Structural studies of phosphine complexes of mercury (II) halides.

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Structural Studies of Phosphine Complexes of Mercury(II) Halides

by

Lorraine Anne March

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ABSTRACT

Previous investigations of the solid-state structures of $(R_3P)_nHgX_2$ (where X = Cl, Br, or I and n = 1 or 2) complexes have been extended by the determination of the structures of the following:

(i) $[(Pr_3P)HgCl_2]_2$	(vi) $[(NCCH_2CH_2)_3PHgCl_2]_n$
(ii) $[(Pr_3P)HgBr_2]_2$	(vii) $[(Ph_3P)HgI_2]_2$
(iii) $[(\alpha\text{-}Pr_3P)HgI_2]_n$	(viii) $[(NCCH_2CH_2)_3P]_2HgCl_2$
(iv) $[(\beta\text{-}Pr_3P)HgI_2]_2$	(ix) $[(NCCH_2CH_2)_3P]_2HgBr_2Me_2CO$
(v) $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$	(x) $[(2\text{-thienyl})_3P]_2HgCl_2$

As with previously solved 1:1 mercury(II) halide tertiary phosphine complexes (i) to (vii) show a wide variety of structures. These vary from symmetrical halogen-bridged dimers (e.g. $[(Pr_3P)HgCl_2]_2$) to a polymeric chain structure for $[(\alpha\text{-}Pr_3P)HgI_2]_n$. Both $[(\beta\text{-}Pr_3P)HgI_2]_2$ and $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$ show the unusual feature for halogen-bridged dimers, of having both phosphine ligands attached to the same metal atom. In the case of $I_2Cd(\mu\text{-}I)_2Hg(PPr_3)_2$ both phosphine groups are attached to the mercury atom, showing mercury to have a stronger affinity than cadmium for phosphorus.

The 2:1 complexes all are distorted monomeric tetrahedral structures, $[(NCCH_2CH_2)_3P]_2HgCl_2$ consisting of two independent monomeric units. However, $[(NCCH_2CH_2)_3P]_2HgBr_2Me_2CO$ which contains a molecule of acetone has a trigonal bipyramidal arrangement due to a weak interaction between the mercury atom and the oxygen atom from the acetone molecule.

The solid-state structures of these complexes have been rationalised in the terms of:

(a) the donor strengths of the R_3P ligands

(b) the donor strengths of the halides

For 2:1 complexes strong σ-phosphine donors give a greater distortion of the structure from the tetrahedral, having large P-Hg-P bond angles and short Hg-P bond lengths. Similarly, for the limited data available, the weaker σ-bonding halides (e.g. Cl) give the predicted trends of short Hg-P bond lengths accompanied by larger P-Hg-P bond angles.

The situation for the 1:1 compounds is more complex with some σ-phosphine donors forming more extended structures. A few of these 1:1 complexes are known to exist in more than one form, for example, Bu_3PHgCl_2 and Pr_3PHgI_2. In both of these cases one form is a halogen-bridged dimer, the other form being a more extended structure; in the former it is tetrameric and in the latter a halogen-bridged chain structure. The expected trend of short Hg-P bond lengths and larger P-Hg-X angles for strong σ-phosphine donors is still apparent in these structures as is the shortening of the Hg-P bonds and increase in the associated X_t-Hg-P angles for weak σ-donor halides.

Objectives

Previous work has shown that a variety of structural types are possible for the 1:1 series of complexes of tertiary phosphines with mercury(II) halides. Additionally, certain molecular parameters found for a limited range of 1:1 and 2:1 complexes appear to be dependent upon the nature of the phosphine ligand. In order to more clearly establish the major factors which influence the type of structure and geometric parameters adopted for $(R_3P)_nHgX_2$ ($n = 1$ or 2, X = Cl, Br or I) the full X-ray structure has been determined for a much wider range of complexes. The mercury(II) halide-tertiary phosphine complexes have been chosen with varying halogen atoms and phosphine ligands, in order to extend an understanding of both the effect of the halogen atom and of the σ-donor capacity of the phosphine upon the nature of the complex and the geometry adopted.

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1. General Introduction

1.1 General Properties of Zinc, Cadmium and Mercury

Mercury is a member of group IIB along with zinc and cadmium and they all have the general outer electronic configuration $nd^{10}(n+1)s^2$. Although all have the common oxidation state of M(II), mercury also has an oxidation state Hg(I), giving rise to several stable compounds. In contrast, zinc(I) and cadmium(I) compounds are very unstable and are not easily isolated. The melting points of zinc and cadmium are 420 °C and 320 °C respectively but mercury is an unusual metal in that it is liquid at room temperature, having a melting point of -39 °C. X-ray diffraction studies of liquid mercury show that each mercury atom is surrounded by six close atoms at 3.00 Å and six more distant atoms at 3.47 Å[1]. Solid mercury shows similar hexagonal packing,[2] whereas the vapour is shown to be monatomic. Both zinc and cadmium adopt hexagonal structures at room temperature.[3]

In their compounds all three metals show a range of co-ordination numbers varying from two to eight. All three give linear two co-ordination, mercury more commonly than zinc and cadmium. All three also adopt tetrahedral four co-ordination, trigonal bipyramidal five co-ordination and octahedral six co-ordination, often distorted from the regular shapes (Figs. 1.1-1.3). Mercury also shows cubic eight co-ordination.

The covalent radii of zinc, cadmium and mercury atoms decrease with increasing co-ordination number. For example, four co-ordinate compounds of Zn, Cd and Hg are found to have covalent radii of 1.31, 1.48 and 1.48 Å respectively whereas in octahedral six-co-ordinate compounds the covalent radii have decreased to 1.27, 1.45 and 1.45 Å respectively.

1.2 Metal(I) Halides

Of the three metals only mercury forms stable M(I) halides, although halides of cadmium(I) and zinc(I) have been detected they have not been isolated. Mercury forms all four Hg(I) halides and all have similar dimeric structures.[10] These would appear to be dominated by linear two co-ordination about each mercury, with two mercury and two halogen atoms being colinear (Fig. 1.4). The co-ordination in this dimeric unit is extended to six by weak interaction of four distant halogen atoms (X').

1.3 Metal(II) Halides

Zinc, cadmium and mercury all form the M(II) halides, those of Hg(II) being the most stable. The fluorides are ionic, with that of zinc having a rutile type structure[11] and those of cadmium and mercury adopting a fluorite type structure (Figs. 1.5, 1.6).[1,12] Zinc chloride and bromide have cubic close-packed arrangements while the iodide has a hexagonal close-packed layer structure (Fig. 1.7). Cadmium chloride, bromide and iodide all have layer lattices. The iodide structure is based on a hexagonal close-packing arrangement of iodine atoms (Fig. 1.7) while the other two halide structures involve cubic close-packing arrangements of the halogen atoms.[1] Mercury(II) chloride has a stacked linear structure (Fig. 1.8). The α-form of mercury(II) iodide has a distorted cubic close-packed structure while the β-form adopts a distorted brucite structure also found in mercury(II) bromide.[1]

1.4 Complexes Formed Between Metal(II) Halides and Monodentate Ligands

The halides of all three metals form a range of complexes with monodentate and polydentate neutral ligands having nitrogen, arsenic, sulphur, oxygen or phosphorus as the donor atom. The complexes have a variety of co-ordination numbers, commonly ranging from two to six, but some eight-co-ordinate complexes are also known. The discussion in this section is limited to a discussion of compounds formed between the metal halides and monodentate ligands; complexes formed with polydentate ligands are not included. A more detailed discussion of complexes formed with tertiary phosphines is included in section 1.5.

1.4.1 Zinc Halide Complexes

Few structures of zinc halide complexes are known with any certainty. A variety of 2:1 complexes L_2ZnX_2 have been prepared and studied mainly by infrared vibrational techniques. Interpretation of infrared data indicates the 2:1 complexes formed between zinc halides and p-toluidine,[13] pyridine and substituted pyridines[14,15] adopt monomeric tetrahedral structures. An X-ray study of (thiourea)$_2$ $ZnCl_2$ shows it to have a simple monomeric structure with slightly distorted tetrahedral co-ordination about zinc (Cl-Zn-Cl, 107.3(2)°; S-Zn-S, 111.5(2)°).[16] The 1:1 phosphine complexes of Zn(II) halides are discussed in section 1.5.1, but few other 1:1 complexes are known.

1.4.2 Cadmium Halide Complexes

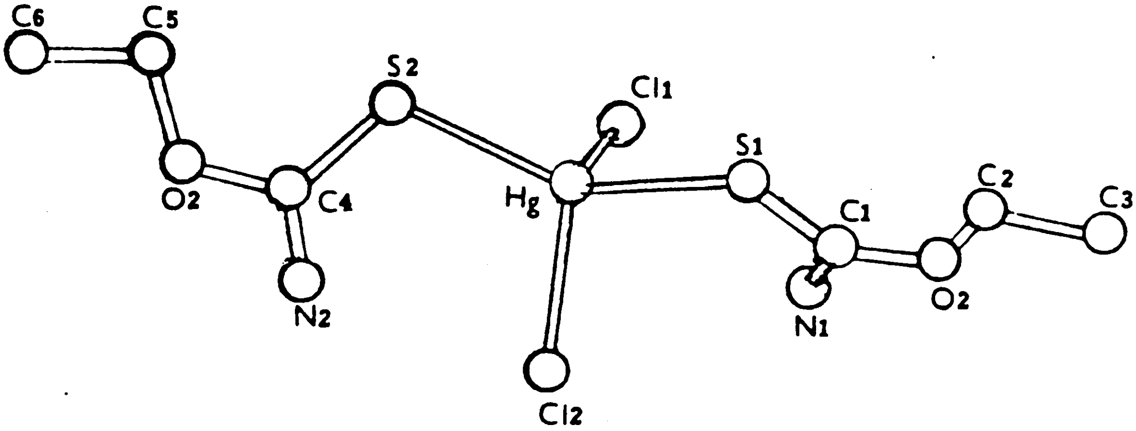
Many examples of 1:1 cadmium halide complexes containing neutral monodentate ligands are known and these are usually polymeric. The structures generally consist of a double chain arrangement involving halogen bridging, resulting in a distorted octahedral arrangement about each cadmium atom (Fig. 1.9). A number of 2:1 cadmium complexes (L_2CdX_2) have a halogen-bridged single chain polymeric structure in which cadmium has an octahedral environment, the fifth and sixth positions being occupied by a neutral monodentate ligand (Fig. 1.10). Other 2:1 complexes give rise to monomeric distorted tetrahedral structures (Fig. 1.11).

1.4.3 Mercury(II) Halide Complexes

Many 1:1 mercury(II) halide complexes of monodentate donor ligands form halogen-bridged dimers (Fig. 1.12) although a few complexes, which have oxygen as a donor have been shown to form oxygen-bridged dimers (Fig.

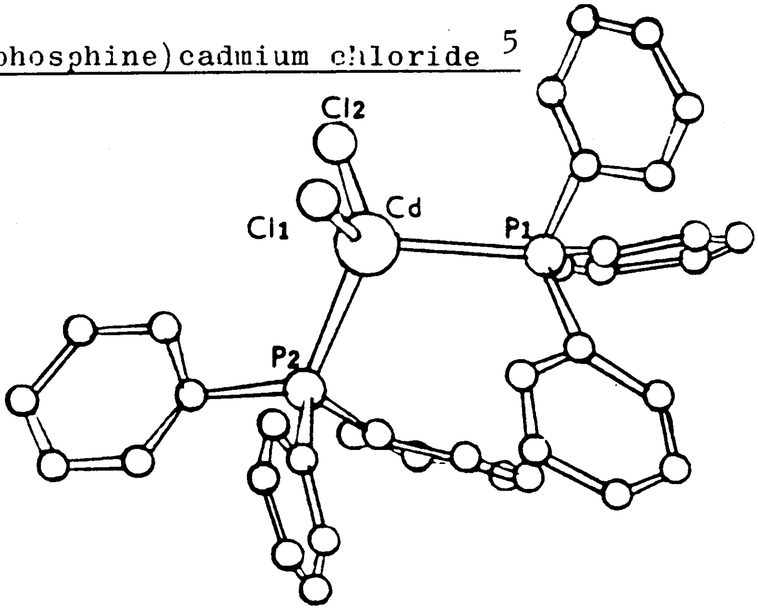
1.13). Some 1:1 complexes have extended five co-ordination resulting in a trigonal bipyramidal structure (Fig. 1.2). For 2:1 complexes (L_2HgX_2) a distorted monomeric tetrahedral structure is common, but some complexes have an effective five co-ordinate trigonal-bipyramidal arrangement (Fig. 1.14). Some 2:1 complexes as for example (pyridine)$_2$HgCl$_2$[27,28] and (methanol)$_2$HgCl$_2$[29] adopt polymeric structures in which mercury occupies a distorted octahedral arrangement (Fig. 1.15).

Bis(o-ethylthiocarbamate)mercury chloride[4]



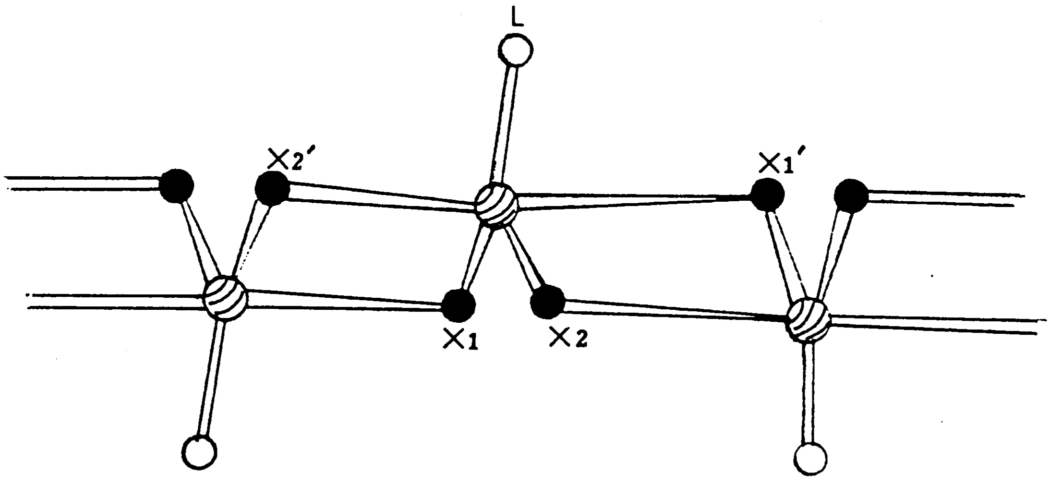
Bond lengths (Å)		Bond angles (°)			
Hg-S1	2.62(1)	S1-Hg-S2	96.2(2)	S2-Hg-Cl1	103.2(2)
Hg-S2	2.58(1)	S1-Hg-Cl1	103.2(2)	S2-Hg-Cl2	112.4(2)
Hg-Cl1	2.45(1)	S1-Hg-Cl2	106.5(2)	S2-Hg-Cl2	129.9(2)
Hg-Cl2	2.43(1)				

Bis(triphenylphosphine)cadmium chloride[5]



Bond lengths (Å)		Bond angles (°)			
Cd-Cl1	2.504(6)	Cl1-Cd-Cl2	113.9(2)	Cl2-Cd-P1	105.7(2)
Cd-Cl2	2.440(6)	Cl1-Cd-P1	104.5(2)	Cl2-Cd-P2	112.1(2)
Cd-P1	2.635(6)	Cl1-Cd-P2	112.2(2)	P1-Cd-P2	107.6(2)
Cd-P2	2.632(6)				

Fig. 1.1 Tetrahedral Four Co-ordination



(2,4-Dimethylpyridine)$HgBr_2$ [6]

Bond lengths (Å)

Hg-Br1	2.621(3)
Hg-Br2	2.486(4)
Hg-Br1'	2.911(3)
Hg-Br2'	3.548(4)
Hg-N	2.21(2)

Bond angles (°)

Br1-Hg-Br1'	92.4(2)
Br1-Hg-Br2	122.2(2)
Br1-Hg-Br2'	83.5(2)
Br1-Hg-N	106(1)
Br1'-Hg-Br2	100.8(2)
Br1'-Hg-Br2'	164.9(3)
Br1'-Hg-N	90(1)
Br2-Hg-Br2'	93.6(2)
Br2-Hg-N	129(1)
Br2'-Hg-N	77(1)

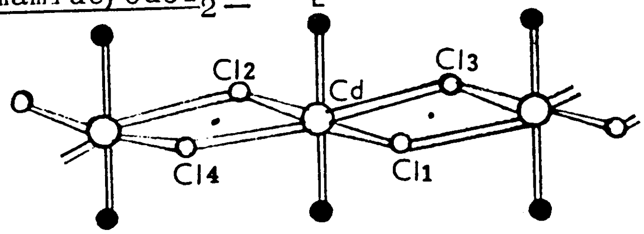
(Collidine)$HgCl_2$ [7]

Hg-Cl1	2.455(18)
Hg-Cl2	2.542(18)
Hg-Cl1'	2.956(18)
Hg-Cl2'	2.948(18)
Hg-N	2.131(18)

Cl1-Hg-Cl1'	85.8
Cl1-Hg-Cl2	110.1
Cl1-Hg-Cl2'	93.3
Cl1-Hg-N	122.5
Cl1'-Hg-Cl2	94.7
Cl1'-Hg-N	89.3
Cl2-Hg-Cl2'	84.3
Cl2 Hg-N	128.4
Cl2'-Hg-N	92.1

Fig 1.2 Trigonal Bipyramidal Five Co-ordination

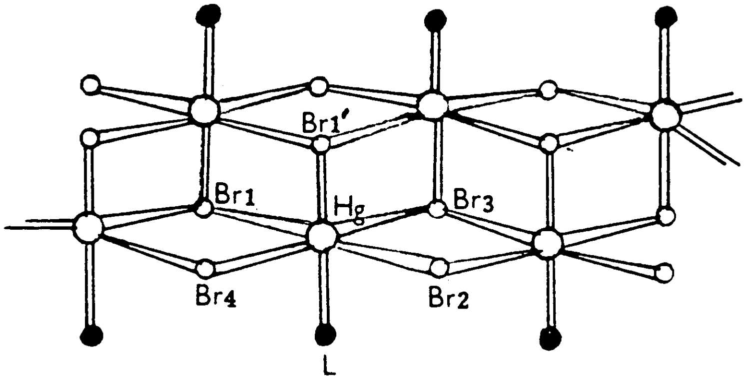
(Bisformamide) CdCl$_2$^{8}



Bond lengths (Å)	
Cd-Cl1	2.383(8)
Cd-Cl2	2.912(8)
Cd-Cl3	2.910(8)
Cd-Cl4	2.379(8)
Cd-O	2.34 (3)

Bond angles (°)	
Cl1-Cd Cl3	90.1(2)
Cl2-Cd-O	83.0(1)
Cl2-Cd-Cl4	89.8(3)
Cl3-Cd-Cl4	180 (-)
Cl3-Cd-Cl2	89.9(-)

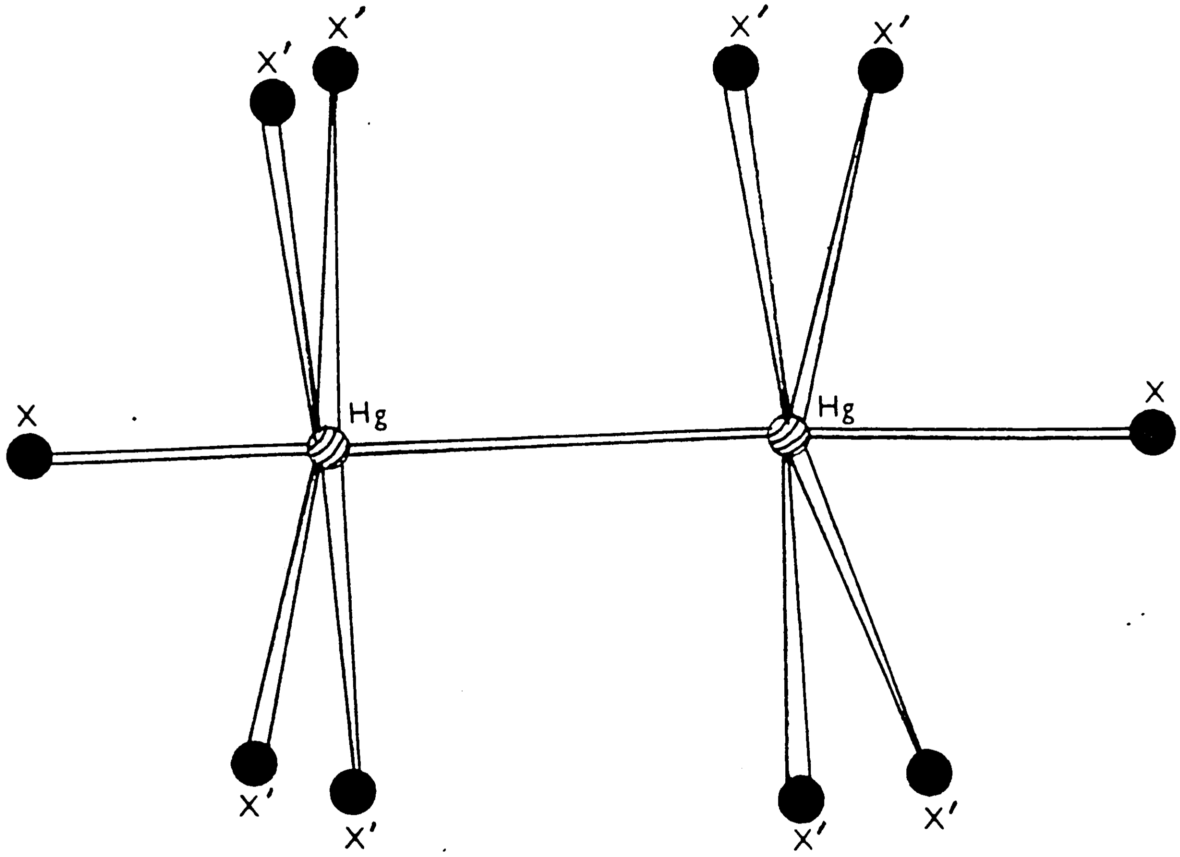
(Tetrahydrofuran)HgBr$_2$^{9}



Bond lengths (Å)			
Hg-Br	2.475(10)	Hg-Br4	3.27(1)
Hg-Br2	2.480(10)	Hg-O	2.67(8)
Hg-Br3	3.15(1)	Hg-Br1′	3.47(1)

Bond angles (°)	
Br1-Hg-Br2	174.6(4)
Br1′-Hg-O	180(-)
Br1 Hg Br4	90(-)

Fig 1.3 Octahedral Six Co-ordination



Bond Distances (Å)

	F	Cl	Br	I
Hg-Hg	2.42	2.53	2.58	2.69
Hg-X	2.31	2.53	2.57	2.69
Hg-X'	2.69	3.17	3.32	3.51

Fig. 1.4 Structures of the Mercury (I) Halides Hg_2X_2 (X=F,Cl,Br,I).[10]

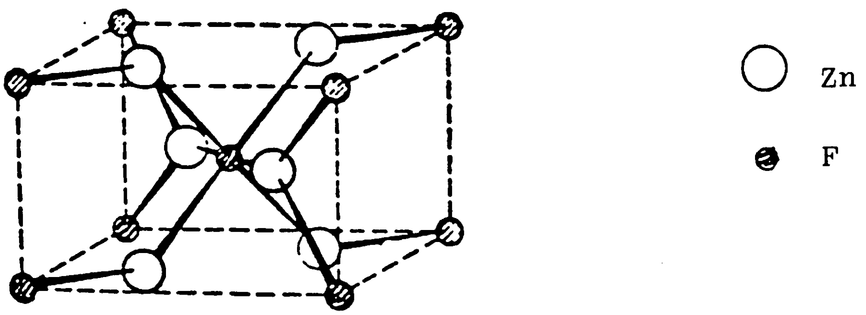


Fig 1.5 Rutile Structure of ZnF_2[1]

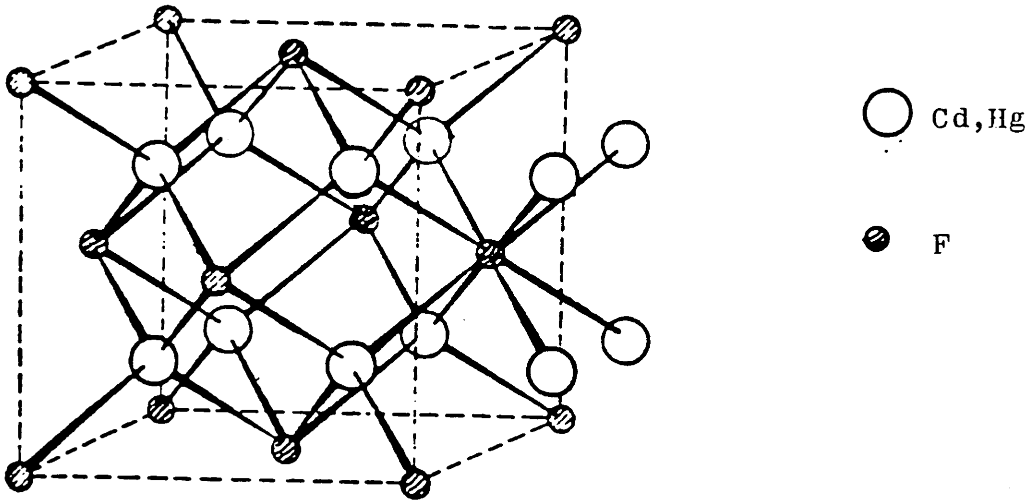


Fig 1.6 Fluorite Structure of MF_2 ,(M=Cd,Hg)[1]

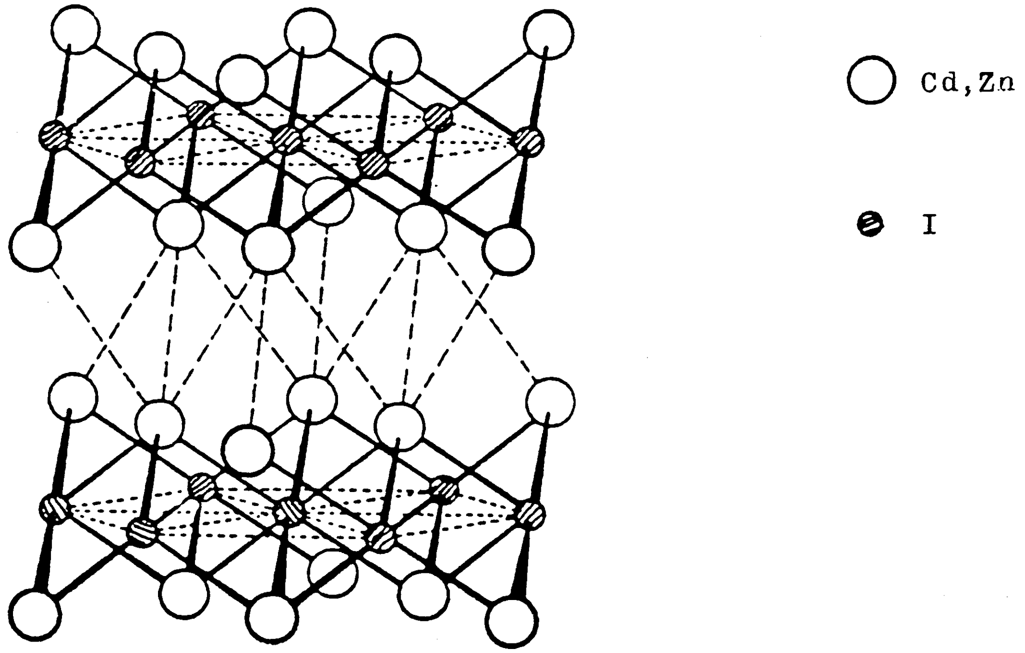


Fig 1.7 Layer Structure of MI_2(M=Cd,Zn)[1]

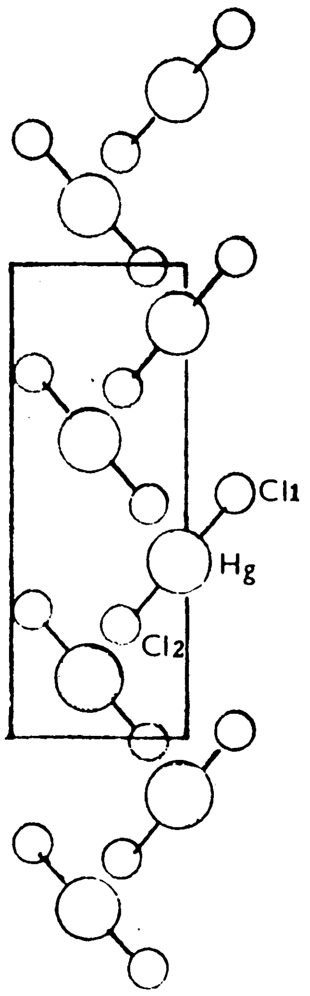
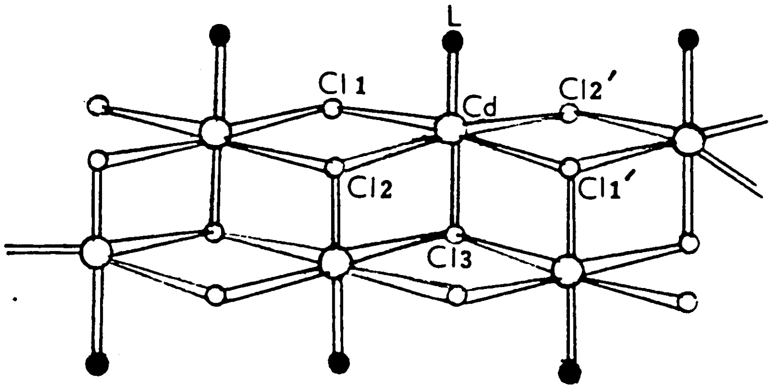


Fig 1.8 Structure of $HgCl_2$[1]



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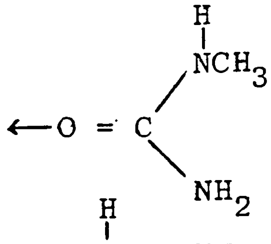

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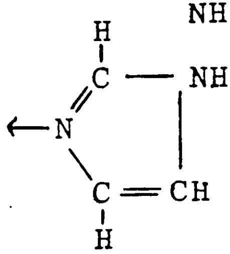

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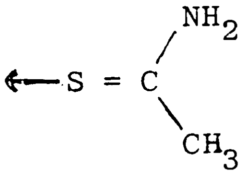
III =



Bond lengths (Å)

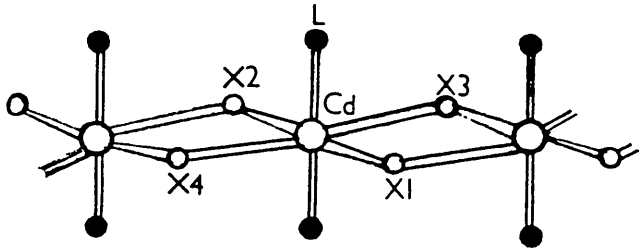
L	Cd-Cl1	Cd-Cl2	Cd-Cl3	Cd-Cl1'	Cd-Cl2'	Cd-L
I	2.62(-)	2 67(-)	2.66(-)	2.58(-)	2.67(-)	2.18(-)
II	2.729(3)	2.604(4)	2.676(3)	2.728(3)	2.601(4)	2.243(5)
III	2.57(2)	2.89(2)	2.63(1)	2.76(2)	2.89(2)	2.55(1)

Bond angles (°)

L	Cl1-Cd-Cl2	Cl1-Cd-Cl1'	Cl1-Cd-Cl3	Cl1-Cd-L
I	87(-)	172(-)	88(-)	99(-)
II	87.5(1)	173.5(1)	90.8(1)	94.1(2)
III	86.1(5)	171.4(4)	90.6(4)	98.2(7)

L	Cl2-Cd-Cl3	Cl2-Cd-L	Cl2-Cd-Cl1'	Cl2-Cd-Cl1
I	88(-)	106(-)	89(-)	91(-)
II	83.1(1)	90.5( )	89.4(2)	95.0(1)
III	79.3(4)	81.7(6)	88.4(5)	97.7(5)

Fig. 1.9. Structure of Selected $LCdCl_2$, Complexes (L=Monodentate Ligand).



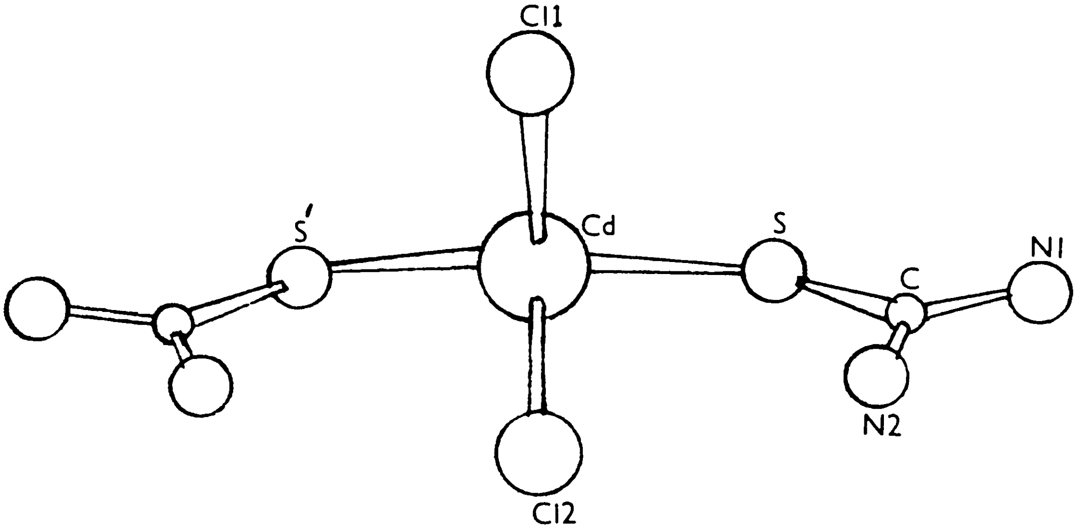
Bond lengths (Å)

L	X	Cd-X1	Cd-L	Cd-X3	Cd-X2
NH_3	Cl	2.71(-)	2.1(-)	2.71(-)	2.71(-)
NH_3	Br	2.86(-)	2.1(-)	2.86(-)	2.86(-)
pyridine	Cl	2.35(4)	2.46(-)	2.35(4)	2.35(4)

Bond angles (°)

L	X	X1-Cd-X3	X1-Cd-L
pyridine	Cl	89.5(-)	90.4(-)

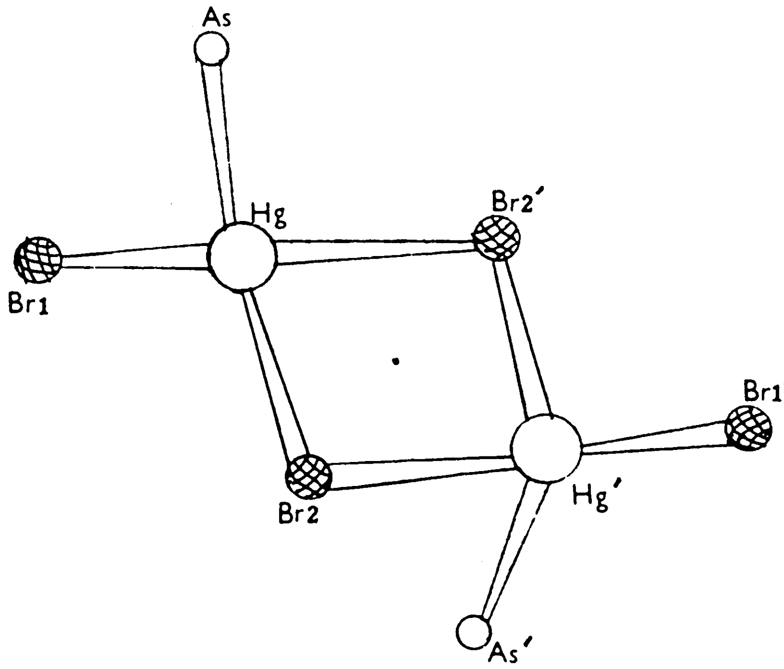
Fig. 1.10. Structures of Selected Octahedral L_2CdCl_2 Complexes (L=NH_3 [20] or Pyridine [21]; X=Cl or Br).



