The Crystal Molecular Structure of Mercury Cobalt Carbonyl

By G. M. SHELDRICK* and R. N. F. SIMPSON

(*University Chemical Laboratory, Lensfield Road, Cambridge*)

DESPITE the current interest[1] in compounds involving transition-metal to mercury bonds, the only relevant crystal structure reported is that of $(BrHg)_2Fe(CO)_4$.[2] We have determined the crystal structure of $Hg[Co(CO)_4]_2$ in order to establish the nature of the co-ordination of the mercury by cobalt atoms, whether or not any of the carbonyls are bridging and whether the co-ordination of the cobalt atoms approximates to trigonal bipyramidal or square pyramidal.

$Hg[Co(CO)_4]_2$ crystallizes in the monoclinic space group $P2_1/a$ with z as needle axis; $a = 12{\cdot}59$, $b = 16{\cdot}44$, $c = 6{\cdot}62$ Å, $\beta = 100{\cdot}7°$. Intensity measurements were made visually using Weissenberg and oscillation photographs and Mo-K_α radiation. Lorentz, polarization, absorption and anomalous dispersion (Templeton) corrections were applied. The structure was solved by Patterson and Fourier methods, and refined by differential Fourier synthesis followed by full-matrix least-squares with anisotropic temperature factors for the heavy atoms; the current R factor is 0·146 for the 1045 observed reflections. The asymmetric unit consists of one molecule with every atom in a general position. The molecule has approximately D_{3d} symmetry, in agreement with the interpretation of the Raman spectra in solution;[3] the carbonyl groups are staggered with respect to one another. The idealized co-ordination about the cobalt atoms is trigonal bipyramidal, but the equatorial carbonyls are bent by an angle of $8 \pm 3°$ towards the mercury atom. A similar effect has been observed in $Ph_3PAuCo(CO)_4$[4] and $Cl_3SiCo(CO)_4$.[5] The $HgCo_2$ unit is linear and symmetrical; the Hg–Co bond lengths are 2·496 and 2·499 ± 0·01 Å; the Co · · · Co distance is 4·994 ± 0·02 Å. All the Co–C–O groups are linear within experimental error; the mean Co–C distance is 1·70 Å and the mean C–O distance is 1·21 Å.

Further refinement is in progress to establish whether the variations in Co–C and C–O distances are significant.

(*Received, August 31st, 1967; Com. 929.*)

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