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Mixed Co-ordination in the Crystal Structures of Tertiary Phosphine Complexes of Mercury(II) Chloride: $(Me_2EtP)_3(HgCl_2)_2$ and $(Bu^n{}_3P)HgCl_2$

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Tertiary phosphines are known [1] to form complexes with mercury(II) chloride having R_3P:$HgCl_2$ ratios of 2:1, 3:2, 1:1, 2:3, or 1:2, and many analogous compounds with other ligands have been described. However, crystallographic data are limited for all of these stoichiometries and the inherent dangers of the indiscriminate use of vibrational spectroscopy for structure elucidation of these systems have already been pointed out [2]. It is therefore to provide the first single crystal X-ray analysis of a 3:2 type complex and to extend the basis of vibrational spectra–structure correlations for such systems, that we report the crystal structures of $(Me_2EtP)_3(HgCl_2)_2$ (I) and $(Bu^n{}_3P)HgCl_2$ (II).

Results and Discussion

Crystals of (I) were selected from a sample thought to be $(Me_2EtP)_2HgCl_2$, but subsequent chemical and X-ray analyses showed that while the bulk of the sample had 2:1 stoichiometry, the larger crystals present had the composition of $(Me_2EtP)_3(HgCl_2)_2$. Complex (II) was obtained as the initial precipitate formed on adding an ethanolic solution of $Bu^n{}_3P$ to a solution of $HgCl_2$ in the same solvent, and was recrystallised from heptane/benzene.

Crystal Data

$C_{12}H_{33}P_3Hg_2Cl_4$ (I), orthorhombic, a = 18.755, b = 13.749, c = 9.740 Å. Space group $P2_12_12_1$, Z = 4, R = 0.055 for 2256 independent reflections.

$C_{12}H_{27}PHgCl_2$ (II), monoclinic, a = 13.698, b = 25.475, c = 10.621 Å, β = 100.78°. Space group $P2_1/n$, Z = 8, R = 0.089 for 1294 independent reflections.

Complex (I) is found to have an extended chain-like structure with the unusual feature of mercury atoms having alternating co-ordination numbers of four and five. The structure can be envisaged as consisting of $[(Me_2EtP)_2Hg]^+$ cations and $[(Me_2EtP)HgCl_3]^-$ anions linked together by chlorine bridges (Figure). Mercury has a distorted tetrahedral

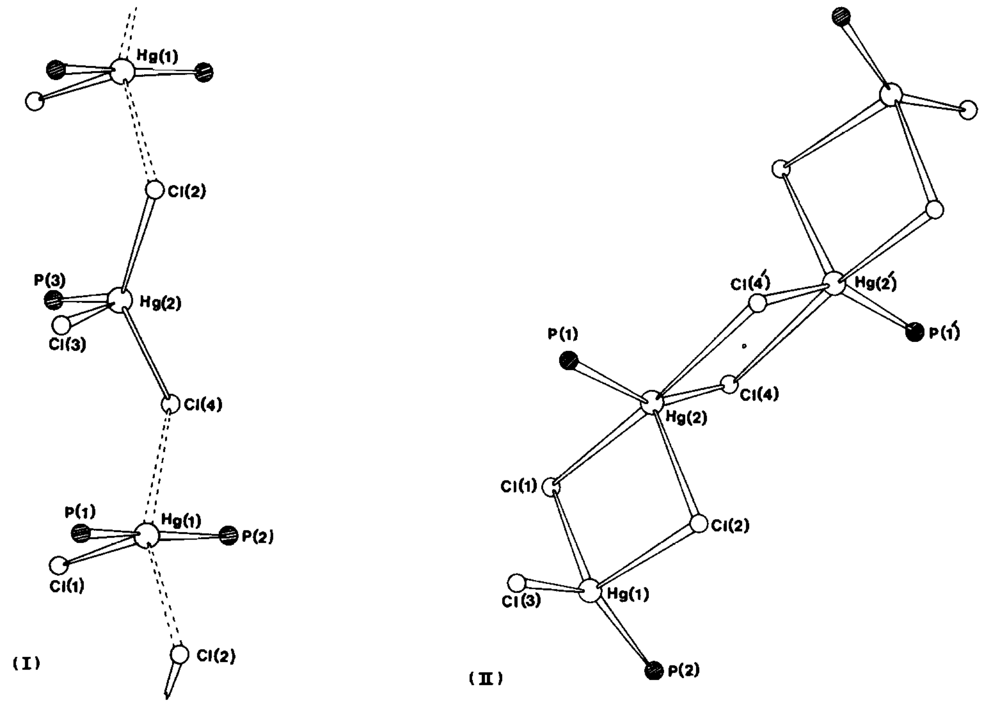

Figure. X-ray structures of $(Me_2EtP)_3(HgCl_2)_2$ (I) and $(Bu^n_3P)HgCl_2$ (II).

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co-ordination within the anionic species with Hg–Cl distances varying from 2.46 to 2.64(1) Å and angles about mercury ranging from 98 to 133°. A 'T-shape' arrangement of one chlorine and two phosphorus atoms gives mercury a primary co-ordination of three within the $[(Me_2EtP)_2HgCl]^+$ cations, with the P–Hg–P bond angle being 172.2(3)°. The presence of two further chlorine atoms associated with the anions increases this coordination number to five, giving a distorted trigonal bipyramidal arrangement about mercury.

The novel feature of alternating four and five co-ordination about mercury is, surprisingly, also found in (II), which has a unique tetrameric structure. The terminal mercury atoms lie in distorted tetrahedral environments (angles at mercury vary from 92 to 148°), while the co-ordination polyhedra about the two central heavy atoms are best described as distorted trigonal bipyramids having a Cl(1)–Hg(2)–Cl(4′) bond angle of 177°. The presence in the tetrameric species of two short Hg–Cl bonds [Hg(1)–Cl(3), 2.29 Å; Hg(2)–Cl(4), 2.29 Å] along with two different asymmetric chlorine-bridged systems can, with hindsight, be correlated with ν(Hg–Cl) frequencies observed for the complex in the 100–300 cm^{-1} region of the i.r. spectrum. The latter consists of a complex pattern of bands, characteristically different from the spectra observed both for chlorine-bridged dimers as found [2] in $(Ph_3P)HgCl_2$, and for polymeric type structures as found [2] for example in $(Et_3P)HgCl_2$. It is therefore evident that the size of the ligand plays a particularly important role in determining the extent of association within such 1:1 phosphine complexes. Thus, while $(Ph_3P)HgCl_2$ is found to contain discrete chlorine-bridged dimers, the smaller Et_3P and Me_3P ligands allow closer approach, giving rise to polymeric structures. The formation of tetramers when $Bu^n{}_3P$ is the ligand in (II) thus represents an intermediate stage.

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