Bond lengths (Å)	
Cd-Cl1	2.51(-)
Cd-Cl2	2.50(-)
Cd-S	2.45(-)

Bond Angles (°)	
Cl1-Cd-Cl2	103(-)
Cl1-Cd-S	106(-)
Cl2-Cd-S	105(-)
S-Cd-S'	129(-)
Cd-S-C	113(-)

Fig 1.11 Structure of Bis(thiourea)Cadmium (II)Chloride [22]



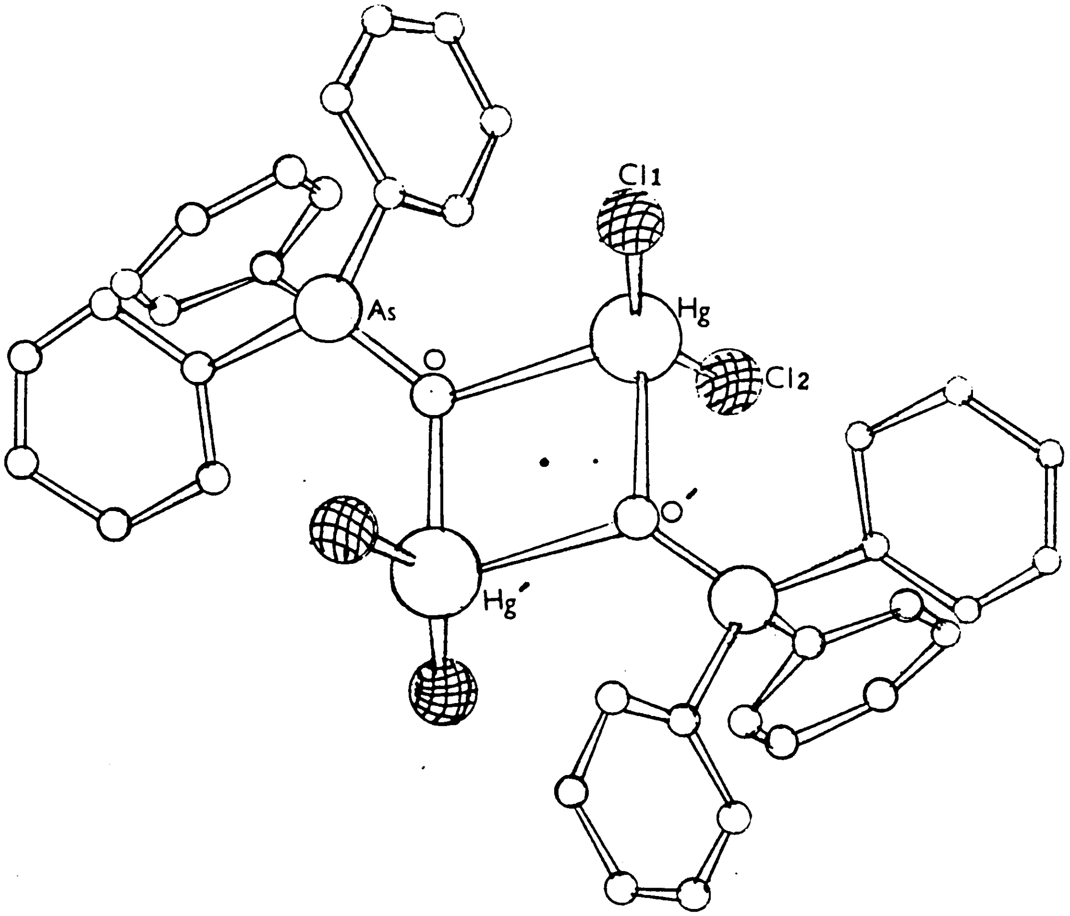
Bond lengths (Å)

Hg-Br1	2.25(-)	Hg-Br2′	2.90(-)
Hg-As	2.25(-)		
Hg-Br2	2.60(-)		

Bond angles (^{o})

As-Hg-Br1	135(-)	Br1-Hg-Br2	102(-)
As-Hg-Br2′	94(-)	Br2-Hg-Br2′	87(-)
As′-Hg′-Br2	94(-)	Hg-Br2-Hg′	93(-)

Fig. 1.12. Structure of $(Bu_3As)HgBr_2$ [24]



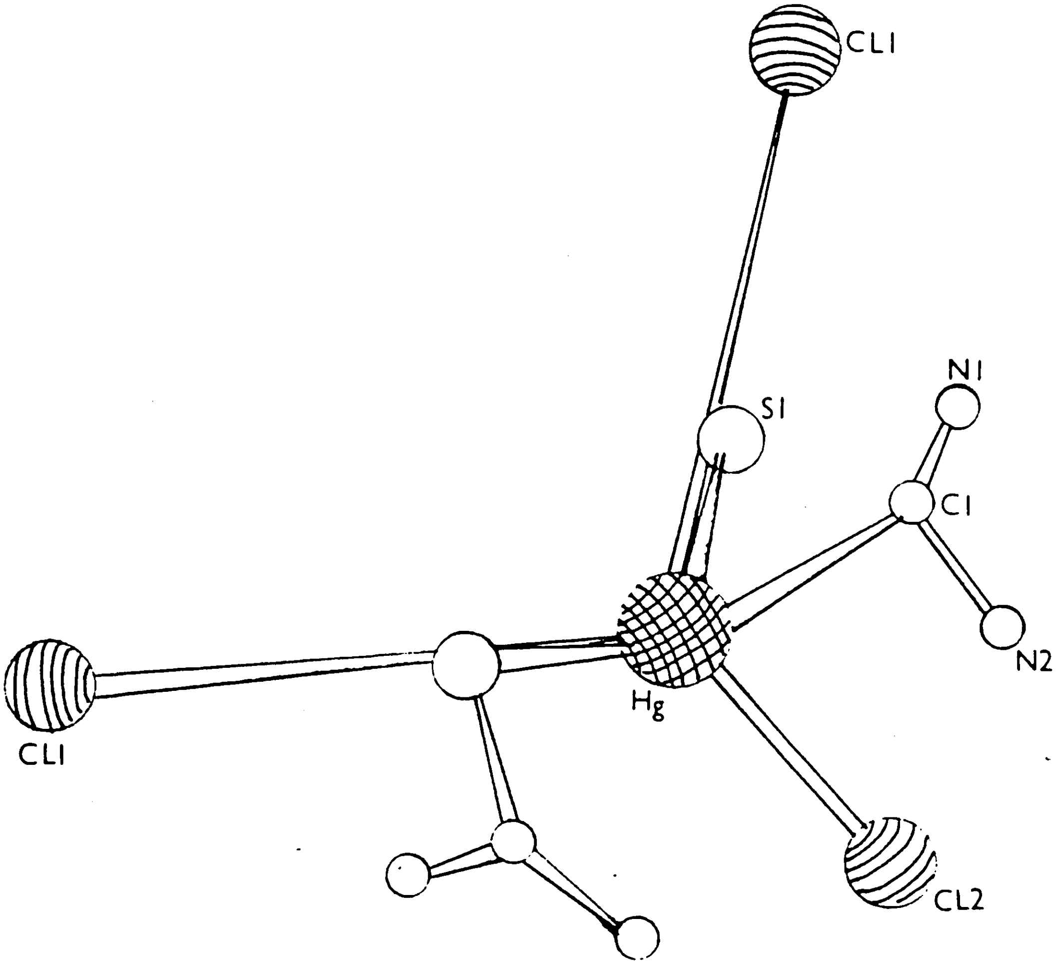
Bond lengths (Å)

Hg-Cl1	2.32(1)	Hg-O′	2.46(2)
Hg-Cl2	2.32(1)	As-O	1.66(2)
Hg-O	2.48(2)		

Bond angles (°)

Cl1-Hg-Cl2	144.8(4)	Cl2-Hg-O′	104.8(7)
Cl1-Hg-O	105.8(7)	O-Hg-O′	78.7(9)
Cl1-Hg-O′	105.4(7)	As-O-Hg	129.3(13)
Cl2-Hg-O	97.6(7)	As-O-Hg′	122.4(13)

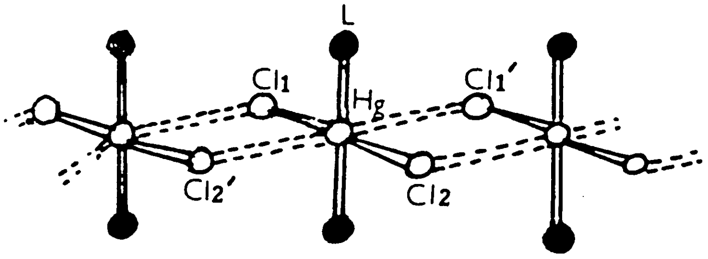
Fig. 1.13. Structure of $(Ph_3AsO)HgCl_2$ [25]



Bond lengths (Å)	
Hg-S1	2.416(6)
Hg-Cl2	2.57(1)
Hg-Cl1	3.22(1)
Hg-Cl1	3.22(1)

Bond angles (°)	
S1-Hg-Cl2	110.8(2)
S1- Hg-S1	138.6(2)
Hg-S1-Cl1	110.0(9)

Fig. 1.14. Structure of $(NH_2CSNH_2)_2HgCl_2$ [26].



Bond lengths (Å)

L	Hg-Cl1	Hg-L	Hg-Cl1	Hg-Cl2	Hg-Cl2
CH_3OH	2.31(3)	2.82(5)	3.07(3)	2.31(3)	3.07(3)
pyridine	2.754(2)	2.266(6)	2.765(2)	2.754(2)	2.765(2)

Bond angles (°)

L	Cl1-Hg-L	Cl1-Hg-Cl2	Cl1-Hg-Cl1	Cl1-Hg-Cl2
CH_3OH	80(1)	180(1)	86(1)	129(1)
pyridine	88.5(2)	180(-)	90.21(6)	-

	L-Hg-Cl1	Hg-Cl1-Hg
pyridine	90.6(2)	90.21(7)

Fig. 1.15. Structures of the 2:1 Complexes L_2HgCl_2 (L=CH_3OH [27] or pyridine [28,29])

1.5 Phosphine Complexes of Zinc, Cadmium and Mercury

Mercury(II) halides form tertiary phosphine complexes having a wide variety of stoichiometries:

$$(R_3P)MX_2,\ (R_3P)_2(MX_2),\ (R_3P)(MX_2)_2,\ (R_3P)_3(MX_2)_2.$$

Zinc and cadmium halides, in contrast, give rise to a limited range of complexes and the moxt extensively studied are the 2:1 and the 1:1 adducts, L_nMX_2 (n = 1,2). These complexes are generally prepared by the reaction of the metal(II) halide with the tertiary phosphine in a suitable solvent.

1.5.1 Complexes Formed by Zinc Halides and Tertiary Phosphine Monodentate Ligands

Few zinc halide tertiary phosphine complexes have been prepared. The complexes $(R_3P)ZnX_2$ (X = Cl, Br or I:R = t-butyl, cyclohexyl) have been studied using infrared and ^{31}P NMR techniques. All these complexes are reported to be halogen-bridged dimers.[30,31] The 2:1 complexes formed with triphenylphosphine, $(Ph_3P)_2ZnX_2$ (X = Cl, Br or I), have been prepared and infrared studies indicate that they have monomeric tetrahedral structures.[32]

1.5.2 Complexes Formed by Cadmium Halides and Tertiary Phosphine Monodentate Ligands

Many cadmium halide 1:1 complexes have dimeric halogen-bridged structures with distorted tetrahedral co-ordination about cadmium. However, $(PhMe_2P)CdCl_2$ adopts a polymeric structure in which cadmium has unusual five co-ordination (Fig. 1.16).[33] The 2:1 complexes appear to be monomeric, $(Ph_3P)_2CdCl_2$ having a distorted tetrahedral structure (Fig. 1.1).[5]

1.5.3 Complexes formed by Mercury Halides and Tertiary Phosphine Monodentate Ligands

Although the literature contains many reports of phosphine complexes

$(R_3P)_nHgX_2$ (n = 1, 1.5, 2), the earlier papers gave little unambiguous evidence for the structure of such complexes. Assignment of far-infrared frequencies of mercury-halogen bands appear to be consistent with a halogen-bridged dimeric arrangement. Indeed, preliminary X-ray analysis confirmed this arrangement for $(Pr_3P)HgBr_2$.[24] A programme of work has been undertaken at Sheffield City Polytechnic to rationalize the range of structures adopted by complexes formed between mercury(II) halides and monodentate tertiary phosphines.[6,34-37]

(A) 3:2 Complexes $(R_3P)_3(HgX_2)_2$

The existence of 3:2 mercury(II) halide complexes was reported by Evans et al.[24] Crystallographic data are available for only one complex $(EtMe_2P)_3(HgCl_2)_2$ which is found to have an extended chain structure with the mercury atoms having alternating co-ordination numbers of four and five[35] (Fig. 1.17).

(B) 1:1 Complexes $(R_3P)HgX_2$

In the series of complexes $(R_3P)HgCl_2$ (R = Me, Et, Bu, Ph, cyclohexyl) and (R_3P = 1,2,5-triphenylphosphole) halogen-bridging is observed as shown in (Figs. 1.18-1.24).[34,36,38,39] Full X-ray structural data are available for these complexes, the structural types being indicated in Table 1.1. Structures have been proposed for several of their bromide and iodide analogues using far-infrared vibrational spectroscopy and from preliminary X-ray photographs. In some cases the availability of ^{31}P NMR data has been used to reinforce these structural assignments.

Although many of the complexes are centrosymmetric dimers they show a wide range of structural arrangements. X-ray studies show that $(Cy_3P)HgCl_2$[39] contains two independent dimers within the unit cell. Though the Hg-P distances are almost identical 2.416(3) and 2.412(3) Å for dimers 1 and 2 respectively, other bond distances and angles vary considerably (Table 1.2). $(Me_3P)HgCl_2$ and $(Et_3P)HgCl_2$[36] are both polymeric, with the mercury atoms in distorted trigonal bipyramidal environments, but the details of the structures differ markedly. $(Et_3P)HgCl_2$ is regarded as an extended chlorine-bridged chain (Fig. 1.19) while $(Me_3P)HgCl_2$ (Fig. 1.20) which has a large P-Hg-Cl angle of 162.1(1)°, is ionic in nature (Table 1.2).

Both $(TPP)HgCl_2$ and $(Ph_3P)HgCl_2$ are centrosymmetric dimers in which the ligands are mutually trans (Figs. 1.21-1.22), but the relative Hg-Cl bridging distances differ considerably. For $(TPP)HgCl_2$ the bridging is very asymmetric, $Hg\text{-}Cl_{br}$ distances being 2.54(1) and 2.75(1) Å, whilst for $(Ph_3P)HgCl_2$ the $Hg\text{-}Cl_{br}$ values are almost equal, being 2.623(8) and 2.658(8) Å.[34]

$(Bu_3P)HgCl_2$ exists in two different forms, the α-form[34] contains a tetrameric unit with mercury in both tetra-co-ordinate and penta-co-ordinate environments. The tetramer comprises two unsymmetrical dimeric units (Fig. 1.23) which are linked by weak chlorine bridges (Hg-Cl, 3.38(3) Å). The terminal mercury atoms have an extremely distorted tetrahedral environment, the angles ranging from 92.6(7) to 147.8(7)°. The angles about the central mercury vary even more, ranging from 78.7(6) to 150.6(7)°. The β-form of $(Bu_3P)HgCl_2$[38] is a centrosymmetric halogen-bridged dimer similar to that found in $(Ph_3P)HgCl_2$[34] and shows no evidence of any further interaction of the dimers (Fig. 1.24).

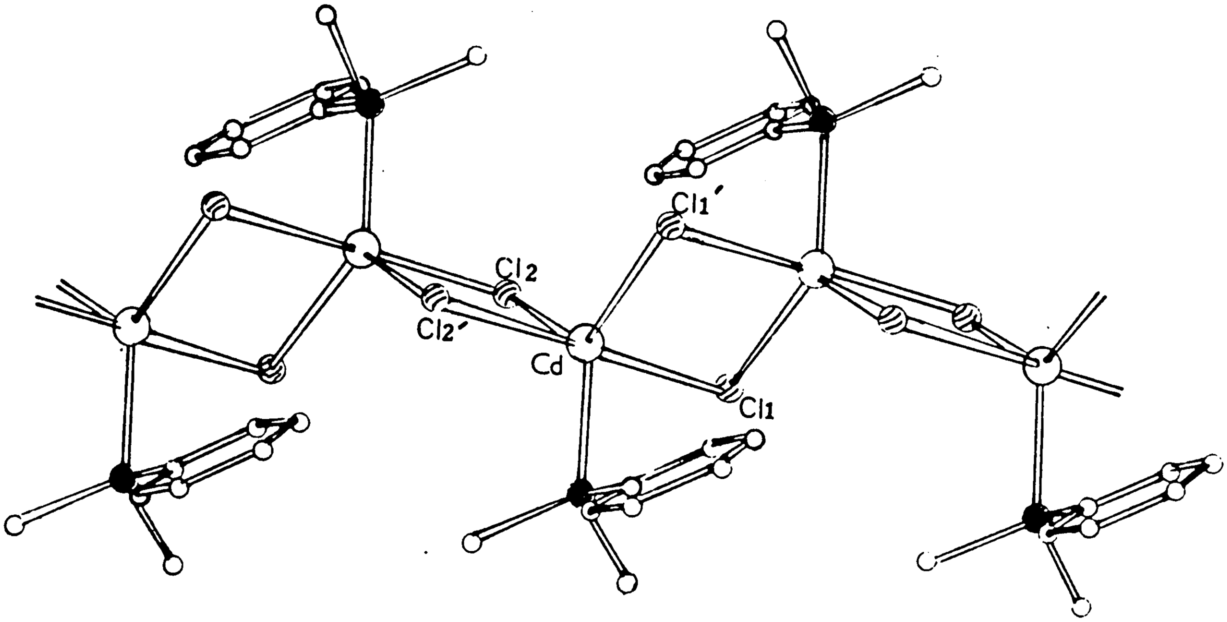
Preliminary photographic evidence indicates that $(TPP)HgBr_2$,[34] $(Me_3P)HgBr_2$,[36] and $(Ph_3P)HgX_2$ (X = Br or I)[34] may be isostructural with their corresponding chlorides. In contrast $(Me_3P)HgI_2$[34] is not isostructural with its chloride analogue.

(C) 2:1 Complexes $(R_3P)_2HgX_2$

The $(R_3P)_2HgX_2$ series of complexes (R = Et, Bu, Ph; X = Cl, Br or I) have been characterised as four co-ordinate monomers, with varying degrees of distortion from regular tetrahedral geometry. $(Ph_3P)_2HgI_2$[40] has an almost regular tetrahedral geometry about the mercury with an I-Hg-I angle of 110.43(8)° and a P-Hg-P angle of 108.15(4)° (Fig. 1.25) In contrast, the complexes $(R_3P)_2HgCl_2$ (R = Bu,[41] Et[42] and Ph[43]) all show a greater distortion from tetrahedral geometry (Table 1.3) (Figs. 1.26-1.28). This distortion may be attributed in the ethyl and butyl complexes to the phosphines having high pKa values of 8.69 and 8.64 respectively. Such high pKa values indicate a higher donor strength than for triphenylphosphine (pKa 2.73). For $(Ph_3P)_2HgCl_2$ the greater distortion from its iodide analogue must be caused by the effect of the halogen atoms. Iodide is a stronger donor than chloride to mercury so that the P-Hg-P angle is less in the iodide (108.15(4)°)[40] than in the chloride (135.2(4)°).[43]

Initial results for $(Ph_3P)_2HgBr_2$ have been reported.[43] These indicate a distorted tetrahedral structure; the P-Hg-P angle being 113.0(5)° in accord with the above results for the iodide and chloride.

NMR data is available for several 2:1 complexes and coupling constants have been determined for $(R_3P)_2HgX_2$[49] complexes (X = Cl, Br or I and R = Et, Bu or Ph). Table 1.3 compares bond distances, angles and coupling constants for these complexes. The factors which influence the degree of distortion of 1:1 and 2:1 complexes are discussed in detail in Section 2.



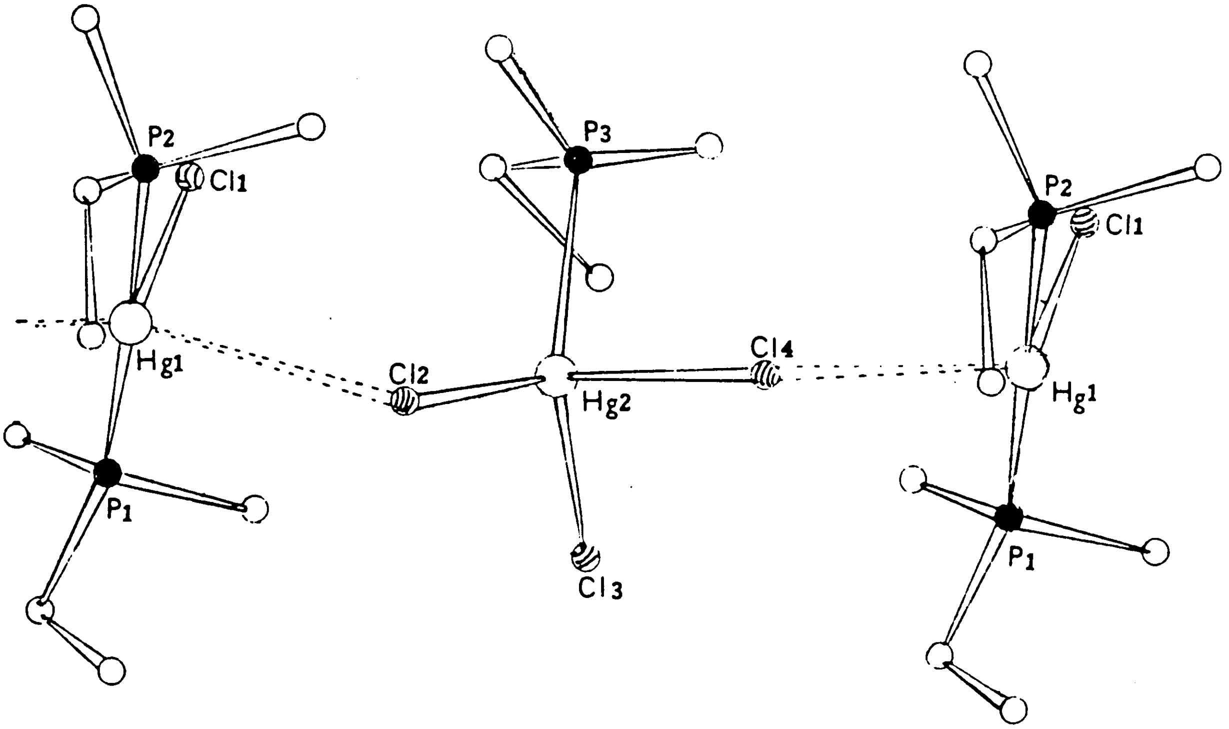
Bond lengths (Å)

Cd-Cl1	2.481(1)	Cd-Cl2′	2.734(1)
Cd-Cl2	2.497(1)	Cd-P	1.825(5)
Cd-Cl1	2.745(1)		

Bond angles (°)

Cl1-Cd-Cl2	110.50(2)	Cl2-Cd-Cl2′	87.10(2)
Cl1-Cd-Cl1′	86.00(2)	Cl2-Cd-P	119.50(3)
Cl1-Cd-Cl2′	92.60(2)	Cl1′-Cd-Cl2′	178.60(4)
Cl1-Cd-P	130.00(4)	Cl1′-Cd-P	88.70(4)
Cl2-Cd-Cl1′	93.40(2)	Cl2′-Cd-P	92.20(2)

Fig 1.16 Structure of $(PhMe_2P)CdCl_2$[33]



Bond lengths (Å)

Hg1-Cl1	2.69(1)	Hg1-P2	2.40(1)	Hg2-P3	2.40(1)
Hg1-Cl2	3.07(1)	Hg2-Cl2	2.62(1)		
Hg1-Cl4	3.25(2)	Hg2-Cl3	2.52(1)		
Hg1-P1	2.40(1)	Hg2-Cl4	2.45(1)		

Bond angles (°)

C-l1Hg1-P1	97.6(5)	Cl2-Hg-Cl3	98.2(5)
Cl1-Hg-P2	90.1(5)	Cl2-Hg2-Cl4	104.1(5)
Cl4-Hg1-Cl2	149.1(4)	Cl3-Hg2-Cl4	98.5(5)
P1-Hg1-P2	172.3(5)	Cl2-Hg2-P3	101.0(5)
Cl3-Hg2-P3	117.2(5)	Hg1-Cl2-Hg2	133.1(5)
Cl4-Hg2-P3	132.9(6)	Hg1-Cl4-Hg2	107.1(5)

Fig 1.17 Structure of $(EtMe_2P)_3(HgCl_2)_2$ [35]

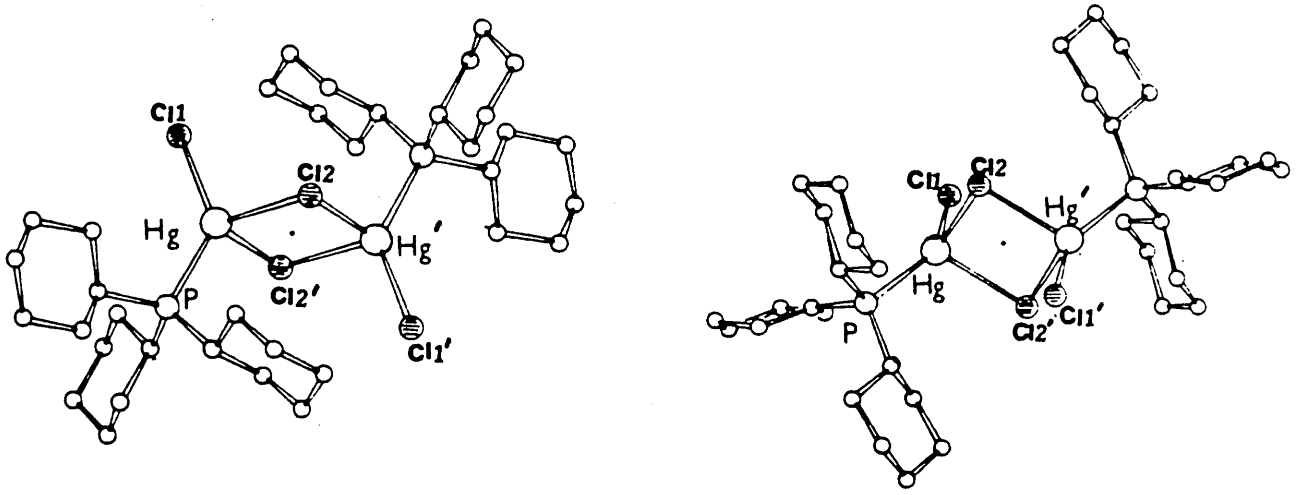


Fig. 1.18 Structure of $(Cy_3P)HgCl_2$ [39]

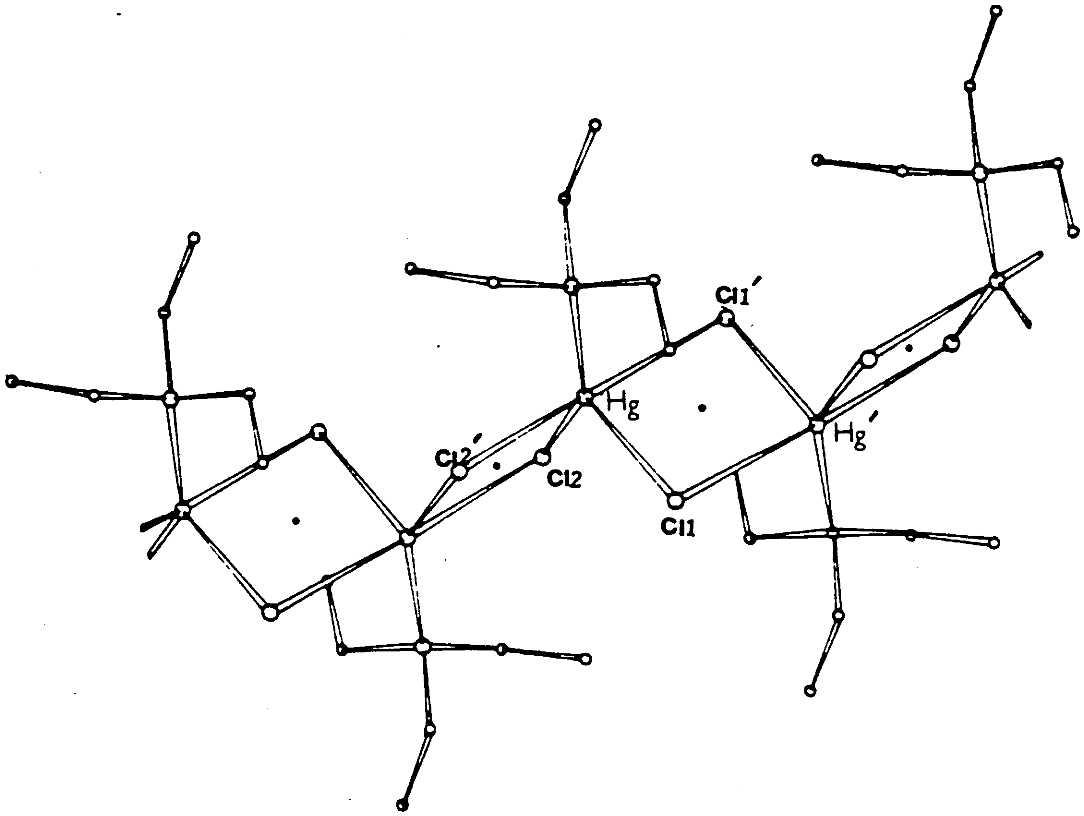


Fig. 1.19 Structure of $(Et_3P)HgCl_2$ [36]

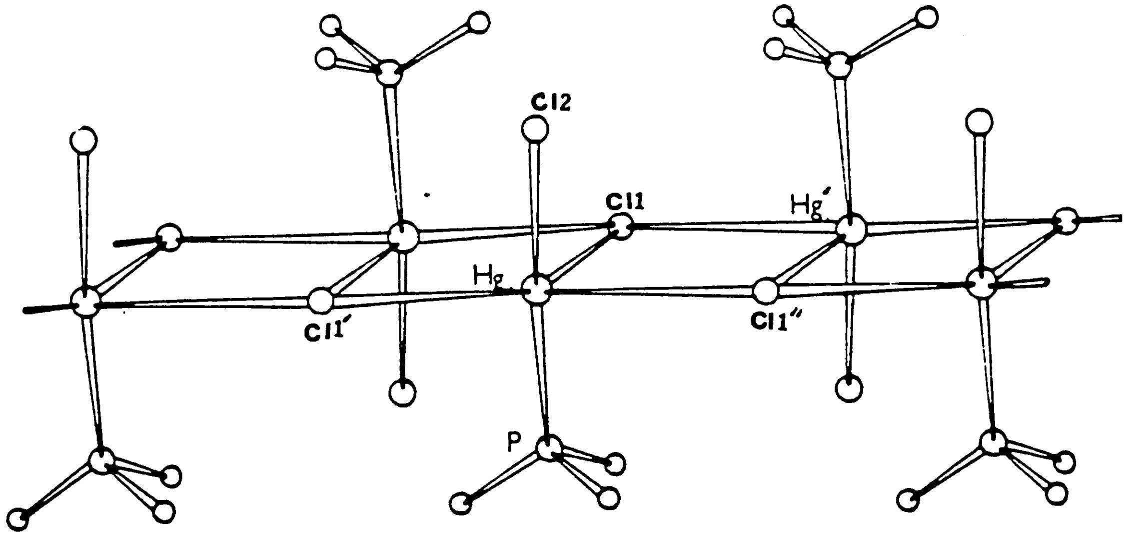


Fig. 1.20 Structure of $(Me_3P)HgCl_2$ [36]

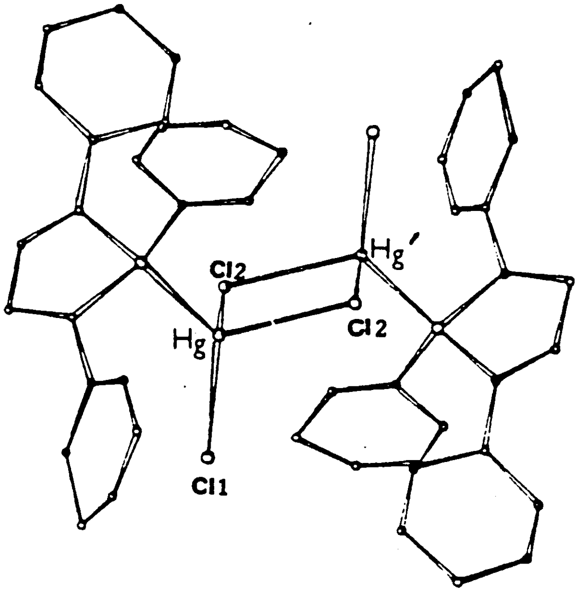


Fig. 1.21 Structure of $(TPP)HgCl_2$ [34]

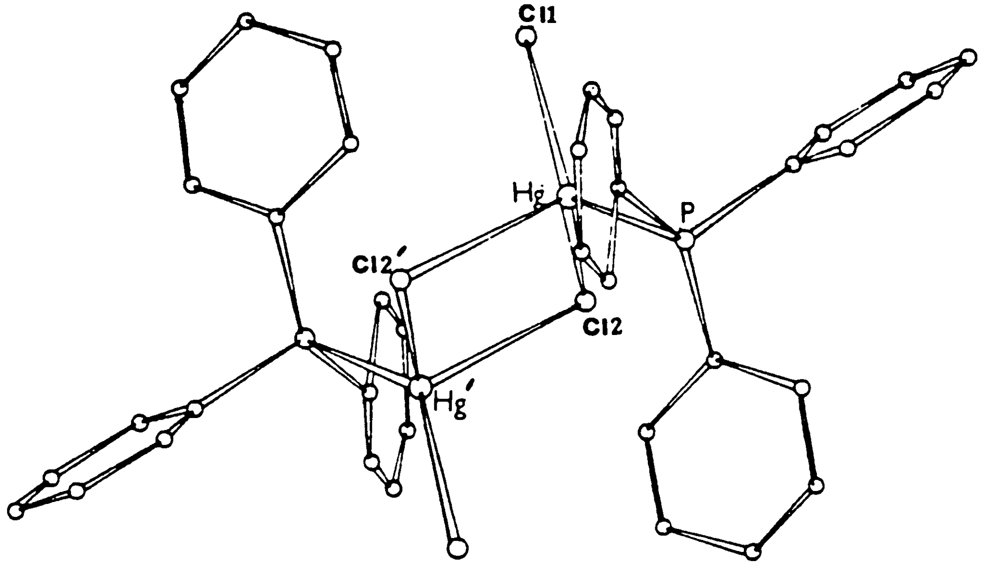


Fig. 1.22. Structure of $(Ph_3P)HgCl_2$ [34]

