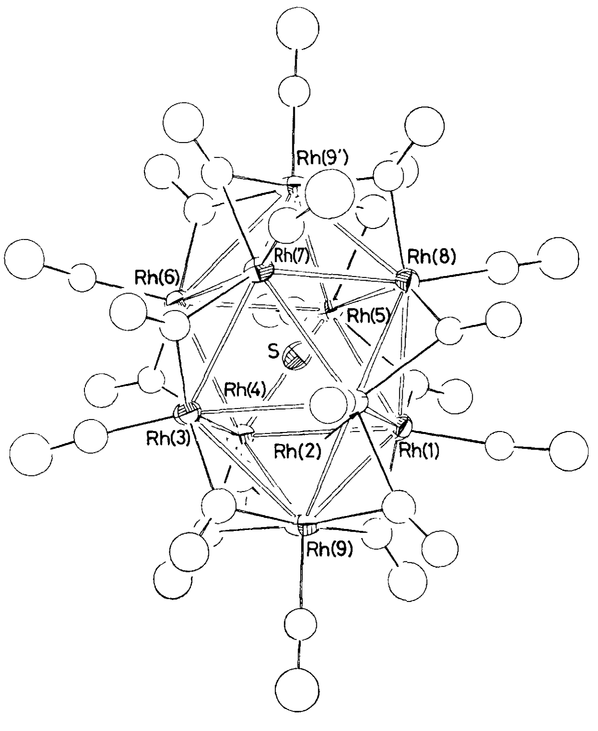

FIGURE 2. A view of the overall $[Rh_{10}S(CO)_{22}]^{2-}$ anion (one component of the disordered structure).

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† *Crystal data*: $C_{94}H_{60}N_2O_{22}P_4Rh_{10}S$, $M = 2754{\cdot}5$, monoclinic, space group $P2_1/c$ (No. 14), $a = 15{\cdot}196(2)$, $b = 16{\cdot}415(3)$, $c = 20{\cdot}204(4)$ Å, $\beta = 103{\cdot}15(2)°$, $Z = 2$. The structure was solved by direct methods which showed the location of the Rh_{10} bicapped square-antiprismatic cluster about an inversion centre (*a* in the Wyckoff notation), resulting in disorder of the eight metal atoms of the square antiprism; the interstitial S atom lies on the crystallographic inversion centre. Successive difference-Fourier maps showed that the positions of most of the carbonyl atoms were not doubled but were coincident for the two disordered models of the cluster, with the exception of the carbon atoms of the terminal CO groups bound to the eight disordered metals, which were treated as half atoms. The structure was refined by block-matrix least-squares on the basis of 4414 significant independent counter data to a current conventional *R* value of 0·072. The PPN^+ cations were not found to be disordered and the disorder in the metal cluster is clearly due to the coincidence of the carbonyl oxygen cages for the two centrosymmetrically related components of the anion. 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.

The metallic skeleton of $[Rh_{10}S(CO)_{22}]^{2-}$, of idealized D_{4d} symmetry, is illustrated in Figure 1. It consists of 8 rhodium atoms arranged at the corners of a square antiprism, with the other 2 metal atoms capping the square faces. A similar arrangement of atoms is present in the *closo* borane deltahedron of $[B_{10}H_{10}]^{2-}$.[11] The sulphur atom occupies the centre of the cluster. The complete anion, of idealized D_4 symmetry, is illustrated in Figure 2. Of the 22 carbonyl ligands, 10 are terminally bound, one per rhodium atom, 8 bridge the edges involving the capping atoms, and the other four bridge alternating edges connecting the two staggered squares. This stereochemistry is very similar to that found in the $[Rh_9P(CO)_{21}]^{2-}$ anion,[7] containing a monocapped square-antiprimsatic cluster, which might be considered the *nido*-derivative of the present Rh_{10} array.

The Rh–Rh distances fall into three classes: the intraplanar ones (within the two squares) ranging from 2·959(3) to 3·156(3) Å (mean 3·026 Å), the interplanar ones in the range 2·817(3)—2·890(3) Å (mean 2·862 Å), and the square-to-capping atoms bond lengths, in the range 2·781(3)—2·953(3) Å (mean 2·853 Å). Although, within each class, the rhodium–rhodium bond distances are rather scattered, the intraplanar bond lengths are, on average, significantly longer than the others. This feature seems to be related to the presence of the two capping atoms, since the $[B_{10}H_{10}]^{2-}$ anion also shows a similar behaviour, while in the $[Rh_9P(CO)_{21}]^{2-}$ and $[Sn_9]^{4-}$ species,[12] both containing a monocapped square antiprism, the intraplanar metal–metal bond distances are longer within the capped square than within the non-capped one.

The sulphur atom shows eight bond contacts (mean Rh–S 2·440 Å) and two longer contacts [3·060(1) Å] with the capping rhodium atoms. In contrast, in the $[Rh_{17}S_2(CO)_{32}]^{3-}$ anion,[8] the sulphur atoms, which are located in distorted monocapped square-antiprismatic cavities, exhibit an unusual 1 : 4 : 4 co-ordination, with mean Rh–S interactions of 2·168, 2·330, and 2·799 Å, respectively.

The Rh–C and C–O bond distances for the terminal carbonyl ligands have mean values of 1·81 and 1·21 Å. Of the bridging CO groups eight, bound to the capping rhodium atoms, are asymmetric (mean Rh_{cap}–C, Rh_{square}–C, and C–O 2·20, 1·97, and 1·16 Å, respectively), while the other four are symmetric (mean Rh–C and C–O 2·00 and 1·19 Å).

The anion possesses 142 valence electrons, in accord both with the M.O. calculations performed by Lauher[13] and also, because the cluster is similar to a borane deltahedron, with Wade's rules.[14]

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