Crystal Structures of the 1:1 Complexes of Mercury(II) Chloride with Phosphines or Arsines: $R_3P,HgCl_2$ (R = Me, Et, or Ph) and $Ph_3As,HgCl_2$

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Summary The crystal structures of a series of mercury(II) chloride complexes $R_3M,HgCl_2$ have been found to range from discrete chlorine-bridged dimers (R = Ph, X = As or P) to chain-like arrangements made up of monomeric $Et_3P,HgCl_2$ units or $[Me_3P,HgCl]^+Cl^-$ ions.

Mercury(II) chloride forms 1 : 1 complexes with a wide range of neutral unidentate ligands. The structures of many of these have been described as discrete chlorine-bridged dimers on the basis of Raman and/or far-i.r. spectroscopic work. The crystallographic and even the spectroscopic evidence for this supposition is limited, yet it is frequently asserted[1] that such structures are prevalent. Hence we have determined the crystal structures of a series of these complexes, $Ph_3P,HgCl_2$ (I), $Me_3P,HgCl_2$ (II), and $Et_3P,HgCl_2$ (III).

We find that only (I) contains discrete chlorine-bridged dimers. The bridge is almost totally symmetrical with Hg-Cl(1) distances of 2·66 and 2·62(1) Å, which is in contrast to the less symmetrical arrangement found[2] in $Ph_3PSe,HgCl_2$ [2·60 and 2·78(1) Å]. Preliminary *X*-ray analysis of $Ph_3As,HgCl_2$ shows it to be isostructural with (I).

In (II) and (III) it is not possible to identify discrete. dimeric units, and both contain chain-like arrangements in which mercury has an overall co-ordination number of five. Thus the structure of (II) is comparable to that found[3] in the tetrahydrothiophen complex $C_4H_8S,HgCl_2$, and may be interpreted as a zig-zag arrangement of $[Me_3P,HgCl]^+$ cations linked together by Cl^- anions. There is only one 'short' Hg–Cl bond, [Hg–Cl(2), 2·36(1) Å], while three further Cl^- anions lie at distances of 2·77, 2·94, and 3·49(1) Å from mercury.

Complex (III) is of yet different structure to the other two phosphine complexes (Figure). There are two short Hg–Cl bonds [Hg–Cl(1), 2·53; Hg–Cl(2), 2·40 Å], and (III) may be considered to contain monomeric $Et_3P,HgCl_2$ units linked together by relatively long intermolecular Hg–Cl interactions [Hg–Cl(1′), 3·03; Hg–Cl(2′), 3·20(1) Å]. The resulting chain-like arrangement is similar to that found[4] in the collidine complex $C_8H_{18}N,HgCl_2$, although the elongated trigonal bipyramidal geometry around mercury is more distorted in (III).

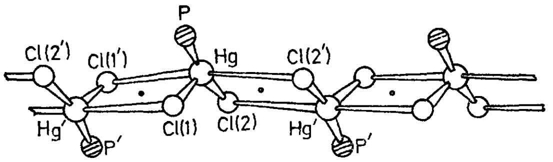

FIGURE. Molecular structure of $Et_3P,HgCl_2$ (III). *Crystal data*: Monoclinic, $a = 7{\cdot}44$, $b = 11{\cdot}54$, $c = 13{\cdot}44$ Å, $\beta = 105{\cdot}9°$; space group $P2_1/c$, $Z = 4$; $R = 0{\cdot}117$ for 1006 independent reflections. Important parameters: Hg–P, 2·36(1); Hg–Cl(2), 2·40(1); Hg–Cl(1), 2·54(1); Hg–Cl(1′), 3·03(1); and Hg–Cl(2′), 3·20(1) Å; and ∠P–Hg–Cl(2), 145·5(5); P–Hg–Cl(1), 115·3(5); Cl(1)–Hg–Cl(2), 99·1(5); and Cl(1′)–Hg–Cl(2′), 170·7(5)°.

It is therefore clear that marked structural differences exist between these 1 : 1 complexes, depending on the nature of the phosphine ligand. It is probably the larger size of the Ph_3P ligand relative to that of Et_3P or Me_3P which inhibits (I) from developing the extended structures found in (II) and (III), leading instead to the formation of discrete dimers. The structural trends are illustrated by comparison of the P–Hg–Cl(2) angles: 128·7(4)° for (I), 145·5(5)° for (II), and 161·8(3)° for (III).

All three phosphine complexes contain one short Hg–Cl bond, *ca.* 2·40 Å in length, and these values may be correlated with ν(Hg–Cl) frequencies that occur in the 280–300 cm^{-1} region of the i.r. spectrum. However, these same bands have often been used to indicate the presence of discrete chlorine-bridged dimers; such descriptions for (II) and (III) are incorrect and care is needed in spectra–structure correlations of this type.

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[1] G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 1969, **25A**, 355; G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166; G. Marcotrigiano and R. Battistuzzi, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3719; I. S. Ahujah and P. Rastogi, *ibid.*, 1970, **32**, 2085; F. G. Moers and J. P. Langhout, *Rec. Trav. chim.*, 1973, 92, 996; H. Schmidbaur and K. H. Rathlein, *Chem. Ber.*, 1973, **106**, 2491.

[2] L. S. D. Glasser, L. Ingram, M. G. King, and G. P. McQuillan, *J. Chem. Soc.* (*A*), 1969, 2501.

[3] C. I. Bränden, *Arkiv Kemi*, 1964, **22**, 495.

[4] S. Kulpe, *Z. anorg. Chem.*, 1967, **349**, 314.