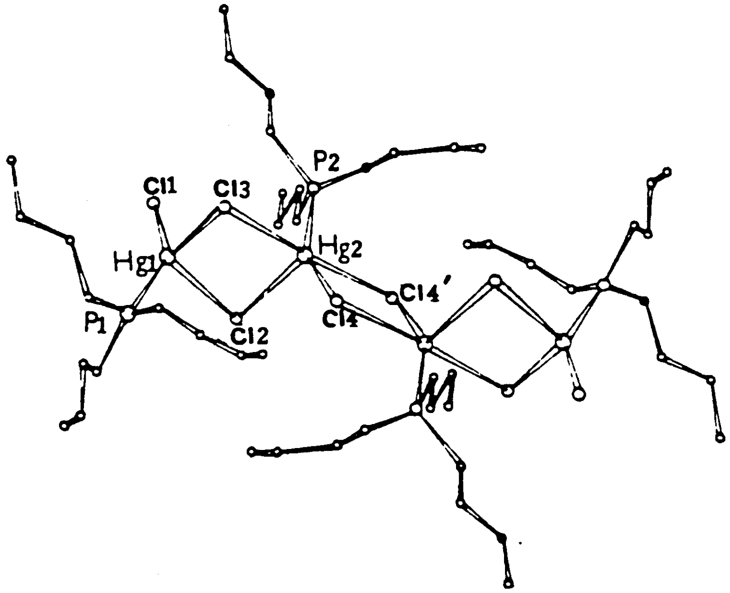


Fig. 1.23 Structure of α-$(Bu_3P)HgCl_2$ [34]

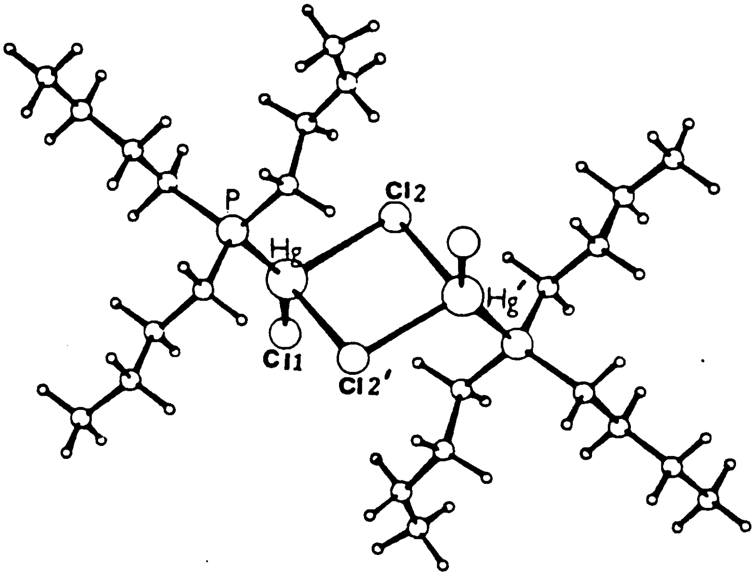


Fig. 1.24. Structure of β-(Bu_3P)$HgCl_2$ [38]

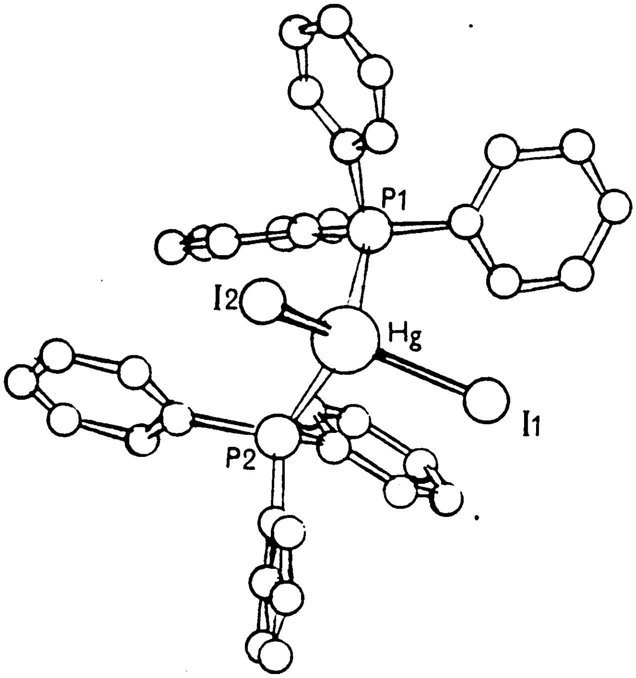


Fig 1.25 Structure of $(Ph_3P)_2HgI_2$ [40]

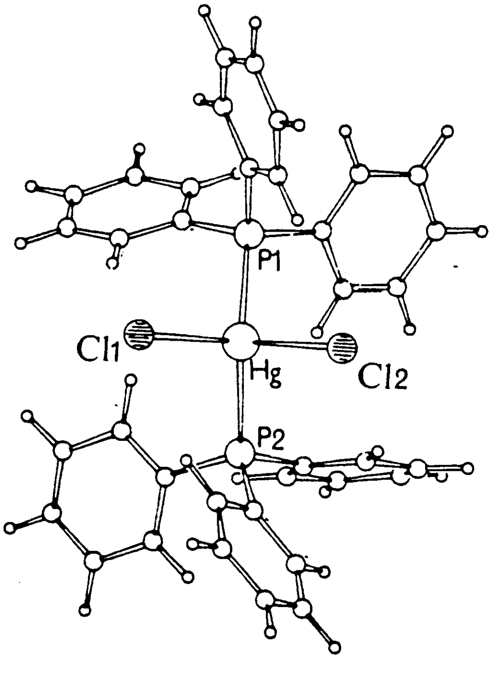


Fig 1.26 Structure of $(Ph_3P)_2HgCl_2$ [43]

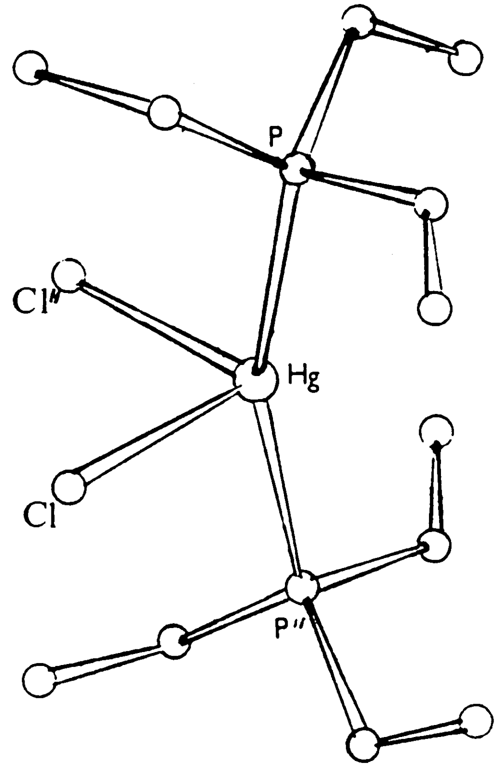


Fig 1.27 Structure of $(Et_3P)_2HgCl_2$ [42]

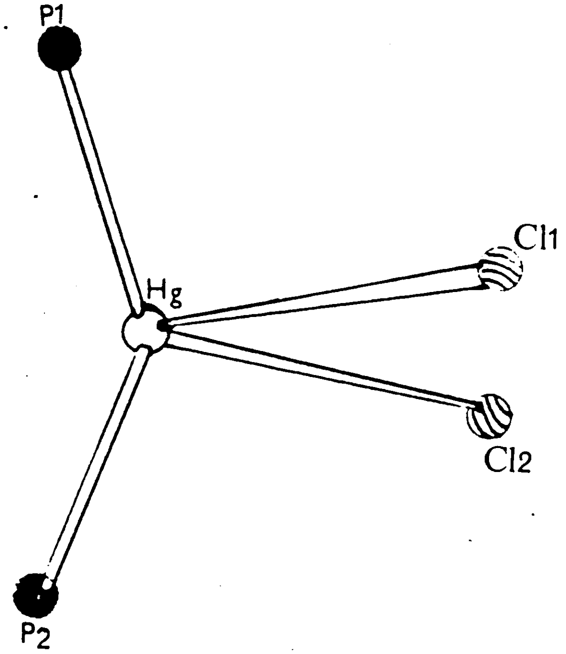


Fig 1.28 Structure of $(Bu_3P)_2HgCl_2$ [41]

TABLE 1.1 Known Structures of $(R_3P)HgX_2$ Complexes

Complex	Structure	Evidence	Ref.
$(Ph_3P)HgCl_2$	Centrosymmetric dimer	Full X-ray structure	34
$(Ph_3P)HgBr_2$	Centrosymmetric dimer	Preliminary X-ray photographs	34
$(Ph_3P)HgI_2$	Centrosymmetric dimer	Preliminary X-ray photographs	34
$(TPP)^{+}HgCl_2$	Centrosymmetric dimer	Full X-ray structure	34
$(TPP)^{+}HgBr_2$	Centrosymmetric dimer	Preliminary X-ray photographs	34
α-$(Bu_3P)HgCl_2$	'Tetramer'	Full X-ray structure	34
β-$(Bu_3P)HgCl_2$	Centrosymmetric dimer	Full X-ray structure	38
$(Cy_3P)^{\ddagger}HgCl_2$	Two independent centrosymmetric dimers	Full X-ray structure	39
$(Et_3P)HgCl_2$	Chain polymer	Full X-ray structure	36
$(Me_3P)HgCl_2$	'Ionic' polymer	Full X-ray structure	36
$(Me_3P)HgBr_2$	'Ionic' polymer	Preliminary X-ray structure	36

$^{+}$TPP = 1,2,5-triphenylphosphole

‡Cy = cyclohexyl

TABLE 1.2 Selected Bond Angles and Bond Lengths of 1:1 $(R_3P)HgCl_2$ Complexes

Ligand	Hg-P(Å)	Hg-Cl_t(Å)	Hg-Cl_{br}(Å)	P-Hg-Cl_t(°)	Cl_1-Hg-Cl_2(°)
PMe_3[36]	2.365(3)	2.355(4)	2.782(4) 2.941(4) 3.489(4)	162.1(1)	98.2(1)
PEt_3[36]	2.35(1)	2.42(1)	2.56(1) 3.04(1) 3.21(1)	145.4(3)	98.7(3)
PBu_3[34] (α-form)	2.363(21) 2.337(19)	2.289(21)	2.709(20) 2.626(19)	147.8(7)	92.6(6)
PBu_3[38] (β-form)	2.377(6)	2.348(8)	2.720(6) 2.736(6)	150.9(3)	89.0(3)
PPh_3[34]	2.406(7)	2.370(10)	2.658(8) 2.623(8)	128.7(4)	84.4(3)
PCy_3[39] mol (1)	2.416(3)	2.391(5)	2.641(4) 2.665(4)	139.6(2)	95.2(2)
mol (2)	2.412(3)	2.413(3)	2.602(4) 2.779(4)	132.0(1)	101.5(1)
TPP[34]	2.438(10)	2.404(11)	2.542(13) 2.747(14)	127.8(5)	86.5(4)

br = bridging
t = terminal

TABLE 1.3

Bond Distances, Angles and Coupling Constants with Estimated Standard Deviations for $(R_3P)_nHgX_2$(n = 1, 2 and X =Cl, Br or I)

$(R_3P)_n$	X	P-Hg (Å)	P-Hg-P (°)	J(^{199}Hg-^{31}P) Hz	pKa	ref.
$(Ph_3P)_2$	Cl	2.462(2) 2.478(2)	134.1(1)	4740	2.73	50
	Br	2.54(3) 2.53(2)	113.0(5)	4178	"	"
	I	2.574(3)	109.0(1)	3073	"	"
$(Ph_3P)_1$	Cl	2.406(7)		7431	"	"
	Br			6464	"	"
	I			4700	"	"
$(Bu_3P)_2$	Cl	2.34(6) 2.64(6)	139.0(2)	5078	8.64	49
	Br			4741	"	"
	I			4110	"	"
$(Bu_3P)_1$	Cl	2.34(3) 2.35(2)		7446		"
	Br			6624		"
	I			5127		"
$(Et_3P)_2$	Cl	2.39(1) 2.39(1)	158.5(1)	5095	8.69	42
	Br			4792	"	"
	I			4004	"	"

Contents

2. Factors which Influence the Solid State Structure of Mercury(II) Halide Complexes

The following factors are believed to influence the solid state structures of mercury(II) halide complexes with monodentate neutral donor ligands:

(i) type of donor atom;

(ii) electronic effect of the substituents attached to the donor atom;

(iii) steric effect of the substituents attached to the donor atom;

(iv) nature of the halogen atom;

(v) entropy effects.

2.1 Influence of the Donor Atom

Hg^{2+} and Cd^{2+} ions are classed as 'soft acids' or 'Class b' metal ions but Zn^{2+} is a 'harder acid' than either Hg^{2+} or Cd^{2+}.[51] Mercury(II) will therefore form strong interactions with 'soft' bases such as sulphur, phosphorus and arsenic but nitrogen, being a harder base, is less likely to form strong interactions. The strong interactions cause distortion of the X-Hg-X unit from a linear arrangement and an increase in the length of the Hg-X bond. Oxygen which is classed as a 'hard' base, only interacts weakly with mercury resulting in polymeric structures with only a slight distortion from linearity of the X-Hg-X units. For $(C_4H_8O)HgBr_2$[9] the Br-Hg-Br angle is 174.6(4)° while the Hg-Br bond distance is 2.475(10) Å. In contrast $(Ph_3P)_2HgBr_2$[43] shows a larger degree of distortion from linearity, having a Br-Hg-Br angle of 106.9(3)° and Hg-Br distances of 2.633(6) and 2.626(8) Å.

The advent of the modern Fourier Transform NMR spectrometer has enabled the ^{31}P and ^{199}Hg spectra of complexes to be studied, the main areas of interest being the chemical shifts and coupling constants.

A clear correlation has been found between the coupling constants and the σ-donor strengths of the ligands (Table 1.3). The stronger donor ligands tend to give larger coupling constants, for example, $(Et_3P)_2HgCl_2$[42] has a larger coupling constant ($J(^{199}Hg-^{31}P)$) than $(Ph_3P)_2HgCl_2$.[50] The 2:1 complexes have smaller coupling constants than the corresponding 1:1 complexes, probably as the donor ability of the ligand is affected by the competition of a second ligand about the mercury atom. This would mean that in the case of the 1:1 complexes the ligand is a stronger donor atom, hence having a larger coupling constant.

2.2 The Electronic Effect of the Substituents Attached to the Donor Atom

The extent of the interaction between mercury and the donor is also dependent on the ability of the donor atom to act as a "Lewis Base". Thus the σ-donor ability of the ligand is dependent on the substituents attached to the donor atom. A considerable amount of work has been carried out on tertiary phosphine complexes,[52] much of which relates the basicity of the phosphine to the Hg-P bond lengths and to the bond angles about Hg. In general, complexes formed with ligands of a high pKa are found to have shorter Hg-P bonds which may reflect a strong mercury-phosphorus interaction.

The 1:1 and 2:1 complexes show an increase in the length of the Hg-Cl bond and a corresponding decrease in the Hg-P distance from Ph_3P to Et_3P. These data appear to support the idea that Ph_3P, with a pKa of 2.73, has a weaker interaction with the mercury atom than Et_3P, which has a pKa of 8.69. For the 1:1 complexes the Cl_t-Hg-P angle increases, while for the 2:1 complexes the P-Hg-P angle increases from Ph_3P to Et_3P (Table 2.21).

2.3 The Steric Effect of the Substituents Attached to the Donor Atoms

The steric requirements of a ligand have been defined by the use of the term 'cone angle'. The cone angle for a symmetric ligand PR_3 (R=R=R) is the apex angle of a cylindrical cone centred 2.28 Å from the centre of the

TABLE 2.21

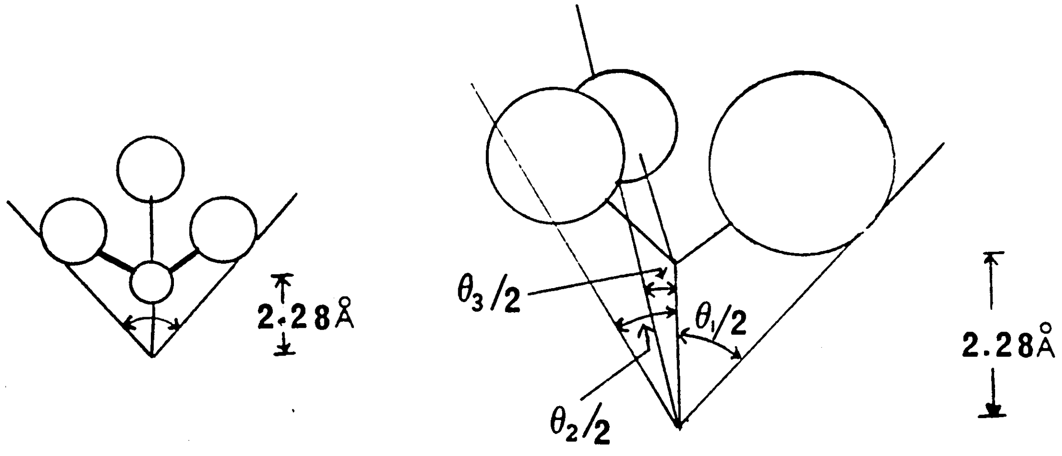
A Comparison of Some Bond Lengths and Angles of $(R_3P)_nHgCl_2$ Complexes

(n = 1 or 2, R = Ph or Et)

n = 1				n = 2				
R_3P	Hg-P(Å)	Hg-Cl(Å)	P-Hg-Cl_t(°)	R_3P	Hg-P(Å)	Hg-Cl(Å)	P-Hg-P(°)	pKa[52]
Et_3P[36]	2.35(1)	2.56(1) 2.42(1)	145.4(3)	Et_3P[42]	2.39(1) 2.39(1)	2.68(1) 2.68(1)	158.5(5)	8.69
Ph_3P[34]	2.406(7)	2.370(10) 2.623(8)	128.7(4)	Ph_3P[43]	2.478(2) 2.462(2)	2.559(2) 2.545(3)	134.1(1)	2.73

Cl_t = terminal chlorine atom

phosphorus atom which touches the Van der Waals' radii of the outermost atoms (Fig. 2.1). For an unsymmetrical ligand the angles are calculated[47] by the equation $\theta = \frac{2}{3}\Sigma_{i=1}^{3}\ \theta i/2$



(a)

(b)

FIGURE 2.1

(a) Cone Angle Measurement for Symmetrical Ligand

(b) Cone Angle Measurement for Unsymmetrical Ligands[47]

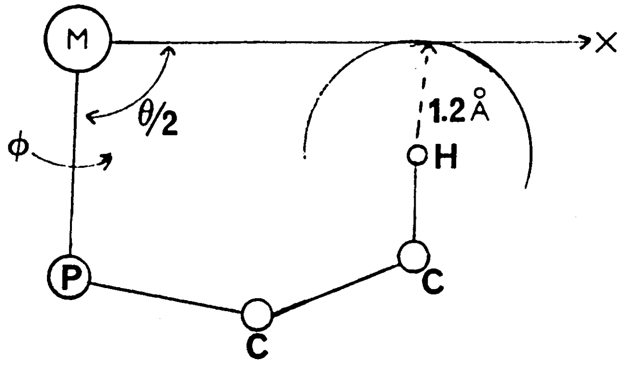


FIGURE 2.2 Details of the Calculation of the Maximum Semicone Angle $\theta/2$[53]

The cone angle is defined as a steric parameter which is a measure of the degree of congestion around the bonding face of phosphorus. Very bulky phosphines such as Cy_3P and $Bu^t{}_3P$ do not behave as solid cones but are described as irregular 'conic cogs'.[53] The concept of 'ligand profile' has been developed to obtain precise maximum cone angle data and information on the gaps between moieties in a ligand (the depth of the tooth of the conic cog). To obtain a 'ligand profile', a plot is made of the maximum semicone angle, $\theta/2$, as a function of the angle ϕ through which the $M \rightarrow X$ vector is rotated about the M-P bond (Fig. 2.2). Cone angles measured for some phosphines are as follows:

Me_3P = 118°, $Cy^{\dagger}{}_3P$ = 170°, $Bu^t{}_3P$ = 180°, Et_3P = 132°[47]

Cy_3P is a "bulky" ligand (cone angle = 170°) but it is known to be a stronger donor than Et_3P and Me_3P ligands. The pKa values are Cy_3P = 9.70, Et_3P = 8.69, and Me_3P = 8.65.[52] It would be expected that Cy_3P complexes would have shorter Hg-P bonds and larger X_t-Hg-P angles than the Et_3P and Me_3P complexes.[36] However, the X_t-Hg-P angles for Cy_3P are 132.0(1) and 139.6(2)° while the Hg-P distances are 2.412(3) and 2.416(3) Å.[39] The corresponding angles for the complexes of Et_3P are 145.4(3) and for Me_3P, 162.1(1)° while the Hg-P bonds are 2.35(1) and 2.365(3) Å.[36] This would indicate that the 'bulky' nature of Cy_3P ligand and the inflexibility of the cyclohexyl rings sterically inhibit the opening up of the Cl_t-Hg-P angle beyond 139.6°.

2.4 The Nature of the Anion in $(R_3P)_nHgX_2$ (n = 1, 2 X = anion)

In the halide complexes the halogen atoms compete with the phosphorus for bonding around the mercury atom. The relative donor strength of halides (Cl^-, Br^- and I^-) towards mercury increases with decreasing

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†Cy = Cyclohexyl

electronegativity of the halogen, chloride being the weakest. This is indicated by comparison of the $\log K_1$ values (where K_1 = first stepwise formation constant) calculated from equation 2.41.

$$Hg^{2+} + X^- \rightleftharpoons HgX^+ \qquad \underline{2.41}$$

$$K_1 = \frac{[HgX^+]}{[Hg^{2+}][X^-]}$$

$\log K_1$ (25 °C)[60] for $[HgCl]^+ = 6.74$

$[HgBr]^+ = 9.05$

$[HgI]^+ = 12.87$

In general for anions, when X is strongly σ-bonding, the X-Hg-X grouping tends towards linearity with longer Hg-P bonds than are found in complexes involving weaker anions. This trend has been illustrated by both X-ray and NMR techniques in the series $(Ph_3P)_2HgX_2$ (X = Cl, Br, I, CF_3, CN, SCN and ONO_2)[42] (Table 2.41). This table shows that for strong σ-donors, for example, where X = CF_3, an X-Hg-X angle of 146.6(9)° and an Hg-P bond length of 2.91 Å are found. In marked contrast for X = ONO_2, which forms a weaker σ-bond, a much smaller X-Hg-X angle of 70.0° and significantly shorter Hg-P bond length of 2.45 Å results. The NMR measurements show weaker σ-bonding groups have larger coupling constants and this has also been illustrated by the series $(EtMe_2P)_2P)_2HgX_2$ (X = Cl, Br, I, CN and SCN),[42] $(Et_3P)_2HgX_2$ and $(Bu^n{}_3P)_2HgX_2$ (X = Cl, Br, I and ONO_2)[42] (Table 2.42).

2.5 Entropy Effects

Entropy is a measure of the disorder of a system; for this reason entropy measurements can give some indication of the number of molecules present in a structure. The higher the entropy of a system the greater the number of independent molecules it contains. Systems tend towards higher entropies and hence the most possible number of independent molecules allowed after consideration of the other factors involved.

TABLE 2.41 Bond Lengths and Interbond Angles in Some Crystalline $(Ph_3P)_2HgX_2$ Complexes (X = CF_3, CN, I, SCN, ONO_2, Br and Cl)[42]

X	(Hg-P)(Å)	(Hg-X)(Å)	P-Hg-P(°)	X-Hg-X(°)	$J(^{199}Hg-^{31}P)Hz$
CF_3	2.91(2)	2.12(2)	94.8(1)	146.6(9)	-
CN	2.515(7)	2.234(26)	108.9(2)	108.5(15)	2617
I	2.565(3)	2.748(1)	108.95(9)	110.43(4)	3074
SCN	2.488(3)	2.571(3)	118.1(1)	96.7(1)	3725
Br	2.533(15)	2.629(7)	113.0(5)	106.9(3)	4156
Cl	2.47(2)	2.552(2)	134.1(1)	110.7(1)	4675
ONO_2	2.451(1)	2.507(4)	131.8(1)	70.0(2)	5925

TABLE 2.42 Coupling Constants ($J(^{199}Hg-^{31}P)Hz$) for $R_3P)_2HgX_2$ (X = Cl, Br, I, CN, SCN and ONO_2)[42]

X	$(EtMe_2P)_2HgX_2$	$(Et_3P)_2HgX_2$	$(Bu^n{}_3P)_2HgX_2$
Cl	5606	5095	5125
Br	5436	4792	4829
I	4702	4033	4089
CN	3225	-	-
SCN	5084	-	-
ONO_2	-	5221	5212

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3. General Introduction to Crystal Structure Analysis

3.1 Single Crystal X-ray Diffraction

A single crystal can be considered as a three-dimensional lattice, with each lattice point occupied by an atom or group of atoms. It is, therefore, possible for a crystal to act as a three-dimensional diffraction grating for X-rays. The conditions required to produce a diffraction maximum from a regular three-dimensional array of scattering atoms are given by the three Laue equations.[54] These may be derived from Figure 3.1.

For a row of scattering atoms of regular spacing b along the y axis, where X-rays are incident at an angle ϕ_2, and are scattered at an angle ψ_2 the path difference (δ_2) between scattered rays is given by

$\delta_2 = AQ - BP$ or $\delta_2 = b\ (\cos \psi_2 - \cos \phi_2)$

For reinforcement of the scattered rays, the path difference must be an integral number of wavelengths.

$$\delta_2 = b\ (\cos \psi_2 - \cos \phi_2) = k\lambda \qquad \underline{3.1}$$

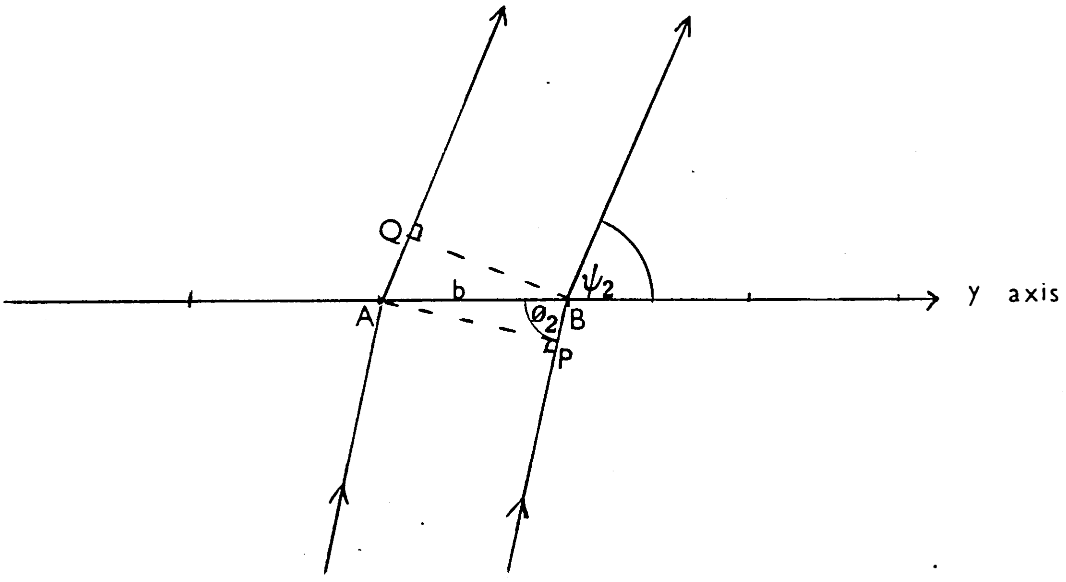


FIGURE 3.1 Diffraction from a Row of Atoms

Equation 3.1 is satisfied by the generators of a cone which is coaxial with the line of scattering atoms and has a semi-vertical angle of ψ_2. For a series of values ϕ_2, there are a number of cones each corresponding to an order of diffraction k and a semi-vertical angle ψ_{2k}. This theory when extended to the x-axis (spacing a) gives the equation

$$a(\cos \psi_2 - \cos \phi_2) = h\lambda \tag{3.2}$$

For three-dimensional systems a third equation corresponding to the third axis of spacing c can be generated.

$$c(\cos \psi_2 - \cos \phi_2) = l\lambda \tag{3.3}$$

Bragg[55] considered diffraction to be analogous to 'reflection' from a set of lattice planes. The waves are 'reflected' only under certain conditions. The length of path between the waves scattered from successive planes must have an integral number of wavelengths (i.e. nλ).

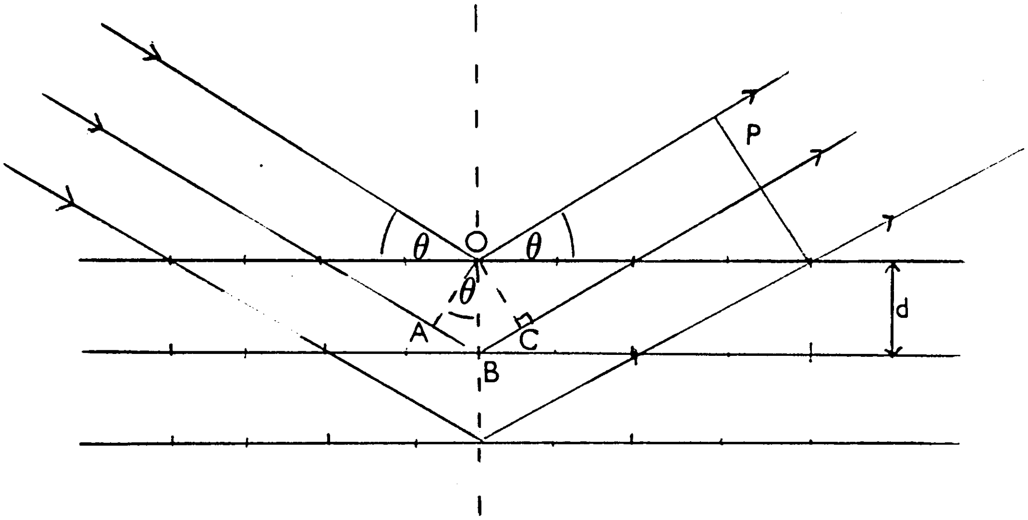


FIGURE 3.2 Diffraction of X-Rays by a Set of Lattice Planes

The path difference δ between successive waves is given by:

$$\delta = AB + BC$$

As AB = BC

$$\delta = 2AB$$

$$\therefore \delta = 2d \sin\theta$$

where d is the interplanar spacing

For reinforcement of the scattered waves the difference δ must be a whole number of wavelengths.

$$n\lambda = 2d \sin\theta \qquad \underline{3.4}$$

This expression is often referred to as 'Braggs Law'.

3.2 The Phase Problem

The phase problem arises from the difficulty in the direct determination of the phase angle associated with each structure factor. While the structure amplitude $|F|$ may be derived directly from the intensity of each reflection (Equation 3.5) the phase angle may not.

$$I_{hkl} = k\,|F_{hkl}|^2(\mathrm{Abs})(\mathrm{LP})(\mathrm{Th}) \qquad \underline{3.5}$$

I_{hkl} is the intensity of the diffraction from the set of planes hkl and may be determined experimentally.

k - scale factor associated with $|F_{hkl}|$, which may be approximated using Wilson's method.[56]

Abs - the absorption factor and is dependent upon the number and type of the atoms present in the unit cell.

L - correction for Lorentz effect which arises as the time required for a reciprocal lattice to pass through the sphere of reflection varies with its position in reciprocal space. The exact nature of the effect depends upon the type and nature of the data collection. For data collected on a Stöe Stadi-2 two circle diffractometer the collection is given by

$$L = \sin\theta/[\sin 2\theta(\sin^2\theta - \sin^2\mu)^{1/2}] \qquad \underline{3.6}$$

P - correction for the polarization of the X-rays. The incident X-ray beam loses intensity due to polarization by both the graphite monochromator crystal and by the crystal under investigation.

Correction for polarization (P) by the data crystal is given by

$$P = \frac{1}{2}(1 + \mathrm{Cos}^2\, 2\theta) \qquad \underline{3.7}$$

The electron density (p) at a point x, y, z in a unit cell of volume V_c is given by equation 3.8 where α_{hkl} is the phase angle and must be evaluated before the map can be computed.

$$p(x,y,z) = \frac{1}{V_c}\,\Sigma_h\Sigma_k\Sigma_l\,|F|\,\mathrm{Cos}[2\pi\,(hx + ky + lz) - \alpha_{hkl}] \qquad \underline{3.8}$$

A plot of p(x,y,z) for appropriate values of x, y and z gives a three-dimensional electron density map from which electron density and hence the atomic positions may be elucidated. Evaluation of the phase angles, i.e. overcoming the phase problem, is normally achieved by one of the following approaches:

Patterson synthesis

Direct methods

3.2.1 Patterson Synthesis

The Patterson function P(uvw) may be calculated without the knowledge of phase angles (equation 3.9). The resulting three-dimensional map gives rise to positive peaks representing vectors between all possible pairs of atoms in the unit cell. The heights of the vectors are proportional to the product of the atomic numbers of the two atoms. Hence, if one or more heavy atoms are present, then their associated vectors may be readily located on the map.

$$P(uvw) = \frac{1}{V_c}\,\sum_{h}\sum_{k}{}_{-\infty}^{\infty}\,\Sigma_l\,|F_{hkl}|^2\,\mathrm{Cos}\,2\pi(hu + kv + lw) \qquad \underline{3.9}$$

The value for $|F_{hkl}|$ is obtained from the measured intensities I_{hkl} using the equation 3.5.

3.2.2 Direct Methods

While this technique has been widely used for organic molecules it has also proved to be useful in locating heavy atoms in, for example, organometallic compounds. These methods were developed assuming that if a structure can be derived from a Fourier synthesis of the measured intensities, such as in the Patterson function, it should be possible to derive the structure directly from the intensities themselves. An initial development of "direct methods" was the derivation of inequalities which expressed the phases of the structure factors in terms of observed structure amplitudes $|F_O|$, where $I \propto |F_O|^2$. Using the general structure factor expression the trivial result

$$|F_{hkl}|^2 < F^2_{000} \qquad \underline{3.10}$$

may be extended by centrosymmetric requirements to give

$$F^2_{hkl} < F_{000}\ (\tfrac{1}{2}F_{000} + \tfrac{1}{2}F_{2h,2k,2l}) \qquad \underline{3.11}$$

If U_{hkl} is defined as $= F_{hkl}/F_{000}$ then $U^2_{hkl} < \frac{1}{2} + \frac{1}{2}U_{2h,2k,2l}$ $\qquad \underline{3.12}$

As the magnitude and sign (+) of U^2_{hkl} are known, only the phase of $U_{2h,2k,2l}$ is unknown. In centrosymmetric systems the phase angle may only take one of two values, 0° or 180°, corresponding to the signs + and - in the structure factor expression. For non-centrosymmetric crystals, however, the phase angle may take any value between 0° and 360°.

