Crystal Structure of Tetrakispentafluorophenyl-μ-bisdiphenylarsinomethane-dimercury(II), a Three-co-ordinate Mercury Complex

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Summary The complex $[(C_6F_5)_2Hg]_2Ph_2AsCH_2AsPh_2$ contains three-co-ordinate mercury with a planar approximately T-shaped stereochemistry and a mercury–arsenic bond length of 3·40 ± 0·02 Å.

MERCURY(II) complexes with three short bonds (characteristic[1] three-co-ordination) are well known[1,2] but usually have one or more additional contacts within the sum of the appropriate van der Waals radii.[1] A series of potentially three-co-ordinate complexes of bispentafluorophenylmercury(II) have recently been prepared,[3] *e.g.* $(C_6F_5)_2HgPh_2NH$ and $(C_6F_5)_2HgPh_3PO$. The title compound was chosen from these for an *X*-ray study because it is one of the least stable in solution and i.r. spectra give no indication of complex formation in the solid.[3] Thus, confirmation of its stereochemistry would support the formulation of the others as three-co-ordinate complexes.

Crystals of $[(C_6F_5)_2Hg]_2Ph_2AsCH_2AsPh_2$ are colourless, elongated in the [001] direction, and are monoclinic with $a = 14·07$, $b = 17·34$, $c = 19·33$ Å, $\beta = 91·05°$, $D_m = 2·15$, $Dc = 2·17$ g cm^{-3}, $Z = 4$, space group $C2/c$. A total of 1218 independent non-zero reflections were collected and measured visually for reciprocal lattice levels $hk0$—$hk12$ using equi-inclination Weissenberg geometry and Cu-K_α radiation. The structure was solved by Patterson and Fourier methods; difference Fourier syntheses indicated anisotropy of the mercury and arsenic atoms, and block-diagonal least-squares refinement with anisotropic temperature factors for mercury and arsenic (all other atoms isotropic) led to a model with a residual index $R = 0·091$. No correction was made for anomalous dispersion.

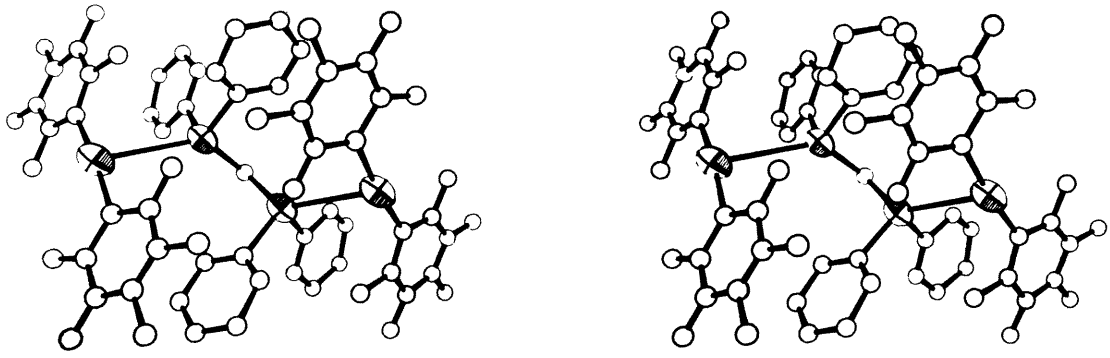

FIGURE. *Stereoscopic illustration of* $[(C_6F_5)_2Hg]_2Ph_2AsCH_2AsPh_2$ *viewed along the* [010] *direction to show the two-fold axis. The figure was drawn by a Fortran thermal-ellipsoid plot program for crystal structure illustrations. (C. K. Johnson, Oak Ridge National Laboratory,* 1965.)

The methylene carbon atom of the diarsine ligand is on the special position $0y\frac{1}{4}$ imposing a two-fold axis on the complex (see Figure). The phenyl and pentafluorophenyl rings are planar and the stereochemistry about the mercury atom is approximately planar, the mercury atom being 0·057 ± 0·006 Å away from the mean co-ordination plane, and approximately T-shaped with a C–Hg–C angle of 173 ± 4°, As–Hg–C angles of 90 and 96 ± 3°, and Hg–C bond distances of 2·07 and 2·15 ± 0·12 Å. The mercury–arsenic distance of 3·40 ± 0·02 Å is only slightly less than the sum of the van der Waals radii of 3·50 Å (with arsenic 2·0 Å[4] and mercury 1·50 Å[1]). However, Grdenić suggests that a limit of 1·73 Å for the radius of mercury can be used as a criterion to indicate some form of bonding.[1] Thus, the mercury–arsenic bond is expected to be weak, in agreement with complete dissociation of the complex in benzene.[3]

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[3] A. J. Canty and G. B. Deacon, *Austral. J. Chem.*, 1971, **24**, 489.
[4] L. Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell, New York.