The Crystal Structure of Bis(chloropyridylmercury)tetracarbonyliron, Fe(CO)$_4$[HgCl(C$_5$H$_5$N)]$_2$

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Summary The crystal structure of Fe(CO)$_4$(HgCl·py)$_2$ has been determined by X-ray diffraction analysis: the iron atom is octahedrally co-ordinated by four carbonyl groups and two mercury atoms but the co-ordination of the mercury atoms involving one iron atom, two chlorine atoms, one pyridine nitrogen atom, and a possible mercury–mercury bond is not simple.

CHALMERS, LEWIS, AND WILD[1] have prepared a series of compounds of adducts of Fe(CO)$_4$(HgY)$_2$ where Y = Cl or Br with amines such as pyridine which form compounds of the formula Fe(CO)$_4$(HgY)$_2$,2py. These authors concluded that the pyridine groups co-ordinate to the mercury atoms.

Crystals of Fe(CO)$_4$[HgCl(C$_5$H$_5$N)]$_2$ are bright yellow, monoclinic needles elongated along the c axis, space group C_{2h}^6—$C2/c$, $a = 1566\cdot3(4)$, $b = 1156\cdot3(3)$, $c = 1268\cdot0(4)$ pm, $\beta = 121°49'(1')$, $Z = 4$. Diffraction data of a small single crystal collected using Mo-K_α radiation in the range $\theta < 23°$ on a computer-controlled[2] diffractometer produced 1474 measurements reducing to 879 unique observed $[I \geq 3\sigma(I)]$ diffraction maxima. The data were not corrected for absorption, extinction, or anomalous dispersion.

The structure was solved by the heavy-atom method and refined by least-squares analysis using anisotropic thermal parameters for Fe, Hg, and Cl and isotropic ones for the other atoms (neglecting H) to a value of R of $0\cdot077$.

The Fe atom lies on a crystal 2-fold axis and thus the complete molecule has 2-fold symmetry. The Fe atom is nearly regularly octahedrally co-ordinated to the four carbonyl groups and to the two Hg atoms in cis positions (see Figure). The Fe–C distances agree with that of 184(3) pm observed in iron pentacarbonyl.[3] There appears to be no other accurate structure analysis available with which to compare the Fe–Hg distance of $255\cdot2(8)$ pm.

Interpretation of the co-ordination of the mercury atom is not simple. In addition to Fe, there is a Cl atom 261(1)

pm and the N atom of the pyridine ring 251(6) pm from the Hg atom. Hg lies 45 pm above the plane of the other three atoms. The interatomic angles at the mercury atom are approximately trigonal being N–Hg–Cl = 90°, N–Hg–Fe = 123°, and Fe–Hg–Cl = 137°. In addition, however, atom Cl(2), related to atom Cl(1) by an inversion centre, is
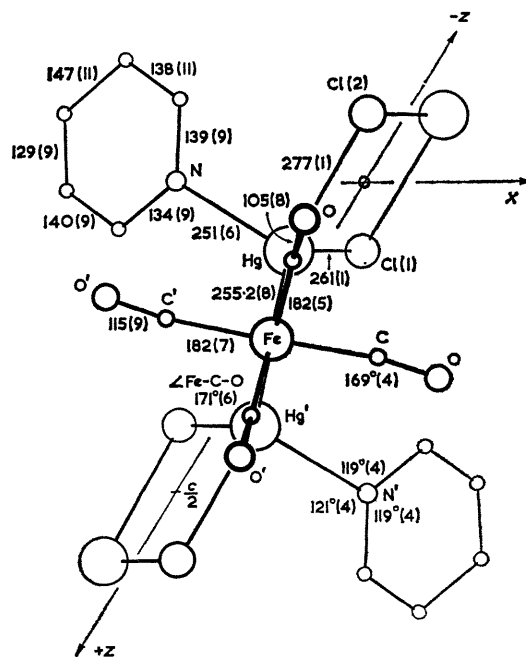

FIGURE. A projection of the crystal structure of Fe(CO)$_4$(HgCl·py)$_2$ down the 2-fold axis parallel to the crystal b axis which passes through the iron atom. Certain interatomic distances and angles are given in picometres and degrees respectively. Standard deviations in terms of the least significant digit given are in brackets.

277(1) pm distant from Hg This distance implies a bond because it is much less than the value 330 pm considered by Grdenic to be the sum of the van der Waals radii [4] Molecules are thus linked together by Hg–Cl bonds to form an infinite polymer in the direction of the *c* axis of the crystal, which is the developed needle axis Atom Cl(2) is not exactly above Hg perpendicular to the plane of the three trigonal ligands but forms angles through Hg of 87°, 93°, and 114° to Cl(1), N, and Fe respectively

There is also a strong possibility of an Hg–Hg bond in this compound The observed Hg–Hg distance is 317 1(4) pm, 40 pm less than the limit of 346 6 pm less than which Grdenic[4] considers some form of bonding to occur In the crystal structure of the parent compound $Fe(CO)_4$-$(HgBr)_2$, Baird and Dahl[5] considered that there is no Hg–Hg bond though the distance between the two atoms is 310 pm More important evidence than the Hg–Hg distance is the Hg–Fe–Hg angle, 77° The rest of the octahedral iron co-ordination is very nearly regular with interatomic angles near to 90° There is no crystalline reason for the Hg–Fe–Hg angle to be less than 90° We conclude from the Hg–Hg distance of 317 pm and the Hg–Fe–Hg angle of 77° that there is some Hg–Hg bonding present Atom Hg′ is not exactly above Hg perpendicular to the plane of the trigonal ligands, but the angles to these ligands through Hg are 95°, 108°, and 52° to Cl(1), N, and Fe respectively The Cl(2)–Hg–Hg′ angle is 158° On this basis the co-ordination polyhedron of the mercury atom is a distorted trigonal bipyramid

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[5] H W Baird and L F Dahl, *J Organometallic Chem*, 1967, **7**, 503