Inequalities proved to be of limited use as often it was not possible to determine sufficient phases from which the structure could be solved. This limitation led to the development of 'probability methods' for the determination of phases which could be used for structural analysis. Karle and Hauptmann found the normalized structure factor $|E_{hkl}|$ to be more suitable for use in probability functions.[64]

$$|E_{hkl}|^2 = \frac{|F_{hkl}|^2}{\varepsilon\ {}^{N}\Sigma_j f_j^2} \qquad \underline{3.13}$$

ε is an integer dependent upon the reflection and upon the space group symmetry.

The distribution of $|E|$ values is independent of the size and content of the unit cell but is dependent whether or not there is a centre of symmetry in the space group.

The tabulated distribution of $|E|$ values are:

Mean Values	Centrosymmetric crystal	Non-centrosymmetric crystal
$\|E\|^2$	1.00	1.00
$\|\|E\|^2 - 1\|$	0.97	0.74
$\|E\|$	0.80	0.89
% $\|E\| > 1$	32.00	36.80
% $\|E\| > 2$	5.00	1.80
% $\|E\| > 3$	0.30	0.01

The most commonly used expression to predict the phases of reflections in centrosymmetric crystals is the Sayre relationship.[57]

$$\text{sign } F_h \approx \text{sign } (F_k F_{h-k}) \qquad \underline{3.14}$$

or in a more general form

$$\text{sign } E_{\underline{h}} \approx \text{sign } \sum_{\underline{k}} E_{\underline{k}} E_{\underline{h}-\underline{k}} \qquad \underline{3.15}$$

where $\approx$ means 'is probably equal to'.

Equation 3.15 is known as the Σ_2 formula but this formula cannot be used for non-centrosymmetric crystal analysis. The phase angle, ϕ_h, for such systems may be derived from the 'tangent formula'.

$$\tan \phi_{\underline{h}} \quad \frac{\Sigma_{\underline{k}} |E_{\underline{k}} E_{\underline{h}-\underline{k}}| \, \mathrm{Sin}(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} |E_{\underline{k}} E_{\underline{h}-\underline{k}}| \, \mathrm{Cos}(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})} \qquad \underline{3.16}$$

A measure of the reliability of the predicted phases $\alpha_{\underline{h}}$ is given by equation 3.17. The higher the $\alpha_{\underline{h}}$ value the better the reliability of the phase prediction.

$$\alpha_{\underline{h}}^{2} = [\sum_{\underline{k}} \kappa_{\underline{hk}} \operatorname{Cos}(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})]^{2} + [\sum_{\underline{k}} \kappa_{\underline{hk}} \operatorname{Sin}(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})]^{2} \qquad \underline{3.17}$$

where $\kappa_{\underline{hk}} = 2\sigma_3\sigma_2^{-3/2}|E_{\underline{h}}E_{\underline{k}}E_{\underline{h-k}}|$

being calculated from equation 3.18

$$\sigma n = \sum_{j=1}^{n} Z_j^n \qquad \underline{3.18}$$

Z_j is the atomic number of the j atom.

Initially $\phi_{\underline{k}}$ and $\phi_{\underline{h}-\underline{k}}$ are unknown, so an estimated value of $\alpha_{\underline{h}}$ must be used and this is given by

$$\langle\alpha_{\underline{h}}^{2}\rangle_e = \sum_{\underline{k}} \kappa_{\underline{hk}}^{2} + 2\sum\sum_{\underline{kk}'} \kappa_{\underline{hk}}\kappa_{\underline{hk}'} \cdot \frac{I_1(\kappa_{\underline{hk}})I_1(\kappa_{\underline{hk}'})}{I_0(\kappa_{\underline{hk}})I_0(\kappa_{\underline{hk}'})} \qquad \underline{3.19}$$

Where I_1 and I_0 are modified Bessel functions.

The expression (3.19) is often modified to the approximate formula

$$\langle\alpha_{\underline{h}}^{2}\rangle_e^{1/2} = \sum_{\underline{h}} \kappa_{\underline{hk}} \frac{I_1(\kappa_{\underline{hk}})}{I_0(\kappa_{\underline{hk}})} \qquad \underline{3.20}$$

Before these expressions may be used, the phases of some of the reflections must be fixed (usually at 0°) in order to determine the position of the origin in the unit cell. The number and type of reflections used depend on the space group. Some reflections have their phases fixed by the structure, and these structure semi-invariants may not be altered. For non-centrosymmetric crystals a further reflection is given fixed values for its phase to distinguish between the two possible enantiomorphous forms of the crystal.

3.3 Refinement of a Trial Structure

Having deduced the initial structure by Patterson or direct methods techniques, further atoms may be located by the successive use of Fourier maps. This method makes use of the fact that the electron density at any point in the unit cell is given by equation 3.8. The structure amplitude, $|F_c|$ may be calculated:

$$|F_{hkl}| = (A_{hkl}^2 + B_{hkl}^2)^{1/2} = |F_c| \qquad \underline{3.21}$$

where

$$A_{hkl} = \Sigma_j f_j \mathrm{Cos} 2\pi(hx_j + ky_j + lz_j)$$

$$B_{hkl} = \Sigma_j f_j \mathrm{Sin} 2\pi(hx_j + ky_j + lz_j)$$

f_j is the atomic scattering factor of the j^{th} atom

x_j, y_j, z_j, is the position of j atoms in the unit cell, and the phase angle is given by

$$\emptyset_{hkl} = \tan^{-1} \left(\frac{B_{hkl}}{A_{hkl}}\right) \qquad \underline{3.22}$$

The resulting observed Fourier map displays areas of electron density corresponding to the initially located atoms plus other unknown atoms in the structure. In the later stages of analysis, a difference Fourier synthesis is normally employed in which the $|F_o|$ coefficients are replaced by $(|F_o| - |F_c|)$ this reveals atoms other than those used to determine $|F|$, providing the calculated phases are close to the observed ones.

3.4 Least-Squares Refinement

When the positions of atoms have been located it is possible to calculate the phase and $|F_c|$ for all observed reflections. These phases and the $|F_o|$ values may be used to obtain further Fourier maps (equation 3.8) from which the positions of further atoms may be located. New values for $|F_c|$ and $\emptyset_{hkl}$ may then be calculated which, since they are based on more atoms, should give a closer approximation to the experimentally determined structure amplitudes and phases. The measure of agreement between $|F_c|$ and $|F_o|$ is given by the reliability or residual index (the R-value) which is calculated from equation 3.23.

$$R = \Sigma_{hkl} \frac{||F_o|-|F_c||}{\Sigma_{hkl}|F_o|} \qquad \underline{3.23}$$

The better the agreement between $|F_o|$ and $|F_c|$ the lower the R-value. A least-squares technique is used to refine the atomic positional parameters (x_j, y_j, z_j), thermal parameters (U or U_{ij} etc.), the overall scale factor, K, and the non-unit population factors.

3.5 Thermal Parameters

The atomic scattering factor as used to calculate $|F_c|$ (equation 3.21), assumes the atoms to be point atoms. However, in practice atoms vibrate and hence a correction for thermal motion needs to be made:

$$f = f_0 \exp \frac{[-8\pi^2 U \sin^2\theta]}{\lambda^2} \qquad \underline{3.24}$$

where U is the isotropic temperature factor and is the mean square amplitude of the atomic vibration. For anisotropic vibration the correction to f_0 is given by:

$$f = f_0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*] \qquad \underline{3.25}$$

Where U_{ij} describes the direction and magnitude of a vibrational elipsoid and are taken as anisotropic thermal factors.

3.6 Weighting Scheme

Unit weights are applied in the early stages of the least squares analysis but a non-unit weighting scheme is introduced in the later stages. If a non-unit weighting scheme is applied then a weighted R - value R_w or R' may be calculated:

$$R_w = \frac{\Sigma_{hkl}|K|F_o| - |F_c||(W_{hkl})^{1/2}}{\Sigma_{hkl}K\,|F_o|(W_{hkl})^{1/2}} \qquad \underline{3.26}$$

Where W is the non-unit weight as calculated using equation 3.27.

$$W = a/[\sigma|F_o|^2 + b|F_o|^2] \qquad \underline{3.27}$$

a and b are refined to give the best consistency of $W\Delta^2$ ($W\Delta^2 = |F_o| - |F_c|$) over ranges of F_o and $\sin\theta/\lambda$

3.7 Anomalous Dispersion

When the scattering factor of an atom is calculated as a real number it is assumed that the frequency of the incident radiation is different from the natural absorption frequency of the atom. Although this may be true for light atoms and the radiations used for X-ray diffraction, it is generally not so for heavier atoms which may absorb the incident radiation. If such absorption occurs there will be an anomalous change in phase of the radiation scattered by the electrons associated with the absorption. This effect, anomalous scattering or anomalous dispersion, causes the scattering factor to become a complex number represented by:

$$f_j^{anom} = f_j + \Delta f'_j + i\Delta f''_j \qquad \underline{3.28}$$

where f_j is the normal scattering factor

$\Delta f'_j$ is a real correction term usually negative

$\Delta f''_j$ is an imaginary correction term

For a centrosymmetric structure the effect of the anomalous dispersion is to alter the phases of certain reflections so they are no longer restricted to 0° and 180°, but for such cases Friedel's law still holds. For non-centrosymmetric crystal systems Friedel's law no longer holds as the phases and magnitudes of the reflections are altered.

Contents

4. Crystallographic Studies of Selected $(R_3P)_nHgX_2$ Complexes

4.1 Crystallographic Methods

The methods used for structure solution and refinement are similar for all the crystals studied and a general description of these is outlined below.

4.1.1 Space Group Determination

The space groups were determined by the examination of oscillation, Weissenberg and precession photographs for:

(i) Symmetry

(ii) Systematic absences

4.1.2 Density Determination and Relative Mass Evaluation

The density D_m of the crystals under examination may be measured by suspending them in a liquid. The density of the liquid is altered until the crystals neither float to the surface of the liquid nor fall to the bottom. At this point the density of the crystals is assumed to be the same as the density of the liquid.

If the crystal contains Z molecules in the unit cell then:

$$D_m = \frac{ZM}{V \times 0.6022 \times 10^{24}} \quad (\mathrm{g\ cm^{-3}}) \qquad \underline{4.1}$$

Where M is the relative molecular mass

V is the unit-cell volume expressed as cm^3

0.6022×10^{24} is the Avogadro constant

The value of Z is related to the number of molecules in the asymmetric unit and the space group. Knowing D_m and M, Z may be calculated, from which the number of molecules in the asymmetric unit can be established. Alternatively, knowing the space group, the value for Z may be assumed, from which the relative molecular mass may be evaluated.

4.1.3 Unit Cell Measurements

The unit cell dimensions, used for alignment of the crystal on the diffractometer, were obtained from measurements of precession photographs and subsequently refined using the diffractometer.

4.1.4 Data Collection

All data were collected using a Stöe Stadi-2 two-circle diffractometer with Mo-K_α radiation (λ = 0.71069 Å), and the background-ω-scan-background technique. By this method the counter remains stationary and the crystal is rotated by small steps in ω (0.01° per second). The scan range, $\Delta\omega$ selected, is dependent upon the equi-inclination angle μ, and upon θ as given in equation 4.2.

$$\Delta\omega = A + \frac{B \sin \mu}{\tan \theta} \qquad \underline{4.2}$$

Values are found for A and B step scanning several reflections before data collection proceeds.

The intensity of a reflection, I_{hkl}, is given by equation 4.3.

$$I_{hkl} = T - \frac{(B_1 + B_2)c}{2t} \qquad \underline{4.3}$$

Where T is the scan count, B_1 and B_2 are background counts at beginning and end of the scan, c is the scan time and t is the time taken for the background measurements. (For all data collected t = 30 seconds). The standard deviation in the intensity measurement $\sigma(I_{hkl})$ is given by equation 4.4.

$$\sigma(I_{hkl}) = [T - \frac{(B_1 + B_2)^2}{4t^2}]^{1/2} \qquad \underline{4.4}$$

Reflections included in the final stages of analysis were those having $I_{hkl}/\sigma(I_{hkl}) \geqslant 3.0$

Corrections were applied to the data for Lorentz and polarisation effects for all complexes but an absorption correction also for $(Pr_3P)HgI_2$ and $[(NCCH_2CH_2)_3P]HgCl_2$.

4.1.5 Structure Solution and Refinement

The mercury co-ordinates for all the structures were determined from a three-dimensional Patterson map. The remaining atoms were located from successive difference electron-density maps. All non-carbon atoms were assigned anisotropic thermal parameters and wherever possible carbon atoms were all given anisotropic thermal parameters. However, for $(Pr_3P)_2HgI_2$ and $[(NCCH_2CH_2)_3P]_2HgCl_2$ only isotropic temperature factors were applied. Where included, hydrogen atoms have been assigned ideal positions (C-H 1.08 Å). Non-unit weighting schemes have been applied to all structures and all calculations were carried out on an IBM 4341 computer using the SHELX (15) computing package.[58]

4.2 The Crystallographic Studies of Some 2:1 Complexes $(R_3P)_2HgX_2$

4.2.1 Crystallographic Examination of the 2:1 Complex $[(2\text{-thienyl})_3P]_2HgCl_2$

TABLE 4.2.1 Crystal Data

Crystal Size	0.30 x 0.23 x 0.40 mm
Crystal System	Monoclinic
	a = 9.556(6), b = 18.280(10), c =16.609(9) Å, β = 102.14(5)°
V	2836.4 Å^3
M_r	832.2
D_c	1.95 g cm^{-3} D_m 1.93 g cm^{-3} Z = 4
Systematic Absences	h0l h + l = 2n + 1
	0k0 k = 2n + 1
Space Group	$P2_1/n$ (a non-standard setting of $P2_1/c$)
μ(Mo-Kα)	59.2 cm^{-1}
F(000)	1608 electrons

Data Collection and Structural Analysis

The crystal was mounted with its c-axis coincident with the ω-axis of the Stöe Stadi-2 two-circle diffractometer. 4774 unique reflections were measured, 4067 had$(I/\sigma(I)) \geqslant 3.0$ and were subsequently used for refinement. The initial co-ordinates of the independent mercury atom in the asymmetric unit were determined using the Patterson function:

For $P2_1/n$ there are four equivalent positions of the mercury atoms in the unit cell, viz.

$x, y, z;\ \ -x, -y, -z;\ \ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\ \ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z.$

These four mercury atoms in the unit cell give rise to sixteen vectors of which four occur at the origin and represent the vector between the atom and itself.

		Hg1	Hg2	Hg3	Hg4
		x,y,z	$-x,-y,-z$	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$
Hg1	x,y,z	$0,0,0$	$-2x,-2y,-2z$	$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	$\frac{1}{2}-2x,\frac{1}{2},\frac{1}{2}-2z$
Hg2	$-x,-y,-z$	$2x,2y,2z$	$0,0,0$	$\frac{1}{2}+2x,\frac{1}{2},\frac{1}{2}+2z$	$\frac{1}{2},+2y,\frac{1}{2}$
Hg3	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$	$-\frac{1}{2},-\frac{1}{2}+2y,-\frac{1}{2}$	$-\frac{1}{2}-2x,-\frac{1}{2},-\frac{1}{2}-2z$	$0,0,0$	$-2x,2y,-2z$
Hg4	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	$-\frac{1}{2}+2x,-\frac{1}{2},-\frac{1}{2}+2z$	$-\frac{1}{2},-\frac{1}{2}-2y,-\frac{1}{2}$	$2x,-2y,2z$	$0,0,0$

Many of the remaining 12 vectors are related by the symmetry allowed in a monoclinic crystal system. Thus, the vectors $2x$, $2y$, $2z$ and $-2x$, $-2y$, $-2z$ are related by a centre of symmetry while in turn to the vectors at $-2x$, $2y$, $-2z$ and $2x$, $-2y$, $2z$ by a mirror plane perpendicular to b. These are three unique vectors:

$\frac{1}{2}$, $\frac{1}{2}-2y$, $\frac{1}{2}$; $2x$, $2y$, $2z$; $\frac{1}{2}-2x$, $\frac{1}{2}$, $\frac{1}{2}-2z$

Examination of the three-dimensional Patterson map generated using the 4067 reflections having $I/\sigma(I) \geqslant 3.0$ enabled the co-ordinates of the independent mercury to be established:

Vector	Fractional Co-ordinate of Peak located on Patterson Map			Height of Vector
$\frac{1}{2},\frac{1}{2}-2y,\frac{1}{2}$	0.5, 0.1906, 0.5			368
	$y = 0.1547$			
$\frac{1}{2}-2x,\frac{1}{2},\frac{1}{2}-2z$	-0.3830, 0.5, 0.0008			363
	$x = 0.4415$	$z = 0.2496$		
$2x,2y,2z$	$x = 0.8830$	$y = 0.3094$	$z = 0.4992$	166

This gives a consistent set of co-ordinates (x, y, z) for the mercury atom of (0.4415, 0.1547, 0.2496). Least-squares refinement of these coordinates (together with the refinement of the overall scale factor and the isotropic temperature factor of the mercury) gave an R-value of 0.33 after four cycles of refinement. The difference Fourier map, using phases derived from the refined position of the mercury atom, enabled the chlorine and phosphorus atoms to be located, together with a number of sulphur and carbon atoms. The remaining atoms were then located from successive difference electron-density maps. Full matrix refinement gave a final R value of 0.049 and R' value of 0.058.

Two of the six thienyl units were found to exhibit rotational disorder. The disordered groups are related to each other by a pseudo two-fold axis about the P2-Cn1 (n = 4 or 6) bonds. Each disordered 2-thienyl group was given an ideal geometry and included in the least-squares refinement with common isotropic temperature factors applied to each atom related by pseudo symmetry. The population parameters applied to each pair of thienyl units were refined, giving final occupancy values of 45% for [C(41), S(42A) -C(45A)], 55% [C(41), S(42B) -C(45B)] and 50% for each of the disordered units associated with C(61). The hydrogen atoms were located for the ordered 2-thienyl groups, and a common isotropic temperature factor applied which refined to a final value of 0.059(13) $\mathring{A}^2$. The weighting scheme $W = 1.000/[\sigma^2(F_0) + 0.0078(F_0)^2]$ was adopted. Final positional parameters are given in the appendix tables 1 and 2, bond distances and angles in Table 4.2.2.

Results and Discussion

The X-ray study of $[(2\text{-thienyl})_3P]_2HgCl_2$ shows it to be a distorted tetrahedral monomer (Fig. 4.2.1) with two of the six thienyl groups showing disorder as discussed in the structural analysis section. The angles about the mercury vary from 99.6(1) to 128.6(1)°. The angles about the phosphorus atoms are less distorted with angles ranging from 110.4(3) to

115.8(3)°. The Hg-Cl bond distances are 2.539(2) and 2.519(2) Å, while the Hg-P bonds are 2.472(2) and 2.513(2) Å in length respectively. A full comparison of the data for this complex with available parameters for other 2:1 structures is made in section 4.2.3.

Fig. 4.2.1 The Molecular Structure of [(2-thienyl)$_3$P]$_2$HgCl$_2$

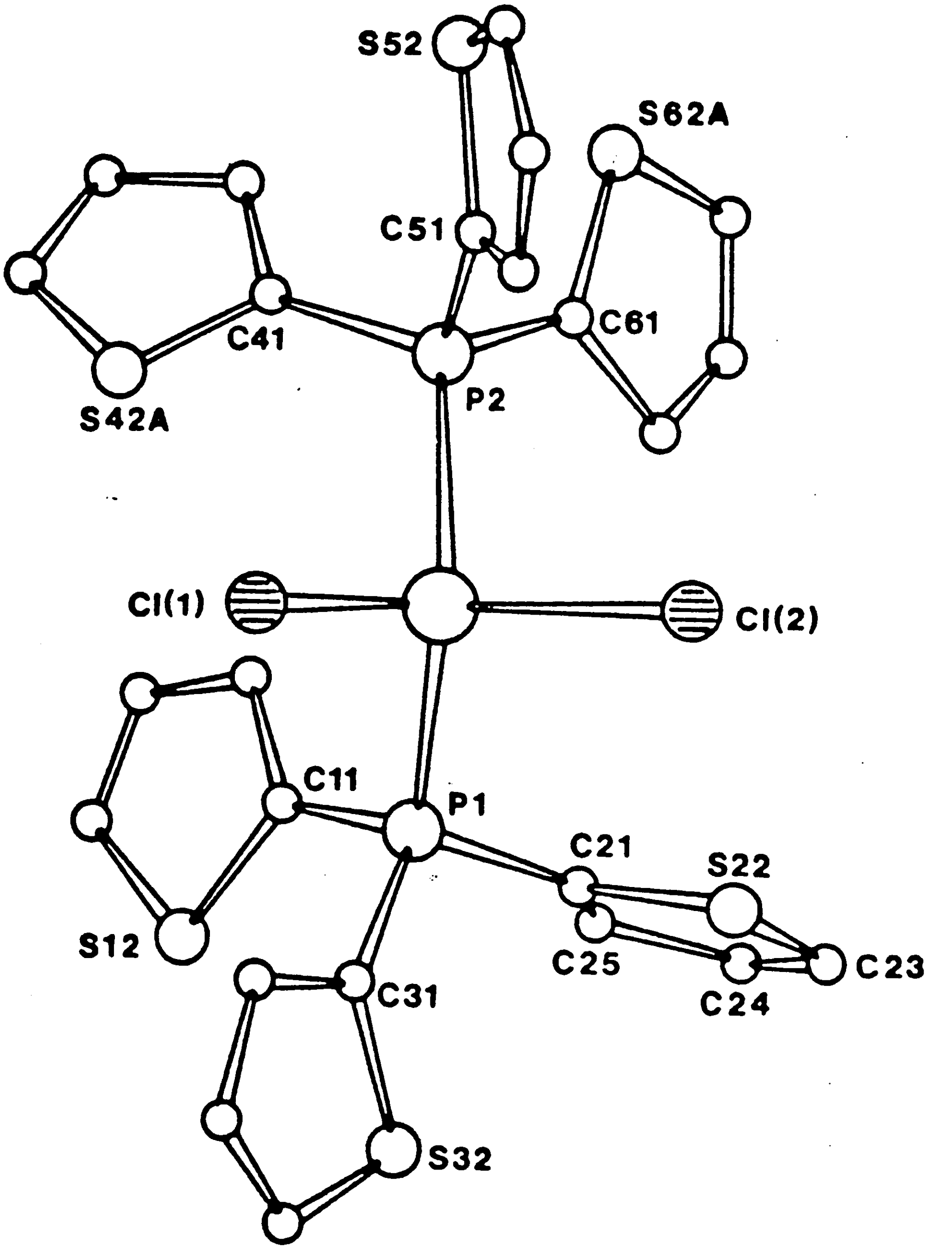


Table 4.2.2 Bond Lengths (Å) and Angles (°) for $[(2\text{-thienyl})_3P]_2HgCl_2$ with Estimated Standard Deviations in Parentheses.

Distances (Å)

Hg -Cl(1)	2.539(2)	Hg -Cl(2)	2.519(2)
Hg -P(1)	2.472(2)	Hg -P(2)	2.513(2)
P(1) -C(11)	1.803(9)	P(2) -C(41)	1.804
P(1) -C(21)	1.785(9)	P(2) -C(51)	1.779(9)
P(1) -C(31)	1.787(9)	P(2) -C(61)	1.795
C(11)-S(12)	1.686(11)	C(41) -S(42A)	1.611
C(11) -C(15)	1.385(14)	C(41) -C(45A)	1.407
S(12) -C(13)	1.726(12)	S(42A) -C(43A)	1.701
C(13) -C(14)	1.285(20)	C(43A) -C(44A)	1.318
C(14) -C(15)	1.395(17)	C(44A) -C(45A)	1.414
C(21) -S(22)	1.717(9)	C(41) -S(42B)	1.631
C(21) -C(25)	1.442(12)	C(41) -C(45B)	1.406
S(22) -C(23)	1.676(12)	S(42B) -C(43B)	1.700
C(23) -C(24)	1.385(16)	C(43B) -C(44B)	1.299
C(24) -C(25)	1.457(13)	C(44B) -C(45B)	1.485
C(31) -S(32)	1.682(10)	C(51) -S(52)	1.720(10)
C(31) -C(35)	1.434(12)	C(51) -C(55)	1.355(12)
S(32) -C(33)	1.708(12)	S(52) -C(53)	1.692(10)
C(33) -C(34)	1.350(17)	C(53) -C(54)	1.346(16)
C(34) -C(35)	1.406(16)	C(54) -C(55)	1.439(15)
C(61) -S(62A)	1.664	C(61) -S(62B)	1.624
C(61) -C(65A)	1.415	C(61) -C(65B)	1.404
S(62A)-C(63A)	1.700	S(62B)-C(63B)	1.701
C(63A)-C(64A)	1.321	C(63B)-C(64B)	1.336
C(64B)-C(65A)	1.444	C(64B)-C(65B)	1.555

Table 4.2.2 (cont.)

Angles (°)

P(1) -Hg -Cl(1)	109.3(1)	P(2) -Hg -Cl(1)	101.6(1)
P(1) -Hg -Cl(2)	108.6(1)	P(2) -Hg -Cl(2)	99.6(1)
P(1) -Hg -P (2)	128.6(1)	C (1)-Hg -Cl(2)	107.3(1)
Hg -P(1)-C (11)	111.1(3)	Hg -P(2)-C(41)	113.1
Hg -P(1)-C (21)	113.0(3)	Hg -P(2)-C(51)	110.4(3)
Hg -P(1)-C (31)	115.8(3)	Hg -P(2)-C(61)	112.4
P(1) -C(11) -S(12)	122.7(6)	P(2) -C(41) -S(42A)	122.6
P(1) -C(11) -C(15)	128.0(9)	P(2) -C(41) -C(45A)	126.2
S(12) -C(11) -C(15)	109.3(8)	S(42A)-C(41)-C(45A)	110.6
C(11) -S(12) -C(13)	91.5(6)	C(41) -S(42A)-C(43A)	92.2
S(12) -C(13) -C(14)	112.9(9)	S(42A)-C(43A)-C(44A)	114.1
C(13) -C(14) -C(15)	112.6.(11)	C(43A)-C44A) -C(45A)	107.8
C(11) -C(15) -C(14)	113.6(12)	C(41) -C(45A)-C(44A)	112.3
P(1) -C(21) -S(22)	121.3(5)	P(2) -C(41) -S(42B)	126.1
P(1) -C(21) -C(25)	125.8(7)	P(2) -C(41) -C(45B)	122.4
S(22) -C(21) -C(25)	112.9(7)	S(42B)-C(41) -C(45B)	110.7
C(21) -S(22) -C(23)	91.8(5)	C(41) -S(42B)-C(43B)	92.3
S(22) -C(23) -C(24)	114.6(8)	S(42B)-C(43B)-C(44B)	117.0
C(23) -C(24) -C(25)	112.2(9)	C(43B)-C(44B)-C(45B)	106.7
C(21) -C(25) -C(24)	108.4(8)	C(41) -C(45B)-C(44B)	112.5
P(1) -C(31) -S(32)	124.0(5)	P(2) -C(51) -S(52)	124.9(5)
P(1) -C(31) -C(35)	123.9(7)	P(2) -C(51) -C(55)	125.7(8)
S(32) -C(31) -C(35)	111.7(7)	S(52) -C(51) -C(55)	109.4(7)
C(31) -S(32) -C(33)	92.6(5)	C(51) -S(52) -C(53)	92.8(5)
S(32) -C(33) -C(34)	111.6(9)	S(52) -C(53) -C(54)	112.8(8)

Table 4.2.2. (cont.)

C(33)-C(34) -C(35)	114.6(10)	C(53) -C(54) -C(55)	110.7(9)
C(31)-C(35) -C(34)	109.5(9)	C(51) -C(55) -C(54)	114.3(9)
P(2) -C(61) -S(62A)	123.0	P(2) -C(61) -S(62B)	120.7
P(2) -C(61) -C(65A)	122.0	P(2) -C(61) -C(65B)	123.2
S(62A)-C(61)-C(65A)	115.0	S(62B)-C(61) -C(65B)	116.1
C(61)-S(62A)-C(63A)	92.2	C(61) -S(62B)-C(63B)	92.3
S(62A)-C(63A)-C(64A)	110.4	S(62B)-C(63B)-C(64B)	113.1
C(63A)-C(64A)-C(65A)	117.6	C(63B)-C(64B)-C(65B)	109.1
C(61) -C(65A)-C(64A)	104.7	C(61) -C(65B)-C(64B)	104.1

4.2.2 Crystallographic Examination of the 2:1 Complexes $[(NCCH_2CH_2)_3P]_2HgX_2$ (X = Cl or Br)

TABLE 4.2.3 Crystal Data

	(I) $[(NCCH_2CH_2)_3P]_2HgCl_2$	(II) $[(NCCH_2CH_2)_3P]HgBr_2.(CH_3)_2CO$
Crystal Size (mm)	.08 x .48 x .04	.44 x .20 x .13
Crystal System	Monoclinic	Monoclinic
a (Å)	25.728(8)	9.174(6)
b (Å)	8.627(7)	15.795(9)
c (Å)	24.482(8)	20.741(11)
β (°)	115.14(1)	93.01(5)
V(Å^3)	4919.49	3001.4
M_r	657.9	821.1
D_c(gcm^{-3})	1.78	1.82
D_m(gcm^{-3})	1.80	1.84
Systematic Absences	$h0l$ $l = 2n + 1$	$h0l$ $h + l = 2n + 1$
	$0k0$ $k = 2n + 1$	$0k0$ $k = 2n + 1$
Z	8	4
Space group	$P2_1/c^+$	$^‡P2_1/n$
μ(Mo-Kα)(m^{-1})	63.6	76.6
F(000)	2544	1544

[+] Two independent molecules in the asymmetric unit.

[‡] Non-standard setting of $P2_1/c$.

Data Collection and Structural Analysis

Details of data collection are given in Table 4.2.4 and both structures were solved using the Patterson method and refined by full-matrix least squares techniques.

TABLE 4.2.4 Details of the Data Collection

	(I)	(II)
Axis crystal mounted about	b	a
No. layers collected	9	11
No. unique reflections	4241	4700
+No. observed reflections	2522	2511
Final R value	0.062	0.043
Final R' value	0.064	0.045
$\underline{W} = a/[\sigma^2(F_o) + b(F_o)^2]$		
a	1.0000	1.0000
b	0.001296	0.0040

+No. of reflections with $I/\sigma(I) \geqslant 3.0$

The data were corrected for Lorentz and polarisation effects, but absorption corrections were not applied. Hydrogen atoms were included for (II) in ideal positions (C-H, 1.08 Å) and were given a common isotropic temperature factor. All other atoms in (II) were assigned anisotropic thermal parameters. In the chloride complex, (I), there is some degree of disorder in the cyanoethyl groups and it proved difficult to resolve this satisfactorily resulting in high errors and widely varying C-N and C-C bond lengths (Table 4.2.5). Hence, anisotropic temperature factors were only applied to mercury, phosphorus and chlorine atoms, and all the remaining atoms were treated isotropically. The degree of disorder made it impossible to include any hydrogen atoms for structure (I).

Results and Discussion

$[(NCCH_2CH_2)_3P]_2HgCl_2$ consists of two independent monomeric units (Fig. 4.2.2). Both units are highly distorted from a regular tetrahedral arrangement, the angles about mercury varying from 92.3(3) to 153.9(3)°.

All the cyanoethyl chains are disordered to some degree, the widest variations being found in the bond lengths for C(A2)-C(A3) and C(A3)-N(A3) (where A = 1-6). The carbon-carbon bonds vary from 1.04(7) to 1.63(7) Å while the carbon-nitrogen bonds have wider variations, 1.08(3) to 1.95(8) Å. There is a weak interaction between the nitrogen atom of three of the cyanoethyl groups, one in one of the units, two in the other. In monomer I the Hg-N distances are 3.51(3) and 3.52(3) Å and for monomer II the Hg-N distance is 3.74(3) Å; these distances being longer than the sum of the van der Waals' radii (3.30 Å). The Hg-N bond distances found for monomer I are very similar to those found for $[(NCCH_2CH_2)_3]PHgCl_2$ 3.51(3) and 3.47(3) Å. Selected bond angles and bond lengths for $[(NCCH_2CH_2)_3P]_2HgCl_2$ are given in Table 4.2.5. The torsion angles (appendix table 16) show that three of the cyanoethyl chains are twisted from their expected geometry of 180° (to 49, 57 and 87° respectively). This allows the nitrogen atoms in these groups to take up positions near the mercury atom.

$[(NCCH_2CH_2)_3P]_2HgBr_2(CH_3)_2CO$ also adopts a monomeric arrangement but with a trigonal bipyramidal polyhedral arrangement about mercury, the oxygen atom of the acetone molecule occupying an equatorial position. The bond angles about the mercury atom vary from 151.3(1)° for P(1)-Hg-P(2) to 75(1)° for P(1)-Hg-O. Further bond lengths and angles are given in Table 4.2.6. The length of the Hg...O bond (3.91(2) Å) is greater than the sum of the van der Waals radii (3.25 Å) and indicates that the mercury-acetone interaction is extremely weak. However, the infrared and thermal studies[59] indicate that the interaction between the mercury and acetone is significant and the presence of the acetone may, at least in part, be responsible for the enlargement of the P-Hg-P angle (151.3(1)°).

Final positional and thermal parameters for both complexes are given in the appendix (tables 3-6). Torsion angles are given in the appendix table 2.1.

