The Crystal Structure of the Dicarbonylcyclopentadienylcobalt–Mercuric Chloride Complex

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METAL–METAL bonds have been classified according to the type of bonding thought to occur between the metal atoms.[1] Of the four classes suggested, *viz.*, (i) metallic, (ii) metal cluster, (iii) covalent, and (iv) metal donor, many examples are now known from the first three classes.[2] Metal–metal bonds of the donor-acceptor type are rare, and reported examples are restricted to the long-range interactions often found between d^8 metal atoms, such as in nickel dimethylglyoxime for instance.

We are now completing the crystal structure determination of the complex between dicarbonylcyclopentadienylcobalt and mercuric chloride,[3] and find that this complex is best formulated as containing a metal–donor bond between mercury and cobalt.

The crystals are monoclinic with $a = 7{\cdot}85$, $b = 13{\cdot}90$, $c = 9{\cdot}38$ Å, $\beta = 91{\cdot}1°$, space group $P2_1/n$, $Z = 4$. The reliability index for 1002 independent reflections is currently 0·094. The molecular stereochemistry is shown in the Figure, estimated standard deviations in the bond lengths are 0·006 Å for Hg–Co and 0·02 Å for Hg–Cl. The bond lengths in the cyclopentadienyl ring and carbonyl groups are normal.

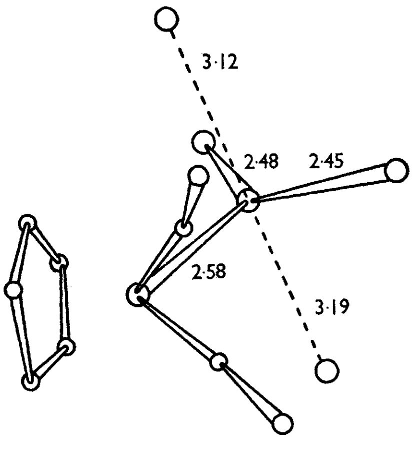

FIGURE. *Molecular stereochemistry of dicarbonylcyclopentadienylcobalt–mercuric chloride complex.*

The analysis confirms the presence of a Hg–Co bond, the bond length of 2·58 Å lies close to the sum of Pauling's single bond metallic radii,[4] 2·55 Å, and the sum of covalent radii obtained by the method of Bennett and Mason,[5] 2·56 Å (using 1·27 Å for Co^I taken from the mean $Co–C(C_5H_5)$ distance in the present structure, and 1·29 Å for Hg from methylmercuric chloride[6]). To a first approximation the Hg–Co bond must be considered a normal single covalent bond. The two shortest Hg–Cl bond lengths of 2·45 and 2·48 Å are equal within 1·5σ, and an ionic formulation such as $[(\pi\text{-}C_5H_5)Co(CO)_2(HgCl)]^+Cl^-$ in the solid is thereby ruled out. This conclusion is also supported by the near equality of the two Co–Hg–Cl bond angles of 125° and 121°. The compound is best described as a Lewis acid–base complex between $(\pi\text{-}C_5H_5)Co(CO)_2$ and mercuric chloride. In view of the structural similarities between this compound and complexes of mercuric chloride with donor molecules, in particular the tetrahydrothiophen complex $C_4H_8SHgCl_2$,[7] the cyclopentadienylcobalt dicarbonyl molecule is here considered to be the Lewis base. The Hg–Cl distances are considerably increased from the value observed in mercuric chloride of 2·25 Å[8] indicating considerable electronic redistribution on the mercury atom in the complex.

The primary co-ordination number of the mercury atom is three, with the $CoHgCl_2$ group planar. Two further chlorine atoms belonging to two different neighbouring molecules increase the overall co-ordination number to five, giving an elongated trigonal bipyramidal geometry about the mercury atom.

Metal–donor bonds are also expected to be found in other reported mercuric halide adducts such as $Fe(CO)_5,HgCl_2$.[9]

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