Fig. 4.2.2(a) The Molecular Structure of [(NCCH$_2$CH$_2$)$_3$P]$_2$HgCl$_2$, Molecule I

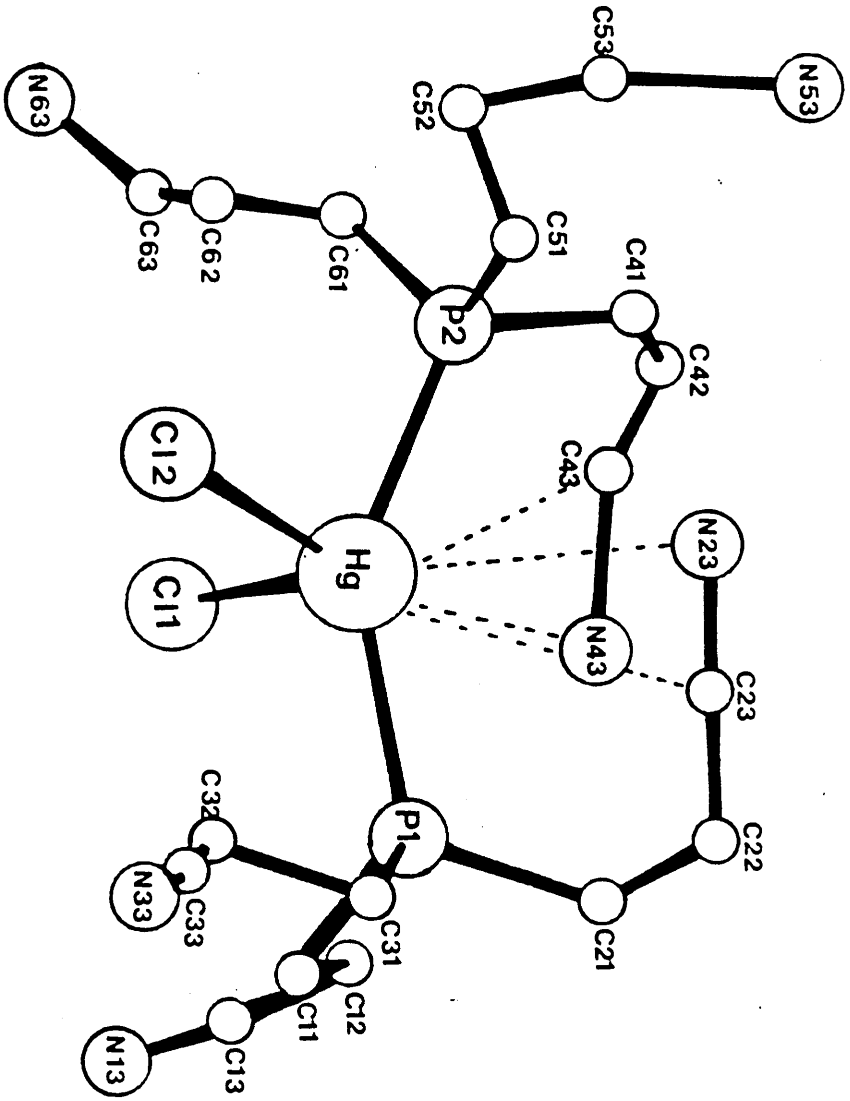


Fig. 4.2.2(b) The Molecular Structure of $[(NCCH_2CH_2)_3P]_2HgCl_2$, Molecule II

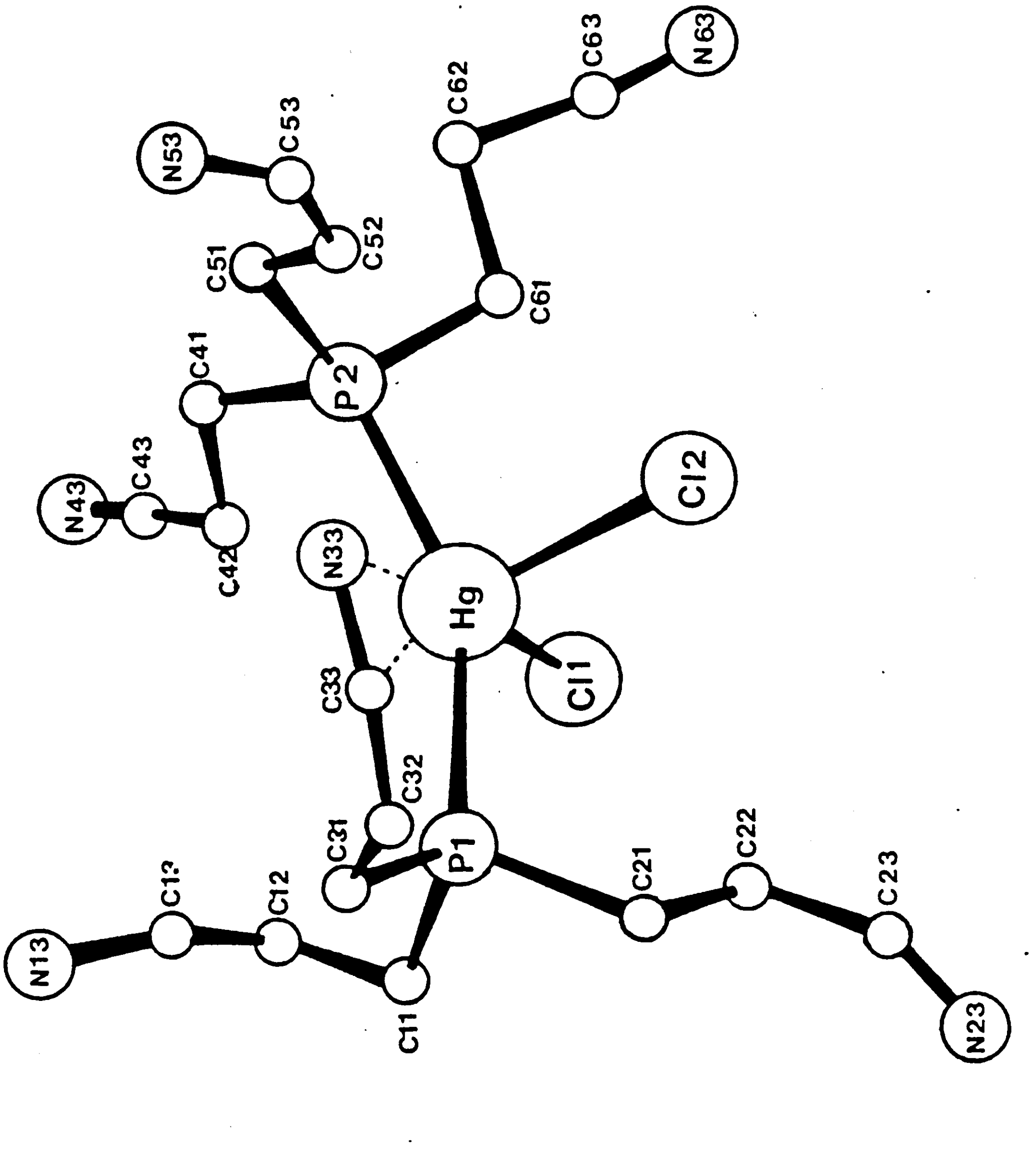


Fig 4.2.3 The Molecular Structure of $[(NCCH_2CH_2)_3P]_2HgBr_2.OC(CH_3)_2$

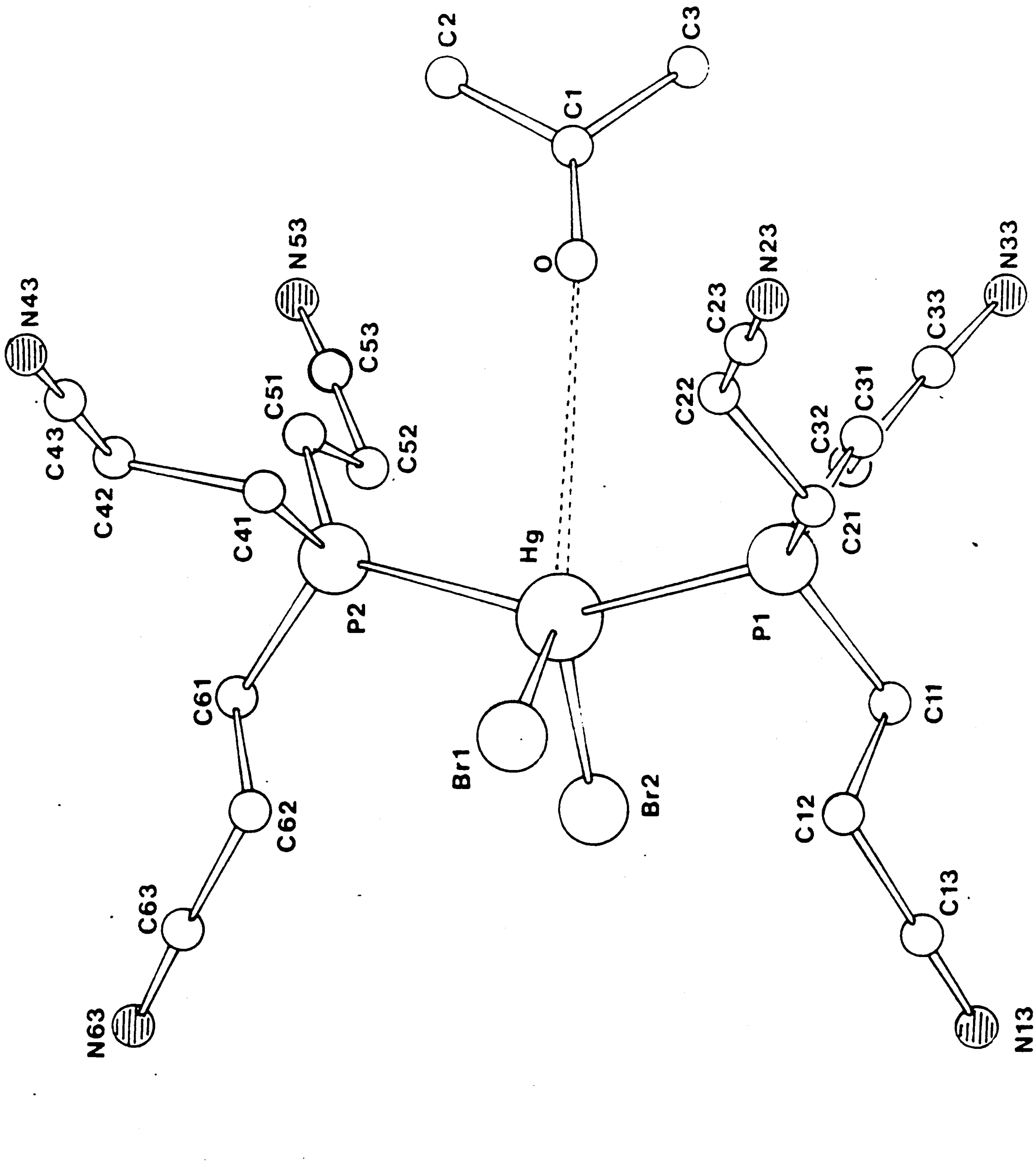


Table 4.2.5 Bond Lengths (Å) and Angles (°) for $[(NCCH_2CH_2)_3P]_2HgCl_2$ with Estimated Standard Deviations in Parentheses

Distances (Å)	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Hg-Cl(1)	2.608(10)	2.669(11)	Hg-Cl(2)	2.622(1)	2.603(10)
Hg-P(1)	2.450(12)	2.411(7)	Hg-P(2)	2.452(11)	2.450(6)
P(1)-C(11)	1.86	1.84	P(2)-C(41)	1.80	1.80
P(1)-C(21)	1.87	1.87	P(2)-C(51)	1.99	1.85
P(1)-C(31)	1.76	1.80	P(2)-C(61)	1.78	1.85
C(11)-C(12)	1.50	1.51	C(41)-C(42)	1.57	1.49
C(12-C(13)	1.30	1.20	C(42)-C(43)	1.04	1.45
C(13)-N(13)	1.36	1.42	C(43)-N(43)	1.59	1.08
C(21)-C(22)	1.44	1.46	C(51)-C(52)	1.25	1.37
C(22)-C(23)	1.33	1.42	C(52)-C(53)	1.34	1.40
C(23)-N(23)	1.28	1.26	C(53)-N(53)	1.95	1.30
C(31)-C(32)	1.63	1.34	C(61)-C(62)	1.46	1.57
C(32)-C(33)	1.51	1.28	C(62)-C(63)	1.04	1.50
C(33)-N(33)	1.15	1.29	C(63)-N(63)	1.62	1.18

Angles (°)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Cl(1)-Hg-Cl(2)	95.0(3)	98.1(3)	P(1)-Hg-P(2)	146.6(3)	153.9(3)
Cl(1)-Hg-P(1)	101.2(4)	95.4(3)	Cl(2)-Hg-P(2)	92.3(3)	96.1(3)
Cl(1)-Hg-P(2)	100.0(4)	94.1(3)	Cl(2)-Hg-P(1)	111.2(3)	106.6(3)
Hg-P(1)-C(11)	113(2)	113(2)	Hg(1)-P(2)-C(41)	120(1)	118(1)
Hg-P(1)-C(21)	116(2)	114(1)	Hg(1)-P(2)-C(51)	105(1)	116(1)
Hg-P(1)-C(31)	118(2)	120(1)	Hg(1)-P(2)-C(61)	114(2)	102(1)
C(11)-P(1)-C(21)	103	99	C(41)-P(2)-C(51)	96	99
C(11)-P(1)-C(31)	103	104	C(41)-P(2)-C(61)	103	108
C(21)-P(1)-C(31)	103	105	C(51)-P(2)-C(61)	119	114
P(1)-C(11)-C(12)	109	115	P(2)-C(41)-C(42)	122	114
C(11)-C(12)-C(13)	93	107	C(41)-C(42)-C(43)	98	115
C(12)-C(13)-N(13)	164	161	C(42)-C(43)-N(43)	158	176
P(1)-C(21)-C(22)	119	111	P(2)-C(51)-C(52)	119	111
C(21)-C(22)-C(23)	114	110	C(51)-C(52)-C(53)	78	124
C(22)-C(23)-N(23)	178	155	C(52)-C(53)-N(53)	159	140
P(1)-C(31)-C(32)	108	114	P(2)-C(61)-C(62)	100	113
C(31)-C(32)-C(33)	107	123	C(61)-C(62)-C(63)	92	103
C(32)-C(33)-N(33)	168	158	C(62)-C(63)-N(63)	150	173

Table 4.2.6 Bond Lengths (Å) and Angles for $[(NCCH_2CH_2)_3P]_2HgBr_2.OC(CH_3)_2$ with Estimated Standard Deviations in Parentheses

Bond lengths (Å)

Hg - Br(1)	2.750(2)	Hg - Br(2)	2.703 (2)
Hg - P (1)	2.441(3)	Hg - P(2)	2.440 (3)
P(1)-C(11)	1.824(14)	P(2)-C(41)	1.806 (15)
P(1)-C(21)	1.795(16)	P(2)-C(51)	1.808 (16)
P(1)-C(31)	1.812(17)	P(2)-C(62)	1.828 (13)
C(11)-C(12)	1.511(26)	C(41)-C(42)	1.551 (20)
C(12)-C(13)	1.465(21)	C(42)-C(43)	1.455 (28)
C(13)-N(13)	1.122(21)	C(43)-N(43)	1.146 (29)
C(21)-C(22)	1.544(20)	C(51)-C(52)	1.518 (22)
C(22)-C(23)	1.426(24)	C(52)-C(53)	1.482 (25)
C(23)-N(23)	1.118(24)	C(53)-N(53)	1.126 (26)
C(31)-C(32)	1.535(25)	C(61)-C(62)	1.518 (24)
C(32)-C(33)	1.448(28)	C(62)-C(63)	1.459 (25)
C(33)-N(33)	1.146(31)	C(63)-N(63)	1.134 (25)

Hg---O	3.91 (2)

TABLE 4.2.6 (cont.)

Bond angles (°)

Br(1)-Hg-Br(2)	107.3(1)	P(1)-Hg-P(2)	151.3(1)
Br(1)-Hg-P (1)	97.2(1)	Br(2)-Hg-P(1)	99.3(1)
Br(1)-Hg-P (2)	95.2(1)	Br(2)-Hg-P(2)	101.5(1)
Hg-P(1)-C(11)	110.9(5)	Hg-P(2)-C(41)	109.1(4)
Hg-P(1)-C(21)	112.3(5)	Hg-P(2)-C(51)	117.1(5)
Hg-P(1)-C(31)	118.5(5)	Hg-P(2)-C(61)	111.3(4)
C(11)-P(1)-C(21)	104.5(7)	C41-P(2)-C(51)	106.0(7)
C(11)-P(1)-C(31)	103.9(7)	C41-P(2)-C(61)	107.5(7)
C(21)-P(1)-C(31)	105.4(7)	C51-P(2)-C(61)	105.2(7)
P(1)-C(11)-C(12)	111.0(11)	P(2)-C(41)-C(42)	115.2(11)
C(11)-C(12)-C(13)	113.2(15)	C(41)-C(42)-C(43)	111.9(14)
C(12)-C(13)-N(13)	176.2(19)	C(42)-C(43)-N(43)	179.3(24)
P(1)-C(21)-C(22)	112.1(11)	P(2)-C(51)-C(52)	111.9(10)
C(21)-C(22)-C(23)	112.2(15)	C(51)-C(52)-C(53)	109.4(13)
C(22)-C(23)-N(23)	178.6(19)	C(52)-C(53)-N(53)	177.7(19)
P(1)-C(31)-C(32)	114.7(11)	P(2)-C(61)-C(62)	112.3(10)
C(31)-C(32)-C(33)	106.7(16)	C(61)-C(62)-C(63)	112.2(15)
C(32)-C(33)-N(33)	174.5(22)	C(62)-C(63)-N(63)	177.1(22)
P(1)-Hg-O	78(1)	P(2)-Hg-O	75(1)
Br(1)-Hg-O	137(1)	Br(2)-Hg-O	116(1)

4.2.3 A Comparison of 2:1 Mercury(II) Halide Complexes

In this section selected parameters for the 2:1 structures presented in this thesis, together with data from previously established structures are rationalised in terms of the factors believed to influence solid state structures of mercury(II) halide complexes (Section 2). Some of the relevant bond lengths and bond angles are given in Table 4.2.7. All complexes have distorted monomeric tetrahedral structures with the exception of $[(NCCH_2CH_2)_3P]_2HgBr_2.OC(CH_3)_2$ which adopts a trigonal bipyramidal polyhedral structure. In this case the oxygen atom of the acetone molecule of crystallisation occupies an equatorial position in the trigonal bipyramidal polyhedron. The complexes $(EtMe_2P)_2HgBr_2$ and $[(NCCH_2CH_2)_3P]_2HgCl_2$, in contrast to the other 2:1 complexes studied, each contains two independent monomeric units. Studies of the $(R_3P)_2HgX_2$ complexes indicate that the structures adopted in the solid state are influenced by (i) the electronic strength and steric requirement of the phosphine ligand, (ii) the nature of the halogen, and (iii) the tendency of mercury(II) to adopt linear two co-ordination. The present comparison of the 2:1 complexes seeks to investigate these influences and tries to establish the key factors and their relative importance. A study of the bond lengths and bond angles about the mercury atoms, given in Table 4.2.7, indicates $[(NCCH_2CH_2)_3P]_2HgCl_2$ and $(Et_3P)_2HgCl_2$ have similar interactions with mercury(II) halides. Triethylphosphine has a high pKa value (8.69), and its 2:1 complex with mercury(II) chloride has a large P-Hg-P angle (158.5(5)°) and short Hg-P bonds (2.39(1) Å) in comparison to some other 2:1 tertiary phosphine mercury(II) chlorides (see below). This indicates a strong interaction of the tertiary phosphine with the mercury(II) halide and as such this phosphine is considered to be a strong σ-donor.

Tris(2-cyanoethyl)phosphine, whose 2:1 mercury(II) chloride complex has comparable bond lengths and bond angles to the triethylphosphine analogue is also considered to be a strong σ-donor to mercury(II) halides, even though the phosphine has a much lower pK_a value (1.37) than Et_3P. This indicates that the electron-withdrawing properties of the cyano groups, while lowering the pK_a value does not appear to reduce the co-ordinating ability of the substituted phosphine to mercury(II) halides. However, a comparison of the parameters of $[(2\text{-thienyl})_3P]_2HgCl_2$ with those of $(Et_3P)_2HgCl_2$ indicates the σ-donor ability of tris(2-thienyl)phosphine to be considerably weaker than that of triethylphosphine. The Hg-P and Hg-Cl bond distances for the heterocyclic phosphine complex are similar to those found in the triphenylphosphine and tributylphosphine 2:1 complexes. The P-Hg-P bond angle found for di(tris(2-thienyl)phosphine) mercury(II) chloride (128.6(1)°) is the smallest of the 2:1 chloride complexes for which data are available which indicates that tris(2-thienyl)phosphine is the weakest σ-donor.

A comparison of the mercury(II) bromide complexes shows a similar trend; in this case the di(tris2-cyanoethyl)phosphine mercury(II) bromide has longer Hg-Br bonds (2.725 Å) and a larger P-Hg-P angle (151.3(1)°) than the complex of the weak σ-donor triphenylphosphine (2.628 Å and 113.0(5)°). The bond lengths and bond angles for $(EtMe_2P)_2HgBr_2$ are comparable to those of $[(NCCH_2CH_2)_3P]_2HgBr_2OC(CH_3)_2$.

From Table 4.2.7 it is clear that the phosphines with the higher pK_a values have the larger P-Hg-P angles and shorter Hg-P bonds in their complexes, i.e. they are the stronger σ-donors to mercury(II), the exception being tris(2-cyanoethyl)phosphine (pK_a 1.36). The pK_a of tris(2-thienyl)phosphine is not available for comparison.

Using the criteria of relative Hg-P distances and P-Hg-P angles, σ-donor strengths to mercury(II) halides vary in the order:

Et_3P > $(NCCH_2CH_2)_3P$ > $EtMe_2P$ > Bu_3P > Ph_3P > (2-thienyl)$_3$P.

A comparison of the P-Hg-P angles for the $(Ph_3P)_2HgX_2$ (X = Cl, Br, I) shows that these decrease from X = Cl to Br to I. This may be related to the relative electronegativity of the halogens (Cl > Br > I) which affords greatest Hg-P interaction in the chlorocomplex, thereby leading to the larger P-Hg-P angle. The presence of a molecule of acetone in $[(NCCH_2CH_2)_3P]_2HgBr_2$ prevents a simple comparison with the chloride complex.

From the NMR shifts and coupling constants given in Table 4.2.8 the stronger σ-donors, Et_3P and $(NCCH_2CH_2)_3P$, have the greater chemical shifts and coupling constants. The complex [(2-thienyl)$_3$P]$_2$HgI$_2$ has the smaller chemical shifts and coupling constant than the triphenylphosphine analogue giving further evidence that the heterocyclic phosphine is an extremely weak σ-donor as suggested by the small P-Hg-P angle and long Hg-P bonds. The chemical shifts and coupling constants show a marked decrease from Cl to Br to I following the trend of decreasing P-Hg-P angle size observed in the $(Ph_3P)_2HgX_2$ (X = Cl, Br or I) complexes. These trends are apparent from the data given in Table 4.2.8 in spite of the effects of varying solvents and temperatures.

TABLE 4.2.7. Selected Molecular Parameters for $(R_3P)_2HgX_2$ (X=Cl, Br, I) Complexes

	Hg-P (Å)		PHgP (°)	Hg-X (Å)		XHgX (°)	pK_a for R_3P [52]
$(Et_3P)_2HgCl_2$ [a]	2.39(1)	2.39(1)	158.5(5)	2.68(1)	2.68(1)	105.5(5)	8.69
$((NCC_2H_4)_3P)_2HgCl_2$ (I) [b]	2.450(12)	2.452(11)	146.6(3)	2.608(10)	2.622(10)	95.0(3)	1.36
(II)	2.411(7)	2.450(6)	153.9(6)	2.669(11)	2.603(10)	98.1(3)	
$((NCC_2H_4)_3P)_2HgBr_2.Me_2CO$ [b]	2.441(3)	2.440(3)	151.3(1)	2.750(2)	2.703(2)	107.3(1)	1.36
$(EtMe_2P)_2HgBr_2$ [c] (I)	2.44(6)	2.50(5)	147(2)	2.72(2)	2.79(2)	101.7(8)	8.61
(II)	2.39(5)	2.48(6)	150(2)	2.79(3)	2.88(2)	106.9(8)	
$(Bu_3P)_2HgCl_2$ [c]	2.3(6)	2.6(6)	139(2)	2.55(5)	2.66(5)	105(2)	8.43
$(Ph_3P)_2HgCl_2$ [d]	2.478(2)	2.462(2)	134.1(1)	2.559(2)	2.545(3)	110.7(1)	2.73
$(Ph_3P)_2HgBr_2$ [d]	2.535(15)	2.540(16)	113.0(5)	2.633(6)	2.626(8)	106.9(3)	2.73
$(Ph_3P)_2HgI_2$ [e]	2.557(3)	2.574(3)	108.95(9)	2.733(1)	2.763(1)	110.43(4)	2.73
$((2\text{-}C_4H_3S)_3P)_2HgCl_2$ [b]	2.472(2)	2.513(2)	128.6(1)	2.539(2)	2.519(2)	107.3(1)	-

a	Ref. 42	d	Ref. 43
b	Ref. This Work	e	Ref. 40
c	Ref. 41		

TABLE 4.2.8. ^{31}P NMR Data for some $(R_3P)_2HgX_2$ Complexes

Complex	δ (ppm)	$J(^{199}Hg-^{31}P)$	Solvent	Temp (°C)
$(Et_3P)_2HgCl_2$ [a]	38.0	5095	$CDCl_3$	27
$(Et_3P)_2HgBr_2$ [a]	32.2	4792	$CDCl_3$	27
$(Et_3P)_2HgI_2$ [a]	16.9	4033	$CDCl_3$	27
$((NCC_2H_4)_3P)_2HgCl_2$ [d]	44.4		$(CD_3)_2CO$	26
$((NCC_2H_4)_3P)_2HgBr_2$ [d]	17.6		$(CD_3)_2CO$	26
$((NCC_2H_4)_3P)_2HgI_2$ [d]	2.6		$(CD_3)_2CO$	26
$(EtMe_2P)_2HgCl_2$ [a]	16.0	5606	$CDCl_3$	-30
$(EtMe_2P)_2HgBr_2$ [a]	13.1	5560	$CDCl_3$	-30
$(EtMe_2P)_2HgI_2$ [a]	2.5	4778	$CDCl_3$	-40
$(Bu_3P)_2HgCl_2$ [b]	28.9	5125	$CDCl_3$	27
$(Bu_3P)_2HgBr_2$ [b]	23.9	4829	$CDCl_3$	27
$(Bu_3P)_2HgI_2$ [b]	9.3	4089	$CDCl_3$	27
$(Ph_3P)_2HgCl_2$ [c]	28.1	4740	CH_2Cl_2	-43
$(Ph_3P)_2HgBr_2$ [c]	21.7	4178	CH_2Cl_2	-43
$(Ph_3P)_2HgI_2$ [c]	7.3	3073	CH_2Cl_2	-43
$((2-C_4H_3S)_3P)_2HgI_2$ [d]	-26.0	2722	CH_2Cl_2	-90
$((2-C_4H_3O)_3P)_2HgCl_2$ [d]	-37.5	4322	CH_2Cl_2	-90
$((2-C_4H_3O)_3P)_2HgBr_2$ [d]	-44.2	3540	CH_2Cl_2	-90

a Ref. 42

b Ref. 49

c Ref. 50

d This Work

4.3 Crystallographic Studies of Selected 1:1 Complexes $(R_3P)HgX_2$

4.3.1 Crystallographic Examination of the 1:1 Complex $[(NCCH_2CH_2)_3PHgCl_2]_n$

TABLE 4.3.1 Crystal Data

Crystal Size	0.04 x 0.08 x 0.52 mm	
Crystal System	Orthorhombic	
a = 20.871(6)	b = 7.853(9)	c = 8.518(8) Å
V 1396.4 Å^3		
M_r 472.8		
D_c 2.25 g cm^{-3}	D_m 2.23 g cm^{-3}	Z = 4
Systematic Absences	h00 h = 2n + 1	
	0k0 k = 2n + 1	
	00l l = 2n + 1	
Space Group	$P2_12_12_1$	
μ (Mo-Kα)	110.6 cm^{-1}	
F(000)	864 electrons	

Data Collection and Structural Analysis

The crystal was mounted with its c-axis coincident with the ω-axis of a Stöe Stadi 2 two-circle diffractometer. 1725 unique reflections were measured; 1121 had $I/\sigma(I) \geqslant 3.0$ and were subsequently used for refinement. The structure was solved via the Patterson function and refined by full-matrix least squares techniques. Hydrogen atoms were included in ideal positions (C-H 1.08 Å) and given a common isotropic temperature factor, all other atoms except one nitrogen and three carbons were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors were used throughout the refinement. The weighting scheme $W = a/[\sigma^2(F_o) + b(F_o)^2]$ was adopted in the final stages of refinement (where a = 0.1965 and b = 0.03781), the final R value being 0.063 and R', 0.068. The final atomic positional and thermal parameters are given in the appendix, tables 7 and 8, and bond distances and angles are listed in Table 4.3.2. A correction for absorption effects was applied for the complex (appendix A2).

Results and Discussion

The complex [$(NCCH_2CH_2)_3PHgCl_2$] is found to be polymeric with almost linear Cl-Hg-PR_3 units bridged by further chlorine atoms (Fig. 4.3.1), resulting in single chains running parallel to the b-axis. The angles about the mercury atom are highly distorted from tetrahedral, varying from 89.7(2)° to 162.3(4)°. However, there is a weak π-interaction between one of the cyanoethyl groups and the mercury atom. From Fig. 4.3.1 it can be seen that C23, N23 and the symmetry related C(23''') and N(23''') lie in positions close to the mercury atom (Table 4.3.2). These distances (3.51, 3.47 Å respectively) are longer than the sum of the van der Waals' radii which is 3.05 Å, indicating a weak interaction. A similar weak bonding between three cyanoethyl groups is found in the 2:1 cyanoethylphosphine complex (Section 4.2.2). A comparison of the Hg-C and Hg-N bond lengths is given in Table 4.3.3. The P-C-C-CN torsion angles for two of the cyanoethyl groups lie close to the expected 180° (173° and 177°), but that for the P-C(21)-C(22)-C(23) is only 81°, allowing N to take up a position near the mercury atom. The resulting co-ordination polyhedron about mercury is distorted octahedral with the two cyano-groups (C(23)-N(23), C(23''')-N(23''')) occupying positions trans to each other, the other four positions being occupied by three chlorine atoms and one phosphorus atom. The angles about the phosphorus are slightly distorted from the tetrahedral, varying from 116.2(10)° to 103.8(10)°.

Fig. 4.3.1 Molecular Structure of $[(NCCH_2CH_2)_3PHgCl_2]_n$

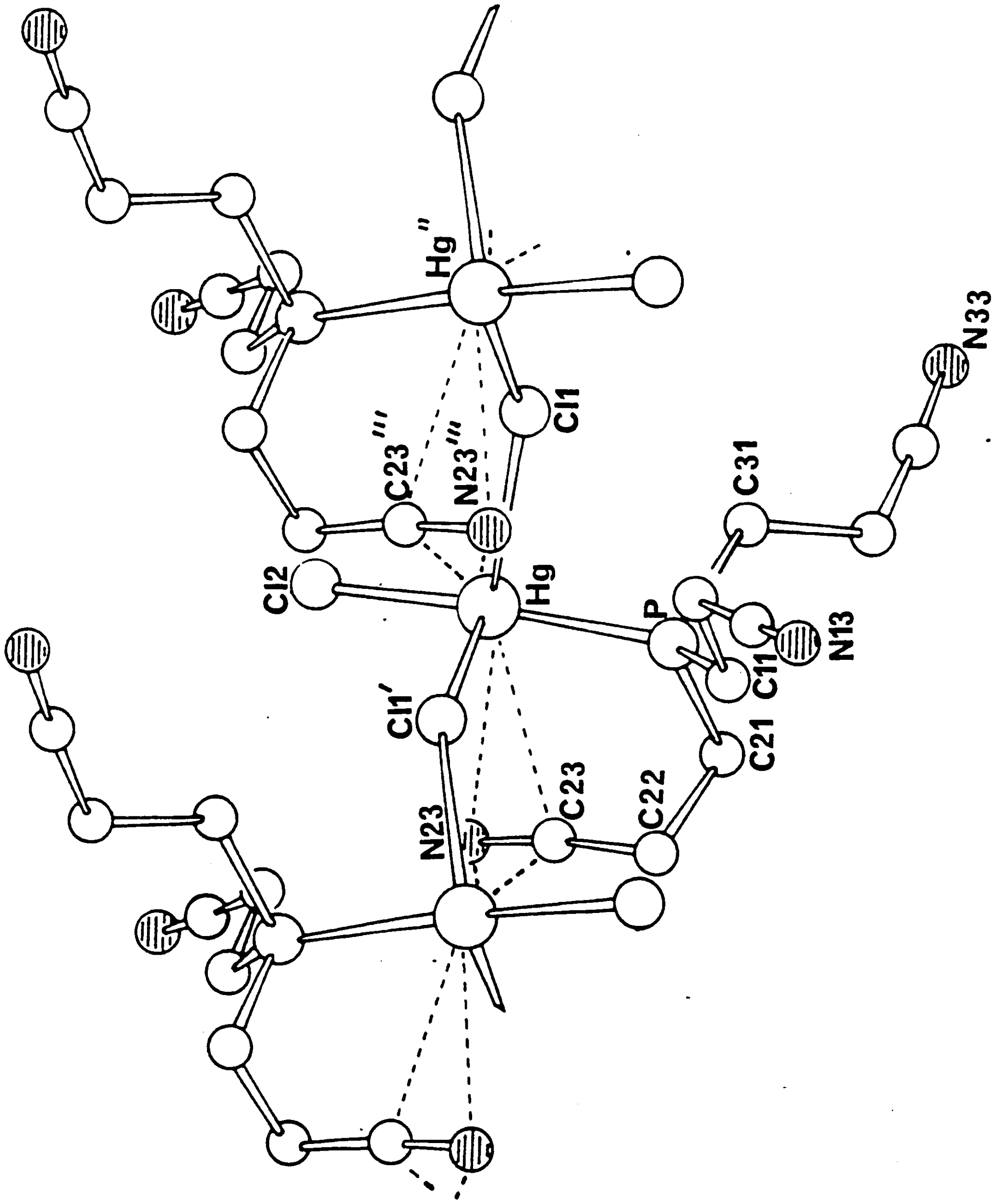


Table 4.3.2 Bond Lengths (Å) and Angles (°) for $[(NCCH_2CH_2)_3PHgCl_2]_n$ with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)

Hg-Cl(1)	2.762(9)	Hg...C(23)	3.44(3)
Hg-Cl(1')	2.754(9)	Hg...N(23)	3.51(3)
Hg-Cl(2)	2.336(7)	Hg...C(23''')	3.61(3)
Hg-P	2.387(6)	Hg...N(23''')	3.47(3)
P-C(11)	1.71(3)		
P-C(21)	1.92(2)		
P-C(31)	1.84(2)		
C(11)-C(12)	1.63(3)		
C(12)-C(13)	1.48(3)		
C(13)-N(13)	1.07(4)		
C(21)-C(22)	1.52(3)		
C(22)-C(23)	1.48(4)		
C(23)-N(23)	1.09(4)		
C(31)-C(32)	1.56(3)		
C(32)-C(33)	1.40(3)		
C(33)-N(33)	1.16(4)		

Bond Angles (°)

Cl(1)-Hg-Cl(1')	99.2(4)	P-C(11)-C(12)	114(2)
Cl(1)-Hg-Cl(2)	99.9(4)	P-C(21)-C(22)	111(2)
Cl(1)-Hg-P	89.7(2)	P-C(31)-C(32)	115(2)
Cl(1')-Hg-Cl(2)	97.3(4)	C(11)-C(12)-C(13)	111(2)
Cl(1')-Hg-P	95.7(2)	C(12)-C(13)-N(13)	177(3)
Cl(2)-Hg-P	162.3(4)	C(21)-C(22)-C(23)	107(2)
Hg-Cl(1)-Hg''	141.4(2)	C(22)-C(23)-N(23)	164(4)
Hg-P-C(11)	116.2(10)	C(31)-C(32)-C(33)	110(2)
Hg-P-C(21)	114.2(8)	C(32)-C(33)-N(33)	174(3)

Table 4.3.2 cont.

Hg-P-C(31)	107.7(7)
C(11)-P-C(21)	103.8(10)
C(11)-P-C(31)	108.8(11)
C(21)-P-C(31)	105.6(11)

symmetry operations

'-x, -0.5 + y, 0.5 - z

''-x, 0.5 + y, 0.5 - z

'''-x, 0.5 + y, -0.5 - z

TABLE 4.3.3 A Comparison of Hg-C and Hg-N Bond Lengths (Å) for $[(NCCH_2CH_2)_3P]_nHgCl_2$, where (n = 1 or 2)

$[(NCCH_2CH_2)_3P]HgCl_2$			$[(NCCH_2CH_2)_3P]_2HgCl_2$(a)	
			Monomer I	Monomer II
Hg...C(23)	3.44(3)	Hg...(C23)	3.600	-
Hg...N(23)	3.51(3)	Hg...N(23)	3.510	-
Hg...C(23''')	3.61(3)	Hg...C(33)	-	3.894
Hg...N(23''')	3.47(3)	Hg...N(33)	-	3.740
		Hg...C(43)	3.703	-
		Hg...N(43)	3.518	-

(a) Section 4.2.2

4.3.2 Crystallographic Examination of the 1:1 Complex $[(Ph_3P)HgI_2]_2$

TABLE 4.3.4 Crystal Data

Crystal Size	0.125 x 0.45 x 0.037 mm
Crystal System	Monoclinic

a = 19.299(4) b = 11.130(3) c = 19.102(2) Å β = 90.50(1)°

V 4103.1 $Å^3$

M_r 1432.8

D_c 2.32 g cm^{-3} D_m 2.41 g cm^{-3} Z = 4

Systematic Absences	h0l l = 2n + 1
	0k0 k = 2n + 1
Space Group	$P2_1/c$
μ(Mo-Kα)	101.06 cm^{-1}
F(000)	2592 electrons

Data Collection and Structural Analysis

The crystal was mounted with its b-axis coincident with a Stöe Stadi 2 two-circle diffractometer. Fourteen layers h0l → h13l were collected; 4444 unique reflections were measured of which 2984 had $I/\sigma(I) \geqslant 3.0$ and were subsequently used for refinement. All non-hydrogen and carbon atoms were assigned anisotropic thermal parameters. All carbon atoms except C(24), C(25), C(26), C(61), C(62), C(63) and C(64) were also assigned anisotropic thermal parameters, these seven carbon atoms could only be assigned isotropic thermal parameters. Hydrogen atoms associated with the anisotropic carbon atoms, were included in ideal positions (C-H 1.08 Å) and were given a common isotropic temperature factor. Complex neutral atom scattering factors were employed throughout the refinement; the weighting scheme $W = 1.000/[\sigma^2(F_o) + 0.0175(F_o)^2]$ was adopted in the final cycles. Full matrix refinement gave a final R value of 0.094 and R' value of

0.091. The final atomic and thermal parameters are given in the appendix tables 9 and 10. Bond angles and distances are listed in Table 4.3.5a.

Results and Discussion

The complex is found to be an asymmetrical halogen bridged dimer (Fig. 4.3.2). The terminal iodine atoms are trans to each other. The mercury atoms are four co-ordinate with the distortion from the tetrahedral being similar for each atom, the angles vary from 94.8(1)° to 128.4(2)°. The geometry about the phosphorus atom is only slightly distorted from the tetrahedral with the angles varying from 104.9(11)° to 112.7(10)°. The Hg-I bridging distances are unequal, being 2.990(2), 2.960(2), 2.860(2) and 2.846(2) Å while the Hg-I terminal bond lengths are similar, 2.671(2) and 2.684(2) Å and are shorter. The Hg-P bond lengths have similar values of 2.461(8) and 2.483(8) Å. The phenyl rings are planar. The angles between the associated mean planes are given in Table 4.3.5b.

Fig. 4.3.2 Molecular Structure of $[Ph_3PHgI_2]_2$

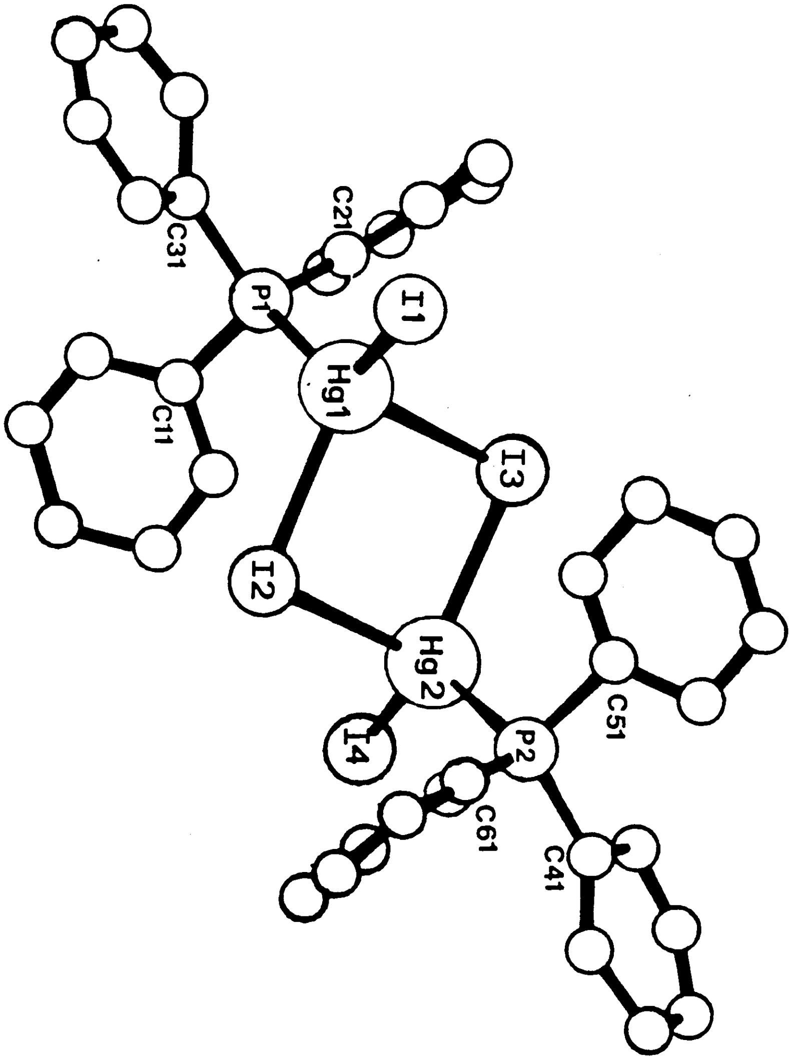


Table 4.3.5a Bond Lengths (Å) and Bond Angles (°) for $[Ph_3PHgI_2]_2$ with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)

Hg(1)-I(1)	2.671(2)	Hg(2)-I(4)	2.684(2)
Hg(1)-I(2)	2.860(2)	Hg(2)-I(2)	2.960(2)
Hg(1)-I(3)	2.990(2)	Hg(2)-I(3)	2.846(2)
Hg(1)-P(1)	2.461(8)	Hg(2)-P(2)	2.483(8)
P(1)-C(11)	1.85(3)	P(2)-C(41)	1.85(3)
P(1)-C(21)	1.80(4)	P(2)-C(51)	1.80(2)
P(1)-C(31)	1.76(2)	P(2)-C(61)	1.75(3)

Bond Angles (°)

I1-Hg1-I2	106.9(1)	I3-Hg2-I4	116.2(1)
I1-Hg1-I3	107.9(1)	I2-Hg2-I4	106.4(1)
I1-Hg1-P1	128.4(2)	I4-Hg2-P2	126.6(2)
I2-Hg1-I3	94.8(1)	I2-Hg2-I3	95.8(1)
I2-Hg1-P1	112.8(2)	I3-Hg2-P2	110.0(2)
C(11)-P1-C(21)	112.0(15)	C(41)-P(1)-C(51)	108.8(11)
C(11)-P(1)-C(31)	104.9(11)	C(41)-P(2)-C(61)	108.0(14)
C(11)-P(1)-Hg(1)	111.2(12)	C(41)-P(2)-Hg(2)	112.7(10)
C(21)-P(1)-C(31)	109.3(14)	C(51)-P(2)-C(61)	108.0(14)
C(21)-P(1)-Hg(1)	109.3(10)	C(51)-P(2)-Hg(2)	108.8(10)
C(31)-P(1)-Hg(1)	110.1(10)	C(61)-P(2)-Hg(2)	110.3(10)
Hg1-I3-Hg2	84.6(1)	Hg2-I2-Hg1	84.9(1)

Table 4.3.5b Angles between mean planes for $(Ph_3P)HgI_2$

Mean Planes	Complexed Ligand	
	1	2
A-B	83.7	89.9
B-C	76.8	78.5
C-A	81.4	82.2

Plane A - ring A (1) C(11), C(12), C(13), C(14), C(15), C(16)

$$-0.5384X + 0.1962Y - 0.8196Z + 18.3945 = 0$$

(2) C(41), C(42), C(43), C(44), C(45), C(46)

$$-0.1830X - 0.9817Y - 0.0534Z + 3.2129 = 0$$

Plane B - ring B (1) C(21), C(22), C(23), C(24), C(25), C(26)

$$0.8217X - 0.3080Y - 0.4795Z - 1.0119 = 0$$

(2) C(51), C(52), C(53), C(54), C(55), C(56)

$$-0.5969X + 0.1523Y - 0.7877Z + 20.8931 = 0$$

Plane C - ring C (1) C(31), C(32), C(33), C(34), C(35), C(36)

$$0.0932X + 0.9956Y - 0.0048Z - 4.5725 = 0$$

(2) C(61), C(62), C(63), C(64), C(65), C(66)

$$0.8526X - 0.2730Y - 0.4455Z - 8.8718 = 0$$

4.3.3 Crystallographic Examination of the 1:1 Complexes $[Pr_3PHgX_2]_2$ (where X = Cl, Br or I)

TABLE 4.3.6 Crystal Data

	(I)	(II)	(III)
	$[Pr_3PHgCl_2]_2$	$[Pr_3PHgBr_2]_2$	$[\beta\text{-}Pr_3PHgI_2]_2$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Dimension (mm)	0.32x0.44x0.6	0.12x0.84	0.4x0.25x0.16
a (Å)	18.474(5)	11.777(5)	10.707(3)
b (Å)	11.328(1)	8.758(5)	13.766(5)
c (Å)	13.891(6)	16.761(1)	22.399(8)
β (°)	101.17(5)	116.18(8)	96.5(1)
V (Å^3)	2852.3	1551.5	3280.3
M_r	863.4	1041.0	1229.6
D_c (g cm^{-3})	2.02	2.23	2.49
D_m (g cm^{-3})	2.00	2.25	2.50
Systematic Absences			
	hkl h+l=2n+1	h0l l=2n+1	h0l l=2n+1
	0k0 k=2n+1	0k0 k=2n+1	0k0 k=2n+1
	0hl h=2n+1		
Z	4	4	4
Space Group	$B2_1/a$‡	$P2_1/c$	$P2_1/c$
μ(Mo-Kα)(cm^{-1})	108.2	146.8	126.3
F(000) electrons	1632	1920	2208

‡A non-standard setting of $P2_1/c$.

Data Collection and Structural Analysis

Details of data collection are given in Table 4.3.7 and all three structures were solved using the Patterson method and refined by full-matrix least squares techniques.

TABLE 4.3.7 Details of the Data Collection

	(I)	(II)	(III)
Axis mounted about	c	b	a
No. layers collected	15	11	11
No. unique reflections	1876	2285	2620
No. observed reflections	1446	1431	1638
Final R value	0.069	0.052	0.103
Final R' value	0.070	0.039	0.103
$\underline{W} = a/[\sigma^2(F_o) + b(F_o)^2]$			
a	1.0000	1.00000	1.00000
b	0.09116	0.000162	0.016547
$I/\sigma(I) \geqslant$	3	2	4

The data were corrected for Lorentz and polarisation effects, but an absorption correction was only applied for (III). For (I) and (II) hydrogen atoms were included in ideal positions (C-H, 1.08 Å) and were given a common isotropic temperature factor. All other atoms in (I) and (II) were assigned anisotropic thermal parameters. In complex (III) only the mercury, iodine and phosphorus atoms were assigned anisotropic thermal parameters; it was also impossible to include hydrogen atoms in this structure. This is probably due to the presence of so many heavy atoms. The application of the absorption correction for this complex did not significantly improve the R value or reduce the errors.

Results and Discussion

All three compounds are halogen bridged dimers with varying degrees of distortion about the mercury atoms. Tripropylphosphine mercury iodide differs from the other two complexes in that both phosphine groups are attached to the same mercury atom (Fig. 4.3.3). In this complex the geometry about the Hg(1) atom to which both phosphine groups are attached is highly distorted from a tetrahedral arrangement with the angles varying from 89.5(1)° to 149.1(5)°. The distortion is less about Hg(2), these angles varying from 93.9(1)° to 123.6(2)°. A full list of bond angles and bond lengths are given in Table 4.3.8, the final positional and thermal parameters are given in the appendix, table (11). Around the phosphorus atom there is significant deviation from the expected tetrahedral arrangement with the bond angles ranging from 104(3)° to 121(2)°, but there is little deviation apparent in the carbon chains.

In tripropylphosphine mercury(II) chloride (Fig. 4.3.4) the distortion from the regular tetrahedral arrangement about the mercury atom is considerable, with angles ranging from 96.5(2)° to 148.7(2)°. Around the phosphorus atom there is only slight deviation from tetrahedral with the angles ranging from 106.4(8)° to 113.6(7)°. A full list of bond angles and bond lengths are given in Table 4.3.9, the final positional and thermal parameters are given in the appendix table (12).

The degree of distortion about the mercury atom in tripropylphosphine mercury(II) bromide (Fig. 4.3.5) is considerable, the angles ranging from 102.5(1) to 135.9(1)°. There is, however, only a slight degree of distortion from tetrahedral about the phosphorus atom, with the angles varying from 112.8(4) to 107.3(7)°. The terminal and bridging mercury-halogen bond lengths for this complex are similar (2.507(2) and 2.667(2) Å respectively). The structure is very unsymmetrical as the bridging bond lengths differ markedly ($Hg\text{-}Br_{br}^{*}$ = 2.667(2) and $Hg\text{-}Br_{br}^{*}$ = 3.051(2) Å). A full list of bond lengths and bond angles are given in Table 4.3.10 and the final positional and thermal parameters are given in the appendix table (13).

Fig. 4.3.3 Molecular Structure of $[\beta\text{-}Pr_3PHgI_2]_2$

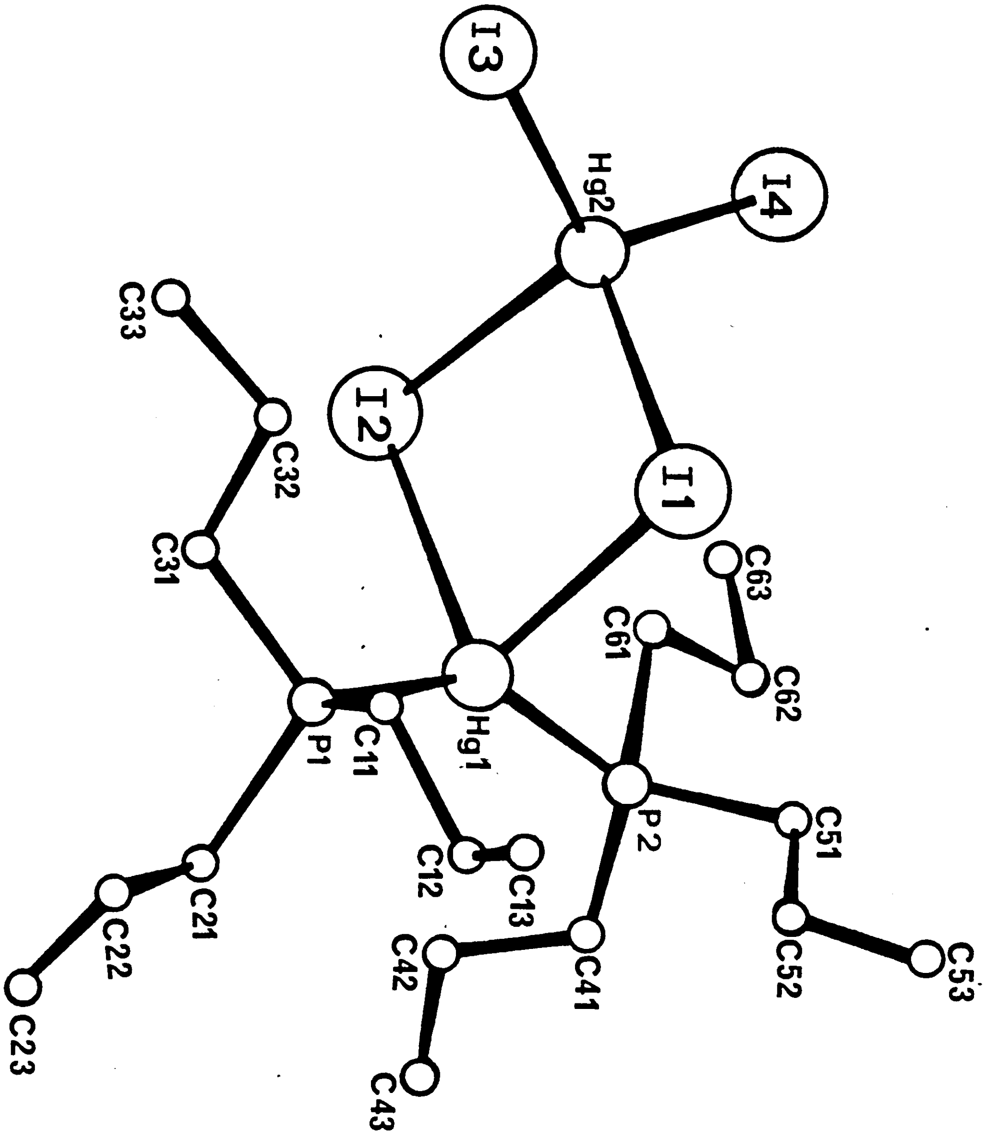


Fig. 4.3.4 Molecular Structure of $[Pr_3PHgCl_2]_2$

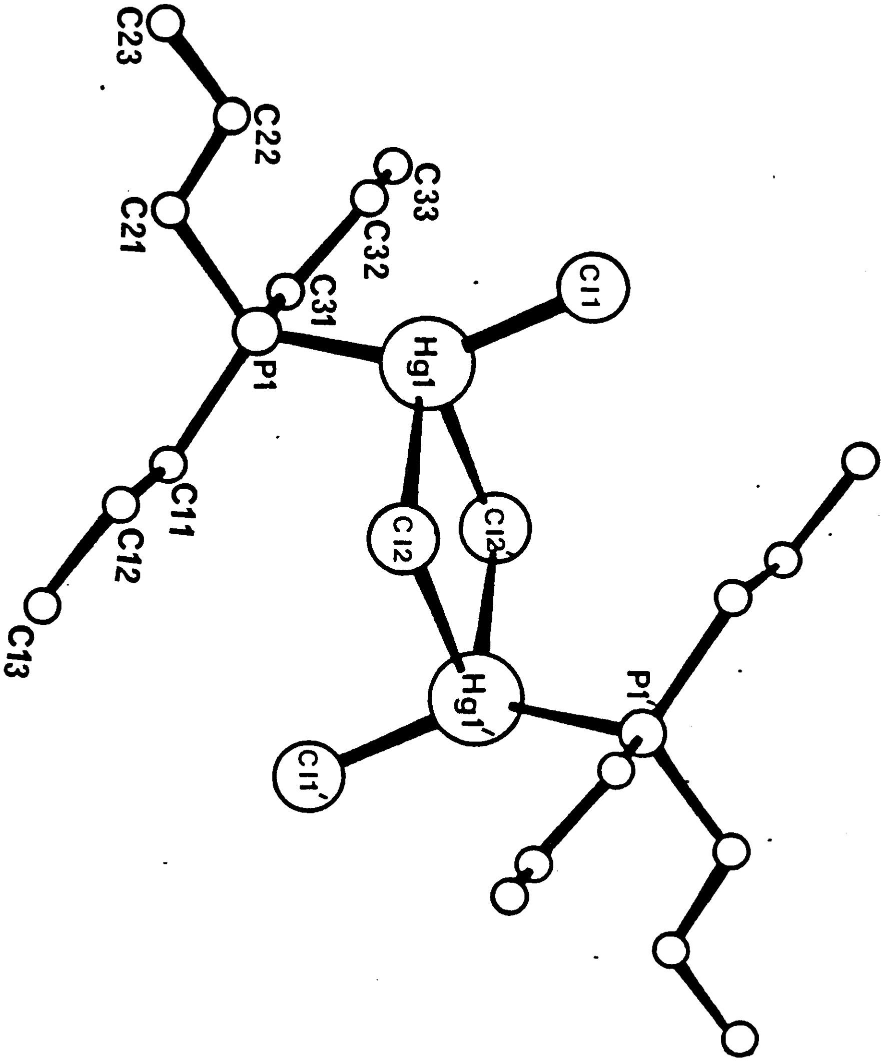


Fig. 4.3.5 Molecular Structure of $[Pr_3PHgBr_2]_2$

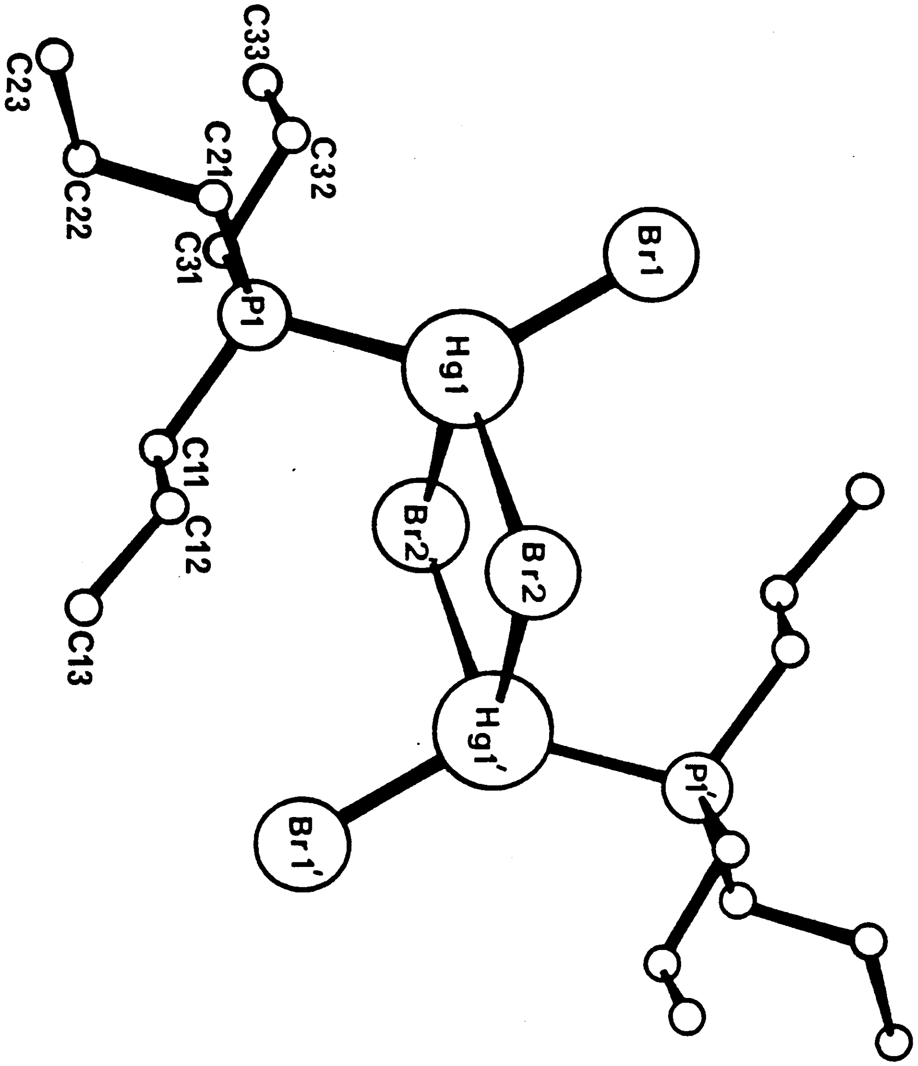


Table 4.3.8 Bond Lengths (Å) and Bond Angles (°) for $[\beta\text{-}Pr_3PHgI_2]_2$ with Estimated Standard Deviations in Parentheses

Bond Distances (A)

Hg1 - I1	3.027(4)
Hg1 - I2	3.050(5)
Hg1 - P1	2.457(14)
Hg1 - P2	2.421(15)
Hg2 - I1	2.937(5)
Hg2 - I2	2.921(4)
Hg2 - I3	2.694(4)
Hg2 - I4	2.685(5)
P1 - C11	1.91(6)
P1 - C21	1.84(5)
P1 - C31	1.81(6)
P2 - C41	1.84(9)
P2 - C51	1.65(6)
P2 - C61	2.09(9)
C11 - C12	1.63(9)
C12 - C13	1.36(11)
C21 - C22	1.53(8)
C22 - C23	1.54(9)
C31 - C32	1.64(8)
C32 - C33	1.58(8)
C41 - C42	1.50(9)
C42 - C43	1.50(12)
C51 - C52	1.45(7)
C52 - C53	1.35(9)
C61 - C62	1.47(11)
C62 - C63	1.65(11)

Bond Angles (°)

I1 - Hg1 - I2	89.5(1)
I1 - Hg1 - P1	100.8(4)
I1 - Hg1 - P2	98.0(4)
I2 - Hg1 - P1	102.2(4)
I2 - Hg1 - P2	102.4(4)
P1 - Hg1 - P2	149.1(5)
I1 - Hg2 - I2	93.9(1)
I1 - Hg2 - I3	106.3(2)
I1 - Hg2 - I4	109.6(2)
I2 - Hg2 - I3	109.5(1)
I2 - Hg2 - I4	109.8(2)
I3 - Hg2 - I4	123.6(2)
Hg1 - I1 - Hg2	88.1(1)
Hg1 - I2 - Hg2	88.0(1)
Hg1 - P1 - C11	109(2)
Hg1 - P1 - C21	109(2)
Hg1 - P1 - C31	112(2)
C11 - P1 - C21	105(2)
C11 - P1 - C31	116(3)
C21 - P1 - C31	105(3)
Hg1 - P2 - C41	113(3)
Hg1 - P2 - C51	121(2)
Hg1 - P2 - C61	104(3)
C41 - P2 - C51	105(3)
C41 - P2 - C61	106(4)
C51 - P2 - C61	107(3)
P1 - C11 - C12	106(4)
C11 - C12 - C13	105(7)
P1 - C21 - C22	110(4)
C21 - C22 - C23	105(5)
P1 - C31 - C32	106(4)
C31 - C32 - C33	104(4)
P2 - C41 - C42	113(6)
C41 - C42 - C43	108(7)
P2 - C51 - C52	113(4)
C51 - C52 - C53	108(6)
P2 - C61 - C62	111(6)
C61 - C62 - C63	103(7)

Table 4.3.9 Bond Lengths (Å) and Bond Angles (°) for $[Pr_3PHgCl_2]_2$ with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)

Hg-Cl1	2.348(5)	C11-C12	1.45(3)
Hg-Cl2	2.638(4)	C12-C13	1.51(3)
Hg-P	2.358(4)	C21-C22	1.45(3)
Hg-Cl2'	2.780(4)	C22-C23	1.58(3)
P-C11	1.815(16)	C31-C32	1.46(3)
P-C21	1.795(17)	C32-C33	1.47(3)
P-C31	1.827(17)	Hg---Hg'	3.813

Bond Angles (°)

Cl2-Hg-Cl1	96.5(2)	P-C11-C12	111.1(15)
P-Hg-Cl1	148.7(2)	P-C21-C22	115.1(14)
P-Hg-Cl2	111.2(2)	P-C31-C32	115.3(16)
Hg-P-C11	112.4(6)	C11-C12-C13	113(2)
Hg-P-C21	110.1(6)	C21-C22-C23	113(2)
Hg-P-C31	113.6(7)	C31-C32-C33	115(2)
C11-P-C21	106.4(8)	Cl1-Hg-Cl2'	103.6(2)
C11-P-C31	107.2(9)	Cl2-Hg-Cl2'	90.6(2)
C21-P-C31	106.6(10)	P-Hg-Cl2'	90.8(2)
		Hg-Cl2-Hg'	89.4(1)

', -x, 1-y, -z

Table 4.3.10 Bond Lengths (Å) and Bond Angles (°) for $[Pr_3PHgBr_2]_2$ with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)

Hg-Br1	2.507(2)	C11-C12	1.507(18)
Hg-Br2	2.667(2)	C12-C13	1.499(20)
Hg-P	2.408(4)	C21-C22	1.514(17)
Hg-Br2'	3.051(2)	C22-C23	1.507(18)
P-C11	1.794(14)	C31-C32	1.553(17)
P-C21	1.806(14)	C32-C33	1.521(19)
P-C31	1.796(14)	Hg---Hg'	4.022

Bond Angles (°)

Br2-Hg-Br1	102.5(1)	P-C11-C12	114.6(11)
P-Hg-Br1	135.9(1)	C11-C12-C13	114.4(15)
P-Hg-Br2	119.7(1)	P-C21-C22	113.1(10)
Hg-P-C11	108.4(5)	C21-C22-C23	111.2(13)
Hg-P-C21	112.8(4)	P-C31-C32	113.8(11)
Hg-P-C31	112.7(5)	C31-C32-C33	110.8(14)
C11-P-C21	107.7(7)	Br1-Hg-Br2'	105.6(1)
C11-P-C31	107.7(7)	Br2'-Hg-Br2	90.9(1)
C21-P-C31	107.3(7)	Br2'-Hg-P	87.2(1)
		Hg-Br2-Hg'	89.1(1)

', -x, 1-y, 1-z

4.3.4 Crystallographic Examination of the Mixed Metal Complex $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$

TABLE 4.3.11 Crystal Data

Crystal Size	0.21 x 0.19 x 0.25 mm				
Crystal System	Monoclinic				
	a = 10.694(6)	b = 13.794(7)	c = 22.415(9) Å	β = 96.25(5)°	
V	3286.7 $Å^3$				
M_r	1141.1				
D_c	2.31 g cm^{-3}	D_m	2.29 g cm^{-3}	Z	= 4
Systematic Absences	h0l l = 2n + 1				
	0k0 k = 2n + 1				
Space Group	$P2_1/c$				
μ(Mo-Kα)	86.2 cm^{-1}				
F(000)	2080 electrons				

Data Collection and Structural Analysis

The crystal was mounted with its a-axis coincident with a Stöe Stadii 2 two-circle diffractometer. Twelve layers 0kl → 11kl were collected; 4159 unique reflections were measured of which 5053 had $I/\sigma(I) \geqslant 3.0$ and were subsequently used for refinement. Hydrogen atoms were included in ideal positions (C-H, 1.08 Å) and were given a common isotropic temperature factor. All other atoms were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors were employed throughout the refinement; the weighting scheme $W = 1.7507/[\sigma^2(F_o) + 0.0009(F_o)^2]$ was adopted in the final cycles. Full matrix refinement gave a final R value of 0.048 and R' value of 0.052. The final atomic parameters and thermal parameters are given in the appendix, tables 14 and 15 and bond distances and angles are listed in Table 4.3.12.

Results and Discussion

The complex is found to be an unsymmetrical halogen bridged dimer (Fig. 4.3.6) in the solid state with, surprisingly, both phosphine ligands being bonded to the mercury atom. The four-membered ring is approximately planar, the angles within the ring ranging from 87.2(1)° to 96.3(1)°. Each metal atom is four co-ordinate and the distortion from a tetrahedral arrangement for the cadmium is not large, the angles varying from 108.3(1)° to 118.6(1)°. However, the tetrahedral arrangement of the mercury is highly distorted, the angles ranging from 88.6(1)° tO 152.8(1)°. The arrangement of the propyl groups about the phosphines is little distorted from the tetrahedral, with the angles varying from 106.3(7)° to 108.2(7)°.

The unsymmetrical structure of this complex was further confirmed by ^{199}Hg NMR studies.[62] The spectra showed a 1:2:1 triplet with a chemical shift of -621 ± 2 ppm which confirmed the bonding of two equivalent phosphine ligands to mercury. The ^{31}P spectrum gave a single sharp peak with a chemical shift of 17.5 ± 0.1 ppm with a coupling constant J(^{199}Hg-^{31}P) of 4340 ± 2.5 Hz.

Fig. 4.3.6 Molecular Structure of $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$

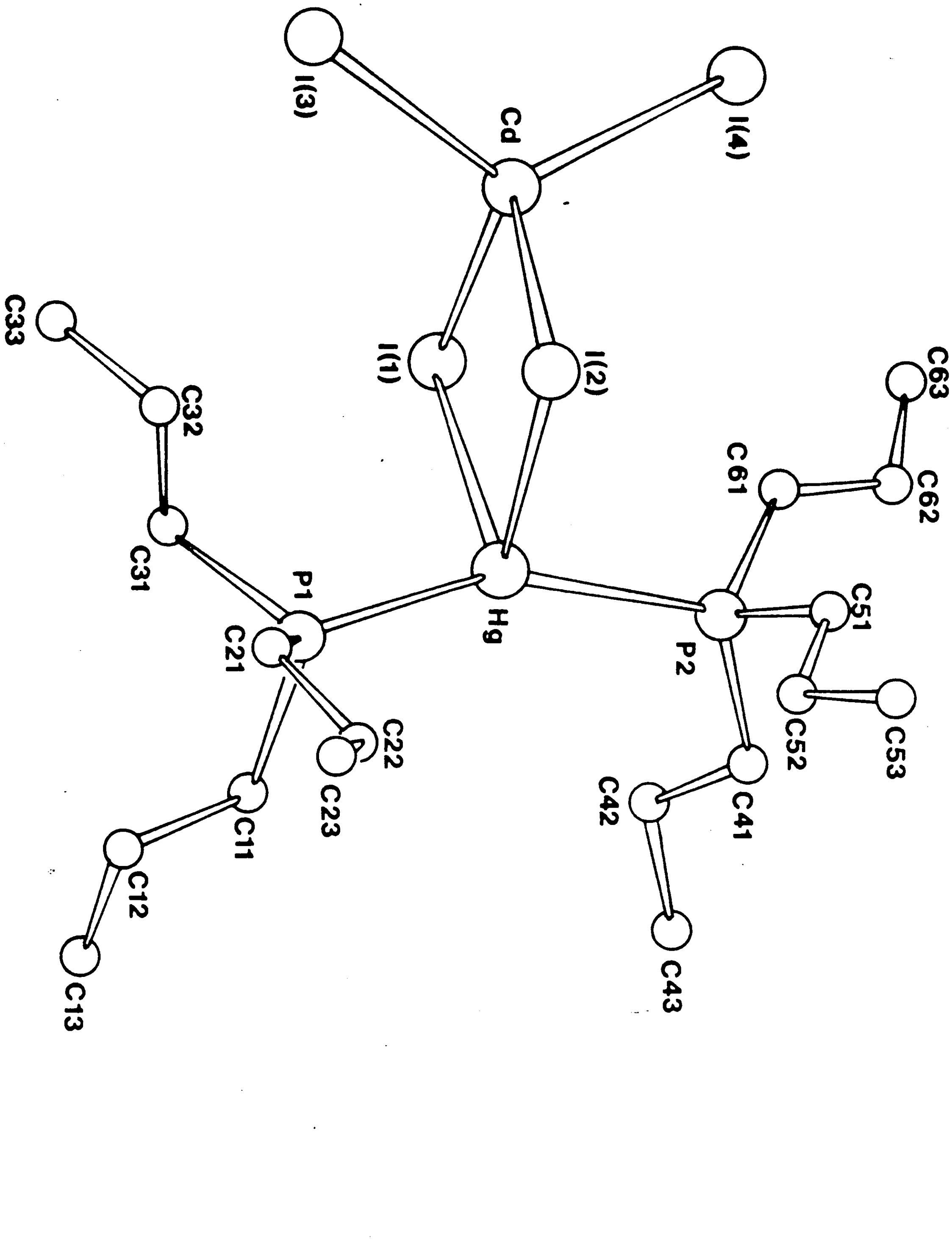


Table 4.3.12 Bond Lengths (Å) and Bond Angles (°) for $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ with Estimated Standard Deviations in Parentheses

(a) Bond lengths (Å)

Hg-I(1)	3.077(1)	Cd-I(4)	2.705(2)
Hg-I(2)	3.056(1)	P(1)-C(11)	1.829(16)
Hg-P(1)	2.424(4)	P(1)-C(21)	1.790(14)
Hg-P(2)	2.410(4)	P(1)-C(31)	1.850(17)
Cd-I(1)	2.866(1)	P(2)-C(41)	1.819(18)
Cd-I(2)	2.882(1)	P(2)-C(51)	1.805(20)
Cd-I(3)	2.705(2)	P(2)-C(61)	1.826(25)

(b) Bond angles (°)

I(1)-Hg-I(2)	88.6(1)	Hg-I(2)-Cd	87.3(1)
I(1)-Hg-P(1)	100.6(1)	Hg-P(1)-C(11)	111.4(5)
I(1)-Hg-P(2)	101.4(1)	Hg-P(1)-C(21)	111.6(5)
I(2)-Hg-P(1)	99.9(1)	Hg-P(1)-C(31)	111.5(5)
I(2)-Hg-P(2)	96.4(1)	C(11)-P(1)-C(21)	107.6(7)
P(1)-Hg-P(2)	152.8(1)	C(11)-P(1)-C(31)	108.2(7)
I(1)-Cd-I(2)	96.3(1)	C(21)-P(1)-C(31)	106.3(7)
I(1)-Cd-I(3)	110.3(1)	Hg-P(2)-C(41)	113.2(6)
I(1)-Cd-I(4)	110.9(1)	Hg-P(2)-C(51)	113.6(7)
I(1)-Cd-I(4)	110.9(1)	Hg-P(2)-C(51)	113.6(7)
I(2)-Cd-I(3)	108.3(1)	Hg-P(2)-C(61)	108.3(8)
I(2)-Cd-I(4)	110.0(1)	C(41)-P(2)-C(51)	107.0(10)
I(3)-Cd-I(4)	118.6(1)	C(41)-P(2)-C(61)	107.8(12)
Hg-I(1)-Cd	87.2(1)	C(51)-P(2)-C(61)	106.6(12)

4.3.5 Crystallographic Examination of the 1:1 Complex $[\alpha\text{-Pr}_3\text{PHgI}_2]_n$

TABLE 4.3.13 Crystal Data

Crystal Size	0.30 x 0.05 x 0.10 mm				
Crystal System	Monoclinic				
	a = 8.670(8)	b = 13.174(9)	c = 14.893(8) Å	β = 106.57(5)°	
V	1630.7 Å^3				
M_r	614.5				
D_c	2.50 g cm^{-3}	D_m	2.47 g cm^{-3}	Z	= 8
Systematic Absences	hkl h + l = 2n + 1				
	0k0 k = 2n + 1				
	h0l h = 2n + 1				
Space Group	$B2_1/a$[‡]				
μ(Mo-Kα)	127.1 cm^{-1}				
F(000)	2208 electrons				

[‡] A non-standard setting of $P2_1/c$

Data Collection and Structural Analysis

The crystal was mounted with its a-axis coincident with the ω-axis of the Stöe Stadi 2 two-circle diffractometer. Ten layers 0kl → 9kl were collected; 1032 unique reflections were measured of which 582 had $I/\sigma(I) \geqslant 2$ and were subsequently used in the refinement. It was impossible to assign positions for the carbon atoms and this was probably due to the small number of reflections available and the presence of a large proportion of heavy atoms. The mercury, iodine and phosphorus atoms were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors were employed throughout the refinement; the final weighting scheme adopted was $W = 2.6953/(\sigma^2|F_o| + 0.002123|F_o|^2)$ and interlayer scaling was applied. Full matrix refinement gave a final R value of 0.092 and R' value of 0.097.

The final atomic parameters and thermal parameters are given in the appendix, table 16 and bond distances and angles are listed in table 4.3.14.

Results and Discussion

The complex is found to consist of a single $(HgI_2)_n$ polymeric chain with each mercury atom co-ordinated to four iodine and one phosphorus atoms (fig. 4.3.7). The mercury atom lies in a distorted trigonal bipyramidal environment with the bond angles varying from 85.8(2)° to 169.7(2)°. The complex has two Hg-I bonds of 2.726(5) Å and 2.715(5) Å and an Hg-P bond of 2.406(17) Å in an approximately planar arrangement (sum of angles is 359.7°). The five co-ordination is completed by bonding of the mercury atom to iodine atoms from two adjacent molecules approximately perpendicular to this HgI_2P plane. These Hg-I bond lengths (3.617 Å and 3.579 Å) are longer than the sum of the van der Waals' radii (3.45 Å) and are considered to be weak interactions.

Fig. 4.3.7 Molecular Structure of $[\alpha\text{-}Pr_3PHgI_2]_n$

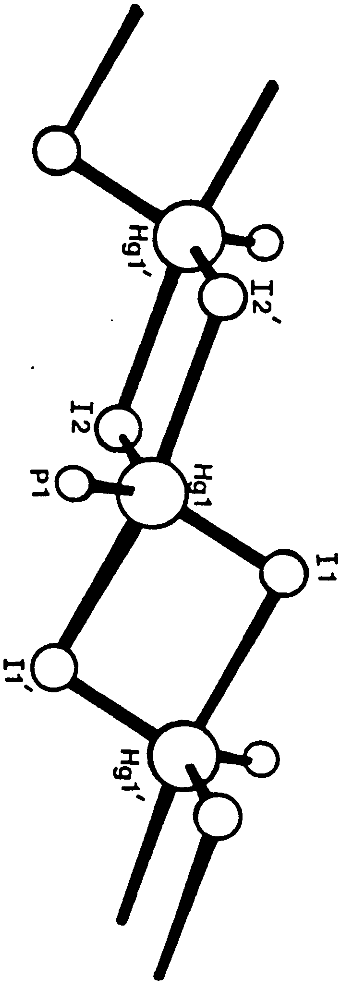


Table 4.3.14 Bond Lengths (Å) and Bond Angles (°) for $[\alpha\text{-}Pr_3PHgI_2]_n$ with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)

Hg-I1	2.726(5)	Hg---Hg'	4.501(4)
Hg-I1'	3.627(5)	Hg---Hg''	4.501(4)
Hg-I2	2.715(5)	symmetry code	
Hg-I2''	3.579(5)	' 1-x, 1-y, -z	
Hg-P	2.406(17)	'' -x, 1-y, -z	

Bond Angles (°)

I2-Hg-I1	112.2(2)	I2''-Hg-I1'	169.7(2)
P-Hg-I2	126.1(5)	Hg-I1-Hg'	89.3(2)
P-Hg-I1	121.4(5)	Hg-I2-Hg''	94.2(2)
I1-Hg-I1'	90.7(2)	P-Hg-I1'	89.0(5)
I2''-Hg-I1	99.1(2)	P-Hg-I2''	88.7(5)
I2-Hg-I2''	85.8(2)		
I1'-Hg-I2	87.4(2)		

4.3.6 A Comparison of 1:1 Mercury(II) Halide Complexes

Although not strictly one of this category, the structure of $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ is included in this section due to its great similarity to $[\beta\text{-}Pr_3PHgI_2]_2$. All the 1:1 mercury(II) halide complexes studied in this work fig. 4.3.8 $(R_3P)HgX_2$ (X = Cl, R = $NCCH_2CH_2$ (e), C_3H_7 (a) and C_6H_5 (f); X = Br, R = C_3H_7 (a); X = I, R = C_3H_7 (b and c) and C_6H_5 (f)) are halogen-bridged dimers with varying degrees of distortion about the mercury atom except for $[(NCCH_2CH_2)_3PHgCl_2]_n$ (e) and $[\alpha\text{-}Pr_3PHgI_2]_n$ (c) which have halogen-bridged polymeric structures. In $[\alpha\text{-}Pr_3PHgI_2]_n$ (c) the mercury atom has a penta-coordinate environment, resulting in an extended distorted trigonal bipyramidal. structure. The structure of polymeric tris(2-cyanoethyl)-phosphine mercury(II) chloride (e) shows the mercury atom to be six-coordination though two of these bonds result from weak CN...Hg π-interactions. Tripropylphosphine mercury(II) iodide exists in two forms; the α-form (c), as reported above,. is polymeric whereas $[\beta\text{-}Pr_3PHgI_2]_2$ (b) is unique among all the 1:1 mercury(II) halide phosphine complexes known having both phosphine ligands coordinated to the same mercury atom. The only bromo mercury(II) complex studied is $(Pr_3PHgBr_2)_2$ (a) which is a halogen bridged dimer similar to its chloro-analogue. Apart from $[Pr_3PHgCl_2]_2$ which has a symmetrical bridged arrangement, all the dimers studied in this work fig. 4.3.8 (a-l) have asymmetrical bridged structures. The structural types established for 1:1 mercury(II) halide complexes with tertiary phosphines from this work and from earlier studies are given in table 4.3.15.

It has been suggested[65] that strong donor ligands give rise to less extended structures. The structures have been established for many tertiary phosphine mercury(II) chloride complexes but insufficient iodide or bromide complexes have been characterised to allow comparisons in these groups. For R_3PHgCl_2 complexes it would appear that 'small' strong σ-donating ligands give rise to extended polymer structures e.g. Me_3P, Et_3P, α-Bu_3P and $(NCCH_2CH_2)_3P$ have structures extended beyond the dimer stage whereas a weak donor such as Ph_3P results in a dimeric structure. The exceptions to this are $[Pr_3PHgCl_2]_2$ and $[Cy_3PHgCl_2]_2$ which have halogen-bridged dimeric structures despite the fact that both ligands have high pKa values (8.64 and 9.7 respectively). However, the large 'size' of the cyclohexyl groups probably inhibits the extension of its structure beyond the dimeric stage. Many R_3PHgX_2 complexes are found to have more than one form and it is possible the Pr_3PHgCl_2 is one of these and may therefore exist in an as yet unknown, more extended form.

The nature of the halogen atoms may play an important role in the extent of the association of $(R_3P)MX_2$ complexes. For example, the structural work on $(R_3P)CdX_2$ complexes[65] has shown that for a given phosphine, the more covalent Cd-I bonding gives rise to a less extended iodine-bridged dimer whilst the chloride gives rise to a more extended penta-coordinate arrangement. However, in the mercury series studied here (Table 4.3.15) for the limited number of structures for a particular phosphine, solved by full X-ray analysis, it appears that the halogen has little effect on the structure adopted. For both Pr_3P and Ph_3P mercury(II) halide complexes a dimeric arrangement is found except for one of the forms of Pr_3PHgI_2 which is polymeric.

In section 2.2 it was proposed that the extent of the interaction between the mercury and the donor ligand was dependent upon the electronic effect and the 'size' of the substituents attached to the donor atom. For the 2:1 series (section 4.2.3) stronger σ-donor ligands gave rise to short Hg-P bonds, long Hg-X bonds and large P-Hg-P bond angles. Parameters for the structures of 1:1 complexes solved in this work and other analogous complexes solved by other workers are listed in table 4.3.16, along with pKa values for the phosphine ligands. Comparison of the Hg-X and Hg-P bond lengths does not show a marked distinction between phosphines of differing pKa values. However, the size of the P-Hg-$Cl_{terminal}$ angle does show marked variation for different strengths of the phosphine ligand. When R is Me, Et, Pr and Bu (pKa 8.65, 8.69, 8.64 and 8.43 respectively) the P - Hg-X angle is found to be large 162.1(1)°, 145.4(3)°, 148.7(2)° and 150.9(3)° respectively, compared to triphenylphosphine mercury(II) chloride (pKa Ph_3P 2.73) which has a much smaller P-Hg-$X_{terminal}$ angle of only 128.7(4)°. Tris(2-cyanoethyl)phosphine mercury(II) chloride has a similar P-Hg-$Cl_{terminal}$ angle (162.0(3)°) to trimethylphosphine mercury(II) chloride (pKa Me_3P is 8.65) which has a P-Hg-$Cl_{terminal}$ angle of 162.1(1)°, indicating $(NCCH_2CH_2)_3P$ is a strong σ-donor to mercury(II) halides although its pKa is only 1.36, as was also found for the 2:1 complex. This is further supported by the NMR data which shows the $(NCH_2CH_2)_3PHgCl_2$ has a similar chemical shift to Pr_3PHgCl_2 but smaller than for the weak donor complex with Ph_3P (table 4.3.17).

Only three mercury(II) iodide structures have been established, those of triphenyl phosphine and the α and β forms of tripropylphosphine. Although these three complexes have vastly differing structures there is little variation of bond angles and bond lengths despite the differing pKa of the phosphines (2.73 and 8.64 respectively). The average Hg-P bond lengths are 2.47 Å, 2.41 Å and 2.44 Å respectively and the P-Hg-$I_{terminal}$ bond angles are 128.4(2)° and for the α-Pr_3PHgI_2 124.8(6)°. This would indicate that for iodides of 1:1 complexes the differing donor strength of the ligands does not markedly affect the bond lengths and bond angles.

The effect of the anion on the geometry of 1:1 mercury(II) halide complexes can be seen from a comparison of the Hg-P and Hg-X_t bond lengths and size of the X_{br}-Hg-X_{br} and P-Hg-X_t angles. The only complete halide series is for tripropylphosphine, where the structures of chloride, bromide and iodide have been fully determined, but data is also available for the chloro and iodo mercury(II) halide complexes with triphenylphosphine. In both these cases the steric and electronic effects of the phosphine ligand may be ignored.

In the case of triphenylphosphine mercury(II) halides a comparison of the appropriate angles and lengths is straightforward, as both complexes being studied have a halogen-bridged dimeric structure, the chloride having a centrosymmetrical structure whilst the iodide has an asymmetric structure. Triphenylphosphine mercury(II) chloride has shorter Hg-P and Hg-X_t bond lengths 2.406(7) Å and 2.370(10) Å respectively and a smaller X_{br}-Hg-X_{br} angle 85.4(3)° than its iodide analogue which has corresponding bond lengths of 2.461(8) Å and 2.671(2) Å and an I-Hg-I angle of 94.8(1)°. The P-Hg-X_t angle in these cases are very similar 128.7(4)° for the chloride and 127.5(2)° for the iodide.

In the case of tripropylphosphine mercury(II) halides the iodides have vastly different structures from the chloride and bromide, both the latter being halogen-bridged dimers. Tripropylphosphine mercury(II) bromide is unusual in that the terminal Hg-Br bond length (2.507(2) Å) and the bridging Hg-Br bond length 2.667(2) Å are similar, whereas there is a marked difference for the chloride which has bond lengths of 2.348(5) Å and 2.638(4) Å respectively. The β-form of the iodide is a halogen-bridged dimer but is most unusual in having both phosphine groups bonded to the same mercury atom. In contrast the α-version of the iodide is a polymeric halogen-bridged structure. Despite the structural variations it is possible to see an increase in the X_{br}-Hg-X_{br} angle from 96.5(2)° for the chloride, 102.5(1)° for the bromide to 112.5(2)° for the α-form of the iodide and 108.3(2)° for the β-form. The P-Hg-X_t angle however shows a decrease from chloride to iodide (148.7(2), 135.9(1) and 123.7(6)° av. respectively) and these variations are accompanied by an increase in the Hg-P (2.358(4), 2.408(4), 2.406(17) and 2.439(14) av. Å) and Hg-X_t (2.348(5), 2.507(2), 2.723(6) and 2.694(4) Å) bond lengths from X= Cl to I. The increase in Hg-P distance from chloride to iodide for both the Ph_3P and Pr_3P complexes may result from both the higher electronegativity of chlorine compared to iodide and also if the iodide is a stronger donor to mercury than chlorine as was discussed in section 4.2.3.

An increase in the Hg-X (X = Cl → Br → I) bond length would be expected due to the electronegativity and bulk of the halogen atoms. A comparison of this bond length (table A) for HgX_2 (I) and Pr_3PHgX_2 (II) shows that Hg-Cl is 2.52 Å in (I) and 2.348(5) Å in (II), Hg-Br for (I) 2.57 Å for (II) 2.507(2) Å and for Hg-I (I) 2.60 Å for (II) 2.69 Å av. The differences between I and II would indicate that in the 1:1 complexes the chlorine atom is acting as the stronger σ-donor. Similarly, a comparison shown below between the Hg-X distances in the complexes and the sum of the covalent radii leads to the same conclusions.

Table A Comparison of Hg-X covalent radii and Hg-X bond distances

sum covalent radii Hg-X (Å)		Hg-X_t bond distance (Å)		Difference (Å)	
		(Pr_3P) (I)	(Ph_3P) (II)	(I)	(II)
X = Cl	2.44	2.348	2.370	0.092	0.07
X = Br	2.58	2.507		0.073	
X = I	2.77	2.69	2.68	0.08	0.09

A similar comparison may be made between the Hg-P bond distances and the sum of the covalent radii for mercury and phosphorus (table B).

Table B Comparison of Hg-P covalent radii and Hg-P bond distances (Å)

sum covalent radii Hg-P (Å)		Hg-P distance (Å)		Difference (Å)	
		(Pr_3P) (I)	(Ph_3P) (II)	(I)	(II)
X = Cl	2.54	2.358	2.406	-.182	-.134
X = Br	2.54	2.408		-.132	
X = I	2.54	2.457	2.483	-.083	-.017

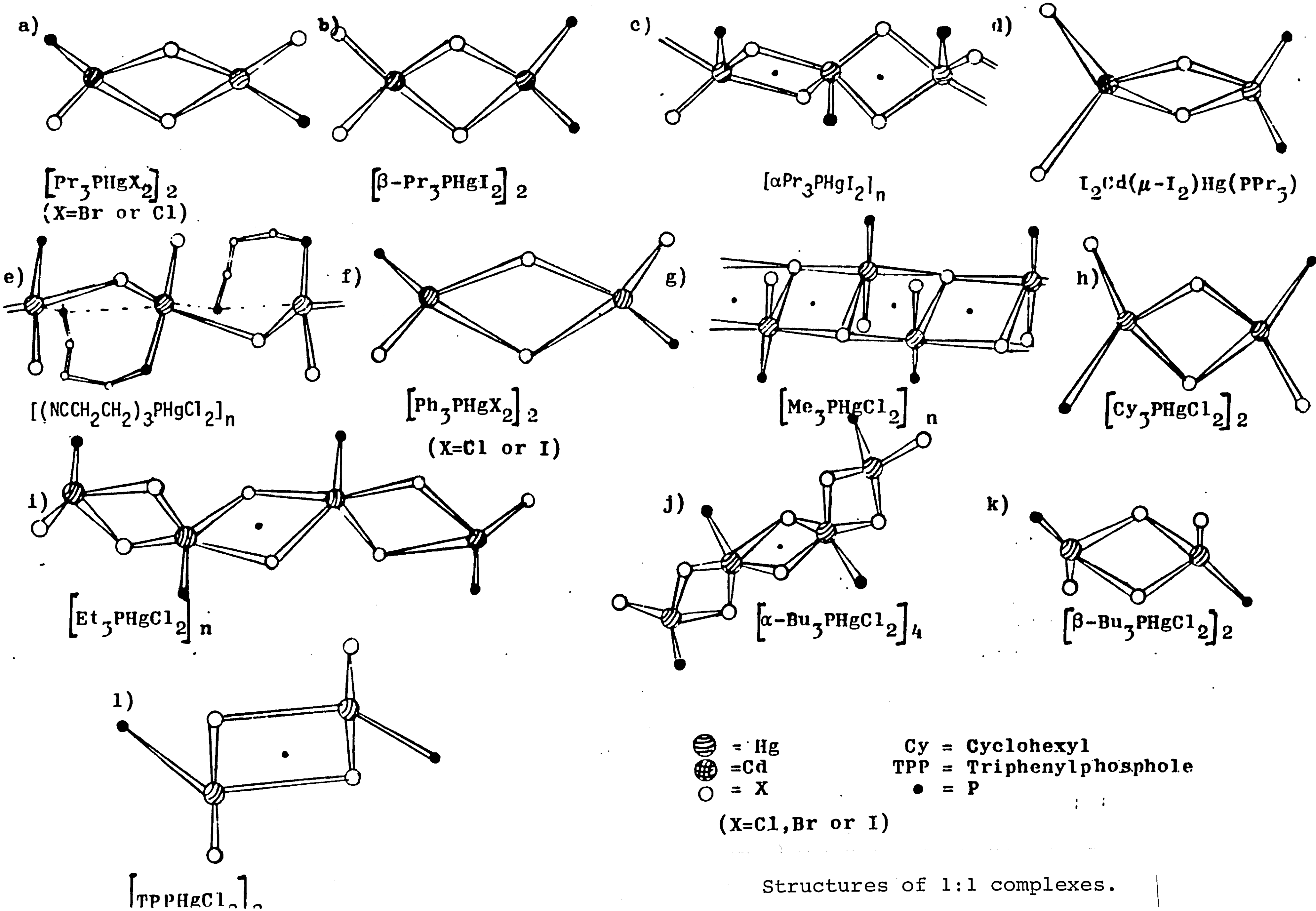
In all cases the Hg-P bond distance is smaller than the sum of the covalent radii indicating a strong mercury-ligand reaction.

Table 4.3.17 shows a decrease from the chloride to the iodide for both chemical shifts and coupling constants with a corresponding increase in the Hg-P bond lengths. The exception being the polymeric $[\alpha\text{-}Pr_3PHgI_2]_n$ which has a Hg-P bond length comparable to its bromo-analogue, but a similar chemical shift and coupling constant to $[\beta\text{-}Pr_3PHgI_2]_2$.

This trend of decreasing chemical shifts and coupling constants is also shown by the 2:1 complexes, but in the case of the 2:1 complexes the chemical shifts and coupling constants are lower.

Comparison of $\beta\text{-}(Pr_3P)_2Hg(\mu\text{-}I)_2HgI_2$ (I) and $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ (II) Fig. 4.3.8

A comparison of the bond lengths and bond angles for the complexes $[\beta\text{-}Pr_3PHgI_2]_2$ (I) and $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ (II) shows them to be remarkably similar. Both have a halogen-bridged dimer structure with the two phosphine ligands coordinated to the same mercury atom and thus (I) is the only 1:1 mercury(II) halide tertiary phosphine complex known to be of this structure. The geometry about the Cd atom in (II) and the analogous Hg atom in (I), which is also bonded to two terminal iodine atoms, is only slightly distorted from the tetrahedral, while the geometries about the other mercury atom, in each case, are highly distorted from tetrahedral and angles range from 89.5° to 149.1° in (I) and from 88.6° to 152.8° in (II). The similarity of the structures is not unexpected as $[\beta\text{-}Pr_3PHgI_2]_2$ can be prepared by the treatment of $(Pr_3P)HgI_2CdI_2$ with excess mercuric iodide.[24] The 1:2:1 triplet nature of the ^{199}Hg NMR spectrum for complex (II) indicates the bonding of two equivalent phosphine ligands to the mercury atom. ^{199}Hg NMR data are not available for $(\beta\text{-}Pr_3PHgI_2)_2$. The ^{31}P NMR data given in table 4.3.17 for both complexes surprisingly shows no similarity, the chemical shifts and coupling constants being markedly different.



Structures of 1:1 complexes.

Fig 4.3.8

Table 4.3.15 Summary of Structures of $HgX_2(PR_3)$ Complexes Determined(a)

PR_3	Cl	Br	I
TPP(b)	Asymmetric dimer(d)	Assymetric dimer(d)	–
PPh_3	Symmetric dimer	Symmetric dimer	Asymmetric dimer
PPh_2Me	(α *Chain polymer* (β *Symmetric dimer*	*Ionic chain*	*Symmetric dimer*
$PPhMe_2$	*Ionic chain*	*Ionic chain*	*Symmetric dimer*
PMe_3	Ionic chain	Ionic chain	*New form*
PEt_3	Chain polymer	*Chain polymer*	*Symmetric dimer*
PPr_3	Asymmetric dimer(d)	Asymmetric dimer(d)	β: Unsymmetric dimer α: Weakly linked monomer units
PBu_3	(α Pseudo-tetramer (β Symmetric dimer	*Pseudo-tetramer*	*Pseudo-tetramer*
PCy_3(c)	Two independent dimers	*Symmetric dimer*	*Symmetric dimer*
$P(CH_2CH_2CN)_3$	Chain polymer		

(a) Structures underlined have been determined by full X-ray analysis: Structures in normal type have been deduced by comparison of preliminary single crystal X-ray data: Structures in *italics* are those proposed from comparative vibrational spectroscopy.

(b) TPP = 1,2,5-triphenylphosphole.

(c) Cy - cyclohexyl.

(d) In an asymmetric dimer the Hg-X bond lengths in the centrosymmetric HgX_2Hg unit are distinctly unequal.

Table 4.3.16 <u>Comparison of Bond Lengths (Å) and Bond Angles (°) for Some $(R_3P)HgX_2$ Complexes</u>

$(R_3P)HgX_2$	Hg-X_{br} (Å)	Hg-X_t (Å)	Hg-P (Å)	X_b-Hg-X_b (°)	P-Hg-X_t (°)	R_3P
$(Me_3P)HgCl_2$[a]	2.782(4) 2.941(4) 3.489(4)	2.355(4)	2.365(3)	98.2(1)	162.1(1)	8.65
$(Et_3P)HgCl_2$[a]	2.56(1) 3.04(1) 3.21(1)	2.42(1)	2.35(1)	98.7(3)	145.4(3)	8.69
$(Pr_3P)HgCl_2$[b]	2.638(4)	2.348(5)	2.358(4)	96.5(2)	148.7(2)	8.64
$(Pr_3P)HgBr_2$[b]	3.051 2.667(2)	2.507(2)	2.408(4)	102.5(1)	135.9(1)	8.64
$(\alpha\text{-}Pr_3P)HgI_2$[b]	3.566(6) 3.612(6)	2.723(6) 2.622(6)	2.406(17)	112.5(2)	122.6(6) 124.8(6)	8.64
$(\beta\text{-}Pr_3P)HgI_2$[b]	3.027(4) 3.050(5) 2.937(5) 2.921(4)	2.694(4) 2.685(2)	2.457(14) 2.421(15)	109.6(2) 109.8(2) 109.5(2) 106.3(2)	-	8.64
$(NCCH_2CH_2)_3PHgCl_2$[b]	2.780(7) 2.714(7)	2.331(7)	2.393(5)	98.8(3) 98.1(3) 99.0(3)	90.2(2) 95.8(2) 162.0(3)	1.36
$(\alpha\text{-}Bu_3P)HgCl_2$[c]	2.709(20) 2.895(21) 2.626(19) 2.304(21) 2.664(18) 3.375(25)	2.289(21)	2.363(21) 2.337(19)	92.6(6) 88.3(7) 87.8(6)	147.8(7)	8.43
$(\beta\text{-}Bu_3P)HgCl_2$[d]	2.720(6) 2.736(6)	2.348(8)	2.377(6)	89.0(3)	150.9(3)	8.43

Ph_3PHgCl_2[c]		2.658(8)	2.623(8)	2.370(10)	2.406(7)	85.4(3)	128.7(4)	2.73
Ph_3PHgI_2[b]		2.990(2)	2.860(2)	2.671(2)	2.461(8)	94.8(1)	128.4(2)	2.73
		2.960(2)	2.846(2)	2.684(2)	2.438(8)	95.8(1)	126.6(2)	
Cy_3PHgCl_2[e]	1	2.641(4)	2.665(4)	2.391(5)	2.416(3)	95.2(2)	139.6(2)	9.7
	2	2.602(4)	2.779(4)	2.413(3)	2.412(3)	101.5(2)	132.0(1)	
$TPPHgCl_2$[c]		2.542(13)	2.747(14)	2.404(11)	2.438(10)	86.5(4)	127.8(5)	-

a = ref. 36

b = this work

c = ref. 34

d = ref. 38

e = ref. 39

t = terminal

Table 4.3.17 NMR Parameters for $(R_3P)HgX_2$ Complexes (where X = Cl, Br or I and R = Pr, Ph and $(NCCH_2CH_2)$)

Complex	(^{31}P)/ppm (±1)	J(Hg-P) Hz (±5)	Hg-P (Å)
$(Pr_3P)HgCl_2$[a]	33.0	7389	2.358(4)
$(Pr_3P)HgBr_2$[a]	27.2	6611	2.407(4)
$CdHgI_4(PPr_3)_2$[c]	17.5	4340	2.436(24)
$\beta(Pr_3P)HgI_2$	6.2	5071	2.431(25)
$\alpha(Pr_3P)HgI_2$[a]	6.9	5053	2.406(17)
$(Ph_3P)HgCl_2$	38.8	7431	2.406(7)
$(Ph_3P)HgBr_2$[b]	36.1	6464	-
$(Ph_3P)HgI_2$[b]	12.2	4700	2.461(8) 2.483(8)
$(NCCH_2CH_2)_3PHgCl_2$[c]	33.39	-	2.393(5)
$(NCCH_2CH_2)_3PHgBr_2$[c]	29.25	-	-
$(NCCH_2CH_2)_3PHgI_2$[c]	-	-	-

All measurements relative to H_3PO_4

[a] ref. 61 solvent 20% CD_2Cl_2 in CH_2Cl_2 at 300 K

[b] ref. 63 solvent DMF at 243 K

[c] Personal communication B. Taylor (solvent acetone)

Summary

The nature of both the phosphine ligand and halogen atom play an important role in the structures adopted by $(R_3P)_nHgX_2$ complexes (where n = 1 or 2).

The 2:1 mercury(II) halide complexes all have distorted monomeric tetrahedral structures in which the σ-donor ability of the phosphine ligand plays a dominant role in the size of the P-Hg-P angles and the lengths of the Hg-P bonds (Table 4.2.7). The stronger σ-donor phosphine ligands give rise to larger P-Hg-P angles, smaller X-Hg-X angles and short Hg-P bond lengths. Insufficient data is available for any meaningful deductions concerning the effect of the halide atom as the full structures are only available for one series $(Ph_3P)_2HgX_2$ (where X = Cl, Br or I). From the limited information available the effects of the halide on the 2:1 structures appears to be a decrease in the size of the P-Hg-P angle where X varies from Cl to Br to I with a corresponding increase of the Hg-P bond lengths.

For the 1:1 mercury(II) halide complexes a variety of the gross structural types has been found, and these are summarised in Table 4.3.15. Complexes which contain strong σ-donor phosphine ligands tend to give a large number of different structures. These vary from symmetrical halogen-bridged dimers (e.g. $(Pr_3PHgCl_2)_2$) to chain polymers (e.g. $(Et_3PHgCl_2)_n$). The only weak σ-donor phosphine studied is triphenylphosphine which results in halogen-bridged dimer structures for both the iodide and chloride complexes. The only complete halide series studied is for tripropylphosphine where the structures vary from a symmetrical halogen-bridged dimer where X = Cl and Br, to an extended pentaco-ordinate iodine-bridged structure or an unusual halogen-bridged dimer, having both phosphine ligands co-ordinated to the same mercury atom in the two forms of Pr_3PHgI_2. A complete study of the iodine analogues where R = Et, Me and $(NCCH_2CH_2)$ would be necessary to provide a meaningful comparison of the effect of the halogen atom on the structures of the 1:1 mercury(II) halide tertiary phosphine complexes.

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Details of Programme of Study

(a) Completed a computing course in Basic at the Polytechnic.

(b) Completed a computing course in the use of IBM 4341 computer at the Polytechnic.

(c) Attended a final year degree course of lectures on X-ray Crystallography, given by the Director of Studies.

(d) Completed the following reading study programme.

  (i) Crystal Structure Analysis. J.P. Glusker and K.N. Trueblood, Oxford University Press, (1972).

  (ii) X-ray Structure Determination, a Practical Guide. G.H. Stout and L.H. Jensen, Macmillan, New York, (1968).

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  (v) Inorganic Chemistry, Principles of Structure and Reactivity, J.E. Huheey, Harper and Row, (1978).

  (vi) The Chemistry of Zinc, Cadmium and Mercury. B.J. Aylett, Pergamon. Texts in Inorganic Chemistry Vol. 18, Pergamon Press.

Appendices

A1. Final Positional Parameters and Thermal Parameters

Anisotropic temperature factors are of the form:-

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*] \quad \underline{1}$$

Isotropic temperature factors are of the form:

$$\exp-8\pi^2U(\sin^2\theta/\lambda^2) \quad \underline{2}$$

Table 1 Final Fractional Coordinates (Hg x 10^5; other atoms x 10^4) with Estimated Standard Deviations in Parentheses[a] for $[(2\text{-thienyl})_3P]_2HgCl_2$

	x	y	z
Hg	44386(3)	15488(2)	25479(2)
Cl(1)	2726(3)	498(1)	2070(2)
Cl(2)	3613(3)	2619(1)	1614(2)
P(1)	4303(2)	1891(1)	3969(1)
P(2)	6592(2)	1169(1)	2004(1)
C(11)	5500(9)	1340(5)	4713(6)
S(12)	5150(4)	1115(2)	5635(2)
C(13)	6690(12)	596(6)	5880(8)
C(14)	7429(13)	609(7)	5317(8)
C(15)	6783(10)	1024(7)	4635(8)
C(21)	4783(9)	2821(5)	4209(6)
S(22)	3989(4)	3524(1)	3592(2)
C(23)	4924(13)	4153(6)	4218(8)
C(24)	5875(11)	3868(6)	4890(8)
C(25)	5810(9)	3072(5)	4920(7)
C(31)	2587(8)	1791(4)	4225(5)
S(32)	2027(3)	2290(2)	4948(2)
C(33)	507(12)	1780(7)	4872(7)
C(34)	425(11)	1247(5)	4301(7)
C(35)	1597(10)	1217(5)	3913(7)
C(41)	7385	328	2451
S(42A)	6473	-299	2789
S(42B)	9009	46	2462
C(43A)	7916	-865	3019
C(43B)	8741	-751	2934
C(44A)	9125	-564	2925
C(44B)	7465	-868	3062
C(45A)	8780	80	2453
C(45B)	6576	-230	2717
C(51)	6112(9)	1016(5)	923(5)
S(52)	7229(3)	654(1)	337(2)
C(53)	5943(11)	679(5)	-535(6)
C(54)	4707(12)	970(5)	-418(6)
C(55)	4828(10)	1175(5)	431(6)
C(61)	8001	1836	2212

	x	y	z
S(62A)	9401	1822	1763
S(62B)	8056	2439	2936
C(63A)	10153	2562	2308
C(63B)	9690	2748	2835
C(64A)	9333	2794	2804
C(64B)	10294	2327	2345
C(65A)	8004	2411	2783
C(65B)	9112	1868	1779

Final Positional Parameters (x 10^4) for Hydrogen atoms

H(13)	6988	289	6446
H(14)	8445	334	5378
H(15)	7230	1086	4094
H(23)	4820	4733	4095
H(24)	6573	4194	5348
H(25)	6419	2726	5394
H(33)	-289	1871	5236
H(34)	-463	871	4154
H(35)	1728	825	3448
H(53)	6100	489	-1125
H(54)	3754	1038	-893
H(55)	3967	1430	658

Table 2 Final Thermal Parameters for Non-hydrogen Atoms with Estimated

Standard Deviations in Parentheses for $[(2\text{-thienyl})_3P]_2HgCl_2$

(a) Anisotropic temperature factors (x 10^4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	334(2)	318(2)	289(2)	-11(1)	96(2)	9(1)
Cl(1)	502(13)	412(13)	412(13)	-119(10)	120(11)	-134(10)
Cl(2)	550(13)	331(11)	398(13)	67(10)	67(11)	54(10)
P(1)	274(10)	242(10)	246(10)	-5(9)	66(8)	-6(8)
P(2)	257(10)	250(10)	305(11)	-18(9)	84(9)	-1(8)
C(11)	309(42)	326(46)	314(50)	-3(42)	94(37)	-27(37)
S(12)	763(20)	804(23)	463(17)	285(16)	253(15)	303(17)
C(13)	646(69)	539(65)	605(73)	287(57)	113(58)	139(53)
C(14)	546(65)	713(78)	602(84)	252(67)	82(60)	93(58)
C(15)	309(47)	658(76)	696(85)	371(67)	96(50)	323(50)
C(21)	334(44)	292(46)	361(50)	-60(41)	101(38)	-31(37)
S(22)	717(19)	342(13)	454(16)	21(11)	12(14)	-7(12)
C(23)	712(76)	289(55)	638(80)	99(56)	115(64)	-96(53)
C(24)	464(52)	431(56)	647(77)	-167(53)	136(53)	-134(44)
C(25)	290(40)	230(45)	643(63)	-108(44)	107(42)	-32(34)
C(31)	322(39)	209(37)	318(47)	-65(35)	28(35)	40(32)
S(32)	457(13)	461(13)	487(15)	-161(12)	189(12)	9(11)
C(33)	524(60)	707(75)	463(62)	70(59)	279(51)	163(58)
C(34)	465(56)	329(49)	652(70)	83(48)	199(51)	-85(42)
C(35)	347(46)	348(49)	569(64)	-116(46)	170(44)	21(38)
C(51)	365(43)	292(42)	268(44)	-64(36)	174(36)	-43(35)
S(52)	488(13)	451(13)	428(14)	-76(11)	207(11)	76(11)
C(53)	691(62)	333(47)	330(50)	-156(42)	174(45)	-152(46)
C(54)	575(62)	428(52)	333(51)	56(44)	76(46)	-42(47)
C(55)	472(53)	403(51)	345(52)	13(43)	153(43)	-16(42)

(b) Isotropic temperature factors (x 10^3)

	U		U
C(41)	38(2)	C(61)	37(2)
S(42A), S(42B)	52(1)	S(62A), S(62B)	47(1)
C(43A), C(43B)	63(4)	C(63A), C(63B)	35(2)
C(44A), C(44B)	64(4)	C(64A), C(64B)	77(5)
C(45A), C(45B)	156(14)	C(65A), C(65B)	167(15)

Table 3 Final Fractional Coordinates for $[(NCCH_2CH_2)_3P]_2HgBr_2.OC(CH_3)_2$ (Hg x 10^5, other atoms x 10^4) with Estimated Standard Deviations in Parentheses

Atom	x	y	z
Hg	26835(7)	12825(4)	26700(2)
Br(1)	5682(2)	1215(1)	2708(1)
Br(2)	1913(4)	2934(1)	2618(1)
P(1)	2393(4)	1019(2)	3816(1)
P(2)	2351(4)	870(2)	1538(1)
C(11)	2793(18)	1971(8)	4291(6)
C(12)	4291(23)	2310(10)	4166(8)
C(13)	4628(21)	3107(9)	4503(7)
N(13)	4822(19)	3735(10)	4745(7)
C(21)	3661(19)	245(9)	4141(6)
C(22)	3604(24)	-585(9)	3747(9)
C(23)	4521(21)	-1255(10)	4034(7)
N(23)	5222(22)	-1738(9)	4254(7)
C(31)	623(18)	685(10)	4069(7)
C(32)	-647(19)	1270(14)	3853(8)
C(33)	-1919(23)	968(15)	4167(8)
N(33)	-2885(25)	764(19)	4460(10)
C(41)	3574(18)	7(8)	1381(6)
C(42)	3589(23)	-275(12)	665(7)
C(43)	4545(27)	-998(11)	582(8)
N(43)	5286(27)	-1571(12)	514(9)
C(51)	551(17)	519(9)	1258(6)
C(52)	-622(18)	1148(10)	1426(7)
C(53)	-2048(22)	869(12)	1132(8)
N(53)	-3108(19)	645(12)	891(8)
C(61)	2789(17)	1742(8)	1002(6)
C(62)	4282(21)	2120(11)	1171(9)
C(63)	4561(24)	2874(10)	790(9)
N(63)	4820(27)	3471(11)	514(9)
O	-556(28)	-332(15)	2626(9)
C(1)	-1536(39)	-882(17)	2559(13)
C(2)	-1880(45)	-1310(20)	1923(13)
C(3)	-2469(38)	-1141(26)	3087(14)

Final Positional Parameters (x 10^4) for Hydrogen atoms

	x	y	z
H(111)	2749	1820	4798
H(112)	1987	2448	4163
H(121)	4351	2415	3653
H(122)	5094	1844	4323
H(211)	3401	105	4631
H(212)	4751	503	4137
H(221)	3953	-455	3267
H(222)	2493	-814	3715
H(311)	673	655	4590
H(312)	399	62	3873
H(321)	-834	1241	3335
H(322)	-405	1914	3996
H(411)	3258	-531	1663
H(412)	4667	200	1535
H(421)	3964	247	380
H(422)	2493	-445	498
H(511)	327	-81	1481
H(512)	528	443	740
H(521)	-356	1766	1241
H(522)	-683	1182	1944
H(611)	1974	2231	1038
H(612)	2770	1508	512
H(621)	5105	1652	1082
H(622)	4344	2289	1676

Table 4 Final Anisotropic Thermal Parameters for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses for $[(NCCH_2CH_2)_3P]_2HgBr_2.OC(CH_3)_2$

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{23}$	$\underline{U}_{13}$	$\underline{U}_{12}$
Hg	501(4)	405(3)	210(2)	-11(3)	35(2)	12(4)
Br(1)	43(11)	978(13)	385(7)	-18(9)	15(6)	3(11)
Br(2)	1643(27)	410(9)	519(10)	11(8)	36(12)	303(12)
P(1)	410(25)	315(17)	212(14)	1(11)	59(13)	14(14)
P(2)	422(26)	318(16)	221(14)	-14(12)	40(13)	-22(15)
C(11)	481(110)	303(70)	402(69)	-31(54)	100(59)	-42(65)
C(12)	638(150)	436(90)	517(86)	-83(66)	118(78)	-123(85)
C(13)	700(131)	336(74)	397(71)	-86(59)	-94(67)	-143(73)
N(13)	960(132)	485(78)	598(76)	-117(77)	54(71)	-171(97)
C(21)	531(119)	361(73)	293(63)	83(55)	5(58)	19(69)
C(22)	774(160)	252(67)	747(106)	-64(70)	-52(91)	107(78)
C(23)	825(134)	301(74)	513(80)	30(71)	90(75)	207(92)
N(23)	1056(161)	454(83)	554(84)	19(68)	-1(83)	94(91)
C(31)	366(107)	406(76)	526(82)	118(63)	110(64)	39(65)
C(32)	440(116)	691(102)	641(94)	12(96)	180(74)	96(110)
C(33)	297(130)	1283(179)	502(94)	265(99)	4(75)	-24(105)
N(33)	585(165)	1942(251)	824(133)	437(148)	15(104)	-140(150)
C(41)	557(116)	317(64)	294(61)	43(49)	71(78)	50(65)
C(42)	714(149)	606(104)	356(82)	-237(75)	161(77)	32(94)
C(43)	922(192)	449(91)	528(92)	-170(71)	237(93)	-146(103)
N(43)	1324(220)	574(98)	869(132)	-130(87)	438(123)	155(115)
C(51)	353(102)	516(86)	382(66)	-37(57)	40(55)	76(68)
C(52)	473(106)	450(94)	471(71)	-110(67)	-19(59)	-108(76)
C(53)	554(139)	755(108)	470(84)	-150(76)	60(76)	30(91)
N(53)	413(114)	1167(131)	656(93)	-289(91)	-11(73)	89(91)
C(61)	577(109)	281(64)	323(64)	80(51)	20(57)	40(61)
C(62)	465(130)	490(94)	659(106)	243(81)	39(80)	-33(80)
C(63)	657(155)	444(87)	634(117)	150(83)	97(93)	-54(83)
N(63)	1311(209)	578(106)	846(124)	211(87)	30(114)	-329(103)
O	1601(226)	1333(169)	933(124)	42(115)	483(125)	-61(149)
C(1)	1174(263)	860(160)	960(174)	275(133)	197(155)	268(165)
C(2)	2733(419)	1046(191)	924(166)	-241(167)	576(193)	-191(259)
C(3)	1246(280)	2334(379)	1107(195)	253(213)	426(176)	-261(245)

Table 5 Final Fractional Coordinates (x 10^4) with Estimated Standard Deviations in Parentheses for $[(NCCH_2CH_2)_3P]_2HgCl_2$

	Molecule 1			Molecule 2		
	x	y	z	x	y	z
Hg	1638(1)	1948(2)	4198(1)	6578(0)	2437(2)	2564(1)
Cl(1)	1606(5)	-721(11)	4683(4)	7244(4)	1005(11)	2132(4)
Cl(2)	2215(4)	3363(14)	5228(4)	6806(4)	5281(11)	2385(5)
P(1)	2256(4)	1341(12)	3692(4)	7179(3)	1856(10)	3608(3)
P(2)	724(4)	3050(14)	4100(4)	5706(3)	2188(11)	1622(3)
C(11)	2526	-683	3827	7482	-116	3717
C(12)	2030	-1759	3526	7068	-1378	3361
C(13)	2308	-2934	3851	6712	8508	3556
N(13)	2454	-4258	4183	6372	7864	3828
C(21)	1906	1497	2849	7858	2999	3934
C(22)	1741	3003	2582	8131	3036	3517
C(23)	1445	3828	2812	8630	3979	3758
N(23)	1163	4674	3022	9131	4322	4125
C(31)	2886	2434	3896	6890	-8001	4160
C(32)	3223	2437	4631	6768	-6546	4263
C(33)	3711	3585	4795	6329	-5792	3897
N(33)	4117	4336	5017	5869	-5518	3414
C(41)	118	3060	3377	5427	265	1383
C(42)	-201	1525	3072	5881	-929	1514
C(43)	160	877	3126	5697	-2320	1148
N(43)	606	4	2942	5556	-3392	903

Table 6 Final Thermal Parameters for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses for $[(NCCH_2CH_2)_3P]_2HgCl_2$

Anisotropic Thermal Parameters ($\times 10^4$)

	Molecule 1						Molecule 2					
	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{23}$	$\underline{U}_{13}$	$\underline{U}_{12}$	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{23}$	$\underline{U}_{13}$	$\underline{U}_{12}$
Hg	605(8)	812(10)	577(8)	16(8)	273(7)	51(8)	524(7)	723(8)	432(6)	7(7)	197(5)	22(7)
Cl(1)	1289(88)	809(70)	577(58)	104(53)	409(59)	69(64)	682(59)	967(70)	871(61)	-50(54)	461(52)	98(53)
Cl(2)	891(74)	1334(101)	855(69)	-391(70)	249(58)	-417(73)	939(68)	661(64)	1115(76)	-22(56)	472(61)	-134(54)
P(1)	623(58)	819(72)	568(59)	57(53)	234(48)	-14(53)	554(50)	690(59)	370(43)	53(45)	149(39)	14(49)
P(2)	559(60)	1156(92)	663(57)	-1(61)	207(49)	184(62)	579(52)	678(64)	454(43)	-6(47)	220(41)	70(49)

Isotropic Thermal Parameters (x 10^4)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(11)	988(138)	1384(175)	C(41)	1212(134)	630(85)
C(12)	1122(132)	1110(140)	C(42)	2554(357)	1168(162)
C(13)	2179(305)	2671(347)	C(43)	2145(316)	1051(126)
N(13)	2198(293)	3335(350)	N(43)	2224(209)	1096(90)
C(21)	1252(151)	1418(141)	C(51)	1505(170)	760(90)
C(22)	1001(137)	1288(134)	C(52)	4628(1317)	1343(153)
C(23)	1618(265)	1660(140)	C(53)	2425(265)	1993(309)
N(23)	1751(170)	2765(139)	N(53)	3571(322)	2586(422)
C(31)	1003(113)	1442(180)	C(61)	1814(170)	640(88)
C(32)	973(115)	1526(270)	C(62)	1862(234)	837(105)
C(33)	1235(172)	1907(333)	C(63)	2231(547)	943(112)
N(33)	1905(167)	2967(319)	N(63)	2528(287)	1403(134)

Table 7 Final Fractional Coordinates for $[(NCCH_2CH_2)_3PHgCl_2]_n$ (Hg x 10^5; other atoms x 10^4) with Estimated Standard Deviations in Parentheses

Atom	x	y	z
Hg	-520(4)	14470(14)	4988(18)
Cl(1)	197(4)	4615(10)	1767(15)
Cl(2)	-1139(3)	1754(17)	-84(15)
P	1072(3)	960(8)	250(12)
C(11)	1469(12)	414(25)	1932(31)
C(12)	1326(9)	1692(28)	3403(31)
C(13)	1746(14)	1306(31)	4749(31)
N(13)	2074(13)	1038(29)	5689(33)
C(21)	1293(11)	-819(26)	-1191(28)
C(22)	933(14)	-2443(31)	-801(33)
C(23)	283(15)	-2267(36)	-1467(39)
N(23)	-235(14)	-2333(33)	-1654(32)
C(31)	1436(10)	2910(27)	-555(33)
C(32)	2173(10)	2809(27)	-796(29)
C(33)	2389(12)	4279(34)	-1558(36)
N(33)	2516(20)	5568(32)	-2147(36)

Final hydrogen positions (x10^4)

	x	y	z
H(111)	1977	428	1695
H(112)	1324	-856	2264
H(121)	833	1549	3761
H(122)	1409	2989	3033
H(211)	1801	-1059	-1122
H(212)	1170	-424	-2367
H(221)	906	-2607	456
H(222)	1173	-3525	-1316
H(311)	1336	3945	244
H(312)	1216	3171	-1677
H(321)	2287	1708	-1502
H(322)	2406	2701	331

Table 8 Final Thermal Parameters for $[(NCCH_2CH_2)_3PHgCl_2]_n$ with Estimated Standard Deviations in Parentheses

Anisotropic Thermal Parameters

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	261(4)	433(5)	441(6)	11(7)	15(5)	25(4)
Cl(1)	540(38)	431(38)	768(81)	-62(48)	10(44)	100(32)
Cl(2)	319(30)	1133(95)	785(102)	34(71)	-7(34)	11(42)
P	278(25)	302(31)	442(61)	42(33)	-19(30)	-48(21)
C(11)	465(127)	134(101)	488(242)	-43(127)	-136(134)	73(90)
C(12)	195(85)	452(185)	490(209)	11(158)	127(109)	27(97)
C(13)	572(147)	559(193)	359(238)	-31(199)	-254(155)	-63(153)
C(21)	371(110)	236(105)	202(158)	-47(11)	73(107)	18(91)
C(23)	353(159)	1170(465)	2202(930)	-840(560)	60(300)	-305(225)
N(23)	648(171)	1171(307)	636(317)	-696(257)	-119(173)	-264(189)
C(33)	269(123)	899(338)	844(394)	145(294)	-110(161)	-128(152)
N(33)	1398(384)	796(265)	1072(511)	841(347)	-451(340)	-646(278)

Isotropic Thermal Parameters

	U		U
C(22)	498(79)	C(31)	347(52)
C(32)	320(55)	N(13)	590(80)

Table 9 Final Fractional Coordinates for $[Ph_3PHgI_2]_2$ (x 10^4) with Estimated Standard Deviations in Parentheses

	x	y	z
Hg1	6775(1)	1399(1)	8340(1)
Hg2	8118(1)	923(1)	6831(1)
I1	6949(1)	36(2)	9479(1)
I2	6766(1)	-187(2)	7162(1)
I3	8141(1)	2511(2)	7999(1)
I4	7928(1)	2166(2)	5641(1)
P1	6002(3)	3138(8)	8177(3)
C11	5204(13)	2975(36)	8698(13)
C12	4907(16)	2050(42)	8774(18)
C13	4307(16)	1887(51)	9184(20)
C14	4029(12)	2803(45)	9463(16)
C15	4347(16)	3951(41)	9400(15)
C16	4943(13)	4029(38)	9070(14)
C21	6466(13)	4491(35)	8392(15)
C22	6836(17)	4474(36)	9013(17)
C23	7145(22)	5395(64)	9264(26)
C24	7151(27)	6484(57)	8828(27)
C25	6741(27)	6493(62)	8106(29)
C26	6405(19)	5316(41)	8010(20)
C31	5712(11)	3213(30)	7302(12)
C32	5022(12)	3384(35)	7114(15)
C33	4825(17)	3439(31)	6414(17)
C34	5308(17)	3250(30)	5878(14)
C35	6033(15)	3227(28)	6043(14)
C36	6208(12)	3200(29)	6776(14)
P2	8949(3)	-749(8)	7026(4)
C41	9278(12)	-812(31)	7938(13)
C42	8826(16)	-672(36)	8416(16)
C43	9020(21)	-863(33)	918[illegible] (15)
C44	9738(24)	-1033(51)	9279(18)

C45	10196(21)	-1197(34)	8773(21)
C46	9968(13)	1016(35)	8028(17)
C51	9673(12)	-559(30)	6445(11)
C52	9974(16)	530(47)	6339(18)
C53	10505(19)	675(38)	5874(21)
C54	10821(18)	-317(43)	5588(17)
C55	10563(14)	-1457(45)	5668(14)
C56	9930(15)	-1573(43)	6058(19)
C61	8553(14)	-2130(30)	6834(13)
C62	8595(18)	-3050(40)	7240(18)
C63	8261(26)	-4251(55)	7115(29)
C64	7978(29)	-4247(63)	6475(28)
C65	7881(21)	-3545(78)	6038(26)
C66	8154(26)	-2254(38)	6196(18)

Final Hydrogen Positions (x 10^4)

	x	y	z
H12	5116	1286	8498
H13	4104	998	9279
H14	3539	2727	9728
H15	4112	4740	9627
H16	5227	4865	9075
H22	6814	3678	9335
H23	7436	5326	9748
H24	7440	7243	9027
H25	6679	7240	7750
H26	6073	5179	7559
H32	4636	3474	7517
H33	4288	3601	6281
H34	5130	3127	5346
H35	6421	3270	5640
H36	6747	3108	6925
H42	8306	-402	8275
H43	8647	-899	9604
H44	9938	-1022	9809
H45	10724	-1442	8896
H46	10325	-1061	7597
H52	9804	1289	6645
H53	10667	1563	5716
H54	11287	-205	5284
H55	10833	-2233	5469
H56	9643	-2406	6037
H62	8935	-2973	7690
H63	8241	-4921	7523
H64	7824	-5136	6308
H65	7590	-3691	5560
H66	8070	-1515	5839

Table 10 Final Thermal Parameters for $[Ph_3PHgI_2]_2$ with Estimated Standard Deviations in Parentheses

Anisotropic Thermal Parameters

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg1	457(6)	536(14)	652(6)	99(6)	17(5)	97(6)
Hg2	425(6)	604(15)	720(7)	47(6)	22(5)	102(6)
I1	764(13)	740(22)	543(9)	101(10)	3(9)	-16(13)
I2	478(9)	643(22)	672(10)	-116(10)	74(8)	-222(10)
I3	430(9)	542(22)	805(12)	-117(11)	59(8)	-122(10)
I4	549(11)	781(23)	685(11)	136(11)	108(8)	106(12)
P1	365(32)	422(75)	652(38)	41(38)	66(28)	70(35)
C11	324(138)	634(362)	610(149)	50(175)	-99(115)	92(171)
C12	485(176)	901(439)	1055(241)	-116(240)	170(164)	-211(218)
C13	456(174)	1872(550)	1447(327)	-719(343)	498(207)	-512(258)
C14	185(128)	1546(478)	819(195)	-43(241)	143(127)	-88(203)
C15	528(181)	1053(408)	782(188)	-316(210)	89(146)	000(221)
C16	304(128)	1069(385)	800(190)	7(205)	98(126)	63(172)
C21	334(130)	1083(358)	802(180)	553(206)	197(125)	134(169)
C22	863(229)	216(326)	950(227)	-342(195)	-213(177)	-108(207)
C23	797(276)	2611(796)	1162(357)	-111(456)	226(256)	808(382)
C31	333(117)	750(274)	528(132)	43(145)	-68(100)	-2(139)
C32	237(118)	1325(385)	856(188)	-44(206)	44(122)	164(172)
C33	766(207)	568(316)	947(214)	277(196)	-408(182)	0(199)
C34	971(229)	642(306)	507(141)	83(151)	-208(149)	380(210)
C35	731(185)	251(277)	721(169)	170(150)	-115(144)	-138(170)
C36	334(126)	792(309)	911(196)	356(188)	160(128)	346(156)
P2	306(30)	498(76)	639(37)	-80(39)	-2(27)	2(35)
C41	336(124)	707(299)	612(150)	50(160)	-7(110)	25(146)
C42	634(187)	1038(396)	866(206)	-464(215)	-6(163)	218(206)
C43	1267(316)	600(340)	593(171)	-244(177)	-160(185)	363(259)
C44	1277(373)	2129(619)	567(198)	-589(282)	-83(231)	-356(400)
C45	1050(278)	384(359)	1272(296)	123(243)	-739(249)	-140(236)
C46	298(127)	952(362)	1088(239)	246(222)	-26(144)	55(170)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C51	371(128)	351(303)	488(126)	-137(140)	27(101)	299(155)
C52	516(186)	1548(500)	930(232)	-200(265)	54(163)	-444(260)
C53	1039(297)	236(336)	1696(350)	-266(260)	833(265)	-26(222)
C54	708(219)	1051(471)	805(210)	-41(231)	261(172)	-234(259)
C55	338(143)	1394(476)	610(162)	-44(210)	-71(121)	39(211)
C56	381(152)	1337(459)	1251(279)	243(288)	6(174)	96(217)
C65	729(258)	3381(979)	1300(370)	-91(528)	-479(254)	364(421)
C66	2171(487)	326(344)	917(250)	-216(217)	-480(275)	-87(324)

Isotropic Thermal Parameters

	U
C24	1504(202)
C25	1564(209)
C26	892(105)
C61	584(71)
C62	937(110)
C63	1488(191)
C64	1501(205)

Table 11 Final Fractional and Thermal Parameters for $[\beta Pr_3PHgI_2]_2$ (x 10^4) with Estimated Standard Deviations in Parentheses

	x	y	z
Hg1	6109(2)	1511(2)	6051(1)
Hg2	2373(2)	2357(2)	5958(1)
I1	4608(4)	2804(3)	6798(2)
I2	3685(4)	946(3)	5281(2)
I3	764(4)	1423(3)	6601(2)
I4	1739(5)	3917(3)	5270(3)
P1	6478(15)	99(11)	6719(7)
P2	6946(15)	2768(11)	5454(7)
C11	7831(55)	-643(44)	6468(25)
C12	8187(76)	-1455(57)	6989(34)
C13	8949(108)	-2100(85)	6746(48)
C21	5102(50)	-709(37)	6617(23)
C22	4008(59)	-250(46)	6902(25)
C23	2949(75)	-1009(57)	6827(34)
C31	6630(56)	453(44)	7500(24)
C32	7979(49)	1024(39)	7633(24)
C33	8064(65)	1277(47)	8325(30)
C41	7320(77)	3895(62)	5881(35)
C42	8265(60)	3736(48)	6418(28)
C43	8680(111)	4712(92)	6665(47)
C51	8188(56)	2555(45)	5102(25)
C52	8327(53)	1539(41)	4958(25)
C53	9363(89)	1446(63)	4674(38)
C61	5464(83)	3108(72)	4799(39)
C62	5796(77)	3922(63)	4422(36)
C63	4677(85)	3885(65)	3853(40)

Anisotropic Thermal Parameters

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg1	84(2)	55(2)	85(2)	11(1)	17(1)	-1(1)
Hg2	81(2)	72(2)	97(2)	6(1)	14(2)	-5(1)
I1	80(3)	91(3)	100(3)	--6(2)	10(2)	-10(2)
I2	80(3)	74(2)	67(2)	-17(2)	6(2)	-7(2)
I3	94(3)	103(3)	112(4)	17(3)	38(3)	-4(3)
I4	140(4)	82(3)	171(5)	54(3)	26(4)	5(3)
P1	80(11)	67(10)	85(10)	18(8)	13(9)	-4(8)
P2	67(10)	72(11)	91(11)	18(9)	-1(9)	-1(8)

Isotropic Thermal Parameters

	U		U		U
C11	9(2)	C21	8(2)	C31	9(2)
C12	13(3)	C22	10(2)	C32	8(2)
C13	20(4)	C23	13(3)	C33	11(2)
C41	14(3)	C51	9(2)	C61	16(3)
C42	10(2)	C52	8(2)	C62	14(3)
C43	21(5)	C53	15(3)	C63	16(3)

Table 12 Final Fractional and Thermal Parameters for $[Pr_3PHgCl_2]_2$ with Estimated Standard Deviations in Parentheses

Final Positional Parameters (Hg x 10^5, other atoms x 10^4)

$[Pr_3PHgCl_2]_2$ with Estimated Standard Deviations in Parentheses

(i) Non-hydrogen atoms

	x	y	z
Hg	-7296(0)	37958(1)	-3011(0)
Cl1	-1593(3)	4242(5)	683(3)
Cl2	456(2)	4031(4)	1089(4)
P	-451(2)	2811(4)	-1680(3)
C11	508(8)	2987(16)	-1782(14)
C12	1055(10)	2399(22)	-1056(18)
C13	1810(10)	2499(31)	-1303(28)
C21	-992(9)	3408(17)	-2786(12)
C22	-1772(11)	3525(20)	-2786(17)
C23	-2223(20)	4065(27)	-3772(25)
C31	-642(13)	1228(14)	-1694(18)
C32	-1274(17)	882(22)	-1270(26)
C33	-1386(16)	-394(22)	-1209(23)

(ii) Hydrogen atoms

	x	y	z
H111	631	3919	-1739
H112	564	2656	-2493
H121	1063	2800	-348
H122	911	1478	-1027
H131	2207	2053	-749
H132	1959	3419	-1330
H133	1807	2096	-2009
H211	-933	2828	-3383
H212	-779	4273	-2903
H221	-1993	2661	-2681

	x	y	z
H222	-1846	4093	-2185
H231	-2798	4129	-3726
H232	-2165	3501	-4380
H233	-2012	4933	-3884
H311	-160	789	-1289
H312	-742	935	-2448
H321	-1197	1240	-537
H322	-1764	1258	-1714
H331	-1863	-562	-888
H332	-905	-789	-759
H333	-1472	-771	-1937

Anisotropic Thermal Parameters ($\mathring{A}^2 \times 10^4$ for Hg, Cl, P, $\times 10^3$ for carbon atoms)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	648(6)	524(5)	503(6)	-40(3)	163(4)	36(3)
Cl1	610(27)	730(29)	652(28)	38(24)	240(23)	71(22)
Cl2	580(25)	550(24)	640(27)	86(21)	31(21)	24(19)
P	488(23)	472(23)	529(25)	-80(20)	150(20)	13(19)
C11	37(8)	56(10)	78(12)	-6(9)	4(9)	3(8)
C12	58(12)	94(16)	104(17)	1(13)	22(12)	11(11)
C13	27(9)	144(25)	216(34)	-19(24)	20(14)	10(12)
C21	47(9)	86(12)	33(8)	-2(9)	5(7)	-15(9)
C22	56(11)	100(17)	79(14)	18(13)	6(10)	16(11)
C23	127(25)	119(24)	125(26)	33(20)	-1(20)	7(18)
C31	77(13)	47(10)	88(14)	-7(9)	31(11)	-7(9)
C32	120(22)	84(16)	172(30)	-19(18)	85(22)	-32(15)
C33	140(23)	66(14)	189(31)	-29(17)	101(23)	-16(15)

Table 13 Final Fractional and Thermal Parameters for $[Pr_3PHgBr_2]_2$

Final Fractional Coordinates (Hg x 10^5; other atoms x 10^4) for $[Pr_3PHgBr_2]_2$ with Estimated Standard Deviations in Parentheses

(i) Non-hydrogen atoms

	x	y	z
Hg	-16426(1)	52282(1)	38966(0)
Br1	-3155(2)	3161(2)	3827(2)
Br2	443(2)	3661(2)	4180(1)
P	-1812(4)	7871(4)	3463(3)
C11	-2632(15)	8877(16)	3984(10)
C12	-3943(17)	8287(22)	3752(13)
C13	-4623(19)	9126(25)	4191(16)
C21	-290(13)	8774(15)	3802(9)
C22	462(15)	8110(19)	3349(10)
C23	1661(16)	9002(23)	3580(12)
C31	-2684(14)	8132(16)	2283(9)
C32	-2838(17)	9830(19)	1987(11)
C33	-3613(15)	9966(20)	985(11)

(ii) Hydrogen Atoms

	x	y	z
H111	-2709	10060	3786
H112	-2079	8792	4696
H121	-3867	7102	3947
H122	-4498	8376	3040
H131	-5549	8631	3989
H132	-4720	10313	3998
H133	-4090	9039	4905
H211	250	8636	4511
H212	-439	9975	3643
H221	-109	8142	2638

	x	y	z
H222	703	6941	3561
H231	2176	8503	3248
H232	2239	8970	4290
H233	1427	10172	3367
H311	-3615	7644	2072
H312	-2195	7537	1962
H321	-1914	10322	2176
H322	-3312	10442	2313
H331	-3707	9966	985
H332	-4540	9480	793
H333	-3142	9359	656

Anisotropic Thermal Parameters (Å^2 x 10^4 for Hg, Br, P; x 10^3 for all carbon atoms) with Estimated Standard Deviations in Parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	828(5)	549(3)	603(4)	13(4)	284(4)	22(5)
Br1	1065(18)	720(11)	1537(21)	-71(13)	575(16)	-189(12)
Br2	850(14)	993(12)	501(11)	52(10)	311(10)	288(12)
P	546(29)	524(21)	574(27)	35(21)	231(24)	51(22)
C11	75(13)	62(9)	71(12)	18(9)	41(11)	8(10)
C12	79(15)	123(16)	149(19)	-11(14)	80(15)	13(14)
C13	123(18)	169(21)	240(28)	-26(20)	130(20)	-14(18)
C21	67(12)	60(9)	45(10)	23(8)	10(9)	14(9)
C22	66(13)	101(12)	78(13)	-5(10)	51(11)	-12(11)
C23	78(15)	140(18)	125(18)	-14(15)	52(14)	-15(14)
C31	64(12)	81(11)	61(11)	5(9)	24(10)	7(10)
C32	115(15)	96(13)	64(12)	29(11)	33(11)	31(13)
C33	92(15)	130(16)	90(16)	43(13)	23(12)	6(14)

Table 14 Final Fractional Parameters of $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ (Hg, Cd, I x 10^5; other atoms x 10^4) with Estimated Standard Deviations in Parentheses

Atom	x	y	z
Hg	38275(5)	15282(4)	89433(2)
Cd	75301(10)	23481(8)	90295(5)
I(1)	62807(9)	9624(7)	97105(4)
I(2)	53776(10)	28099(9)	81895(5)
I(3)	92599(11)	14569(9)	84250(5)
I(4)	82386(14)	39229(10)	97022(7)
P(1)	3529(4)	127(3)	8290(2)
P(2)	3068(4)	2818(3)	9533(2)
C(11)	2200(15)	-611(10)	8471(6)
C(12)	1882(19)	-1464(14)	8056(9)
C(13)	984(28)	-2118(19)	8222(11)
C(21)	3231(13)	474(11)	7518(6)
C(22)	2062(16)	1038(12)	7378(7)
C(23)	1756(19)	1291(14)	6693(8)
C(31)	4947(16)	-649(11)	8348(7)
C(32)	6017(15)	-271(12)	8069(7)
C(33)	7112(17)	-966(14)	8137(8)
C(41)	1672(15)	2490(14)	9884(8)
C(42)	1614(19)	1505(15)	10081(9)
C(43)	452(18)	1268(15)	10381(8)
C(51)	2699(24)	3916(14)	9113(9)
C(52)	1812(21)	3847(17)	8597(10)
C(53)	1048(26)	4787(18)	8272(11)
C(61)	4305(23)	3128(20)	10130(11)
C(62)	4196(29)	3820(23)	10513(14)
C(63)	5330(24)	3774(19)	11094(11)

Atom	x	y	z
H(111)	1381	-150	8454
H(112)	2417	-888	8921
H(121)	2741	-1864	8024
H(122)	1540	-1178	7620
H(131)	845	-2687	7891
H(132)	106	-1742	8250
H(133)	1306	-2428	8654
H(211)	3165	-175	7248
H(212)	4011	909	7405
H(221)	1289	621	7516
H(222)	2152	1708	7628
H(231)	893	1702	6627
H(232)	1652	630	6435
H(233)	2515	1716	6547
H(311)	4685	-1336	8139
H(312)	5248	-761	8819
H(321)	5735	-155	7597
H(322)	6308	409	8278
H(331)	7884	-664	7926
H(332)	6831	-1647	7926
H(333)	7403	-1083	8608
H(411)	861	2621	9563
H(412)	1629	2953	10270
H(421)	1632	1038	9696
H(422)	2430	1364	10397
H(431)	480	516	10516
H(432)	-376	1396	10070
H(433)	422	1723	10771
H(511)	3565	4188	8970
H(512)	2337	4433	9413

H(521)	2214	3384	8279
H(522)	976	3511	8733
H(531)	735	4626	7890
H(532)	2221	5137	8121
H(533)	983	5263	8574
H(611)	5124	3303	9908
H(612)	4484	2476	10392
H(621)	4256	4508	10287
H(622)	3292	3759	10681
H(631)	5202	4361	11400
H(632)	6239	3839	10931
H(633)	5275	3091	11325

Table 15 Final Thermal Parameters for $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$ with Standard Deviations in Parentheses

Anisotropic Thermal Parameters (C x 10^3, other atoms x 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	752(4)	601(4)	703(4)	-84(3)	256(3)	4(3)
Cd	643(6)	656(7)	770(7)	-15(6)	260(6)	41(5)
I(1)	712(6)	791(7)	636(6)	167(5)	156(5)	42(5)
I(2)	748(7)	989(8)	922(7)	438(6)	216(6)	18(6)
I(3)	851(7)	1048(9)	995(8)	-172(7)	426(6)	50(7)
I(4)	1308(12)	887(9)	1738(14)	-498(9)	410(10)	-19(8)
P(1)	744(26)	677(24)	624(23)	-109(20)	185(20)	21(21)
P(2)	764(26)	736(27)	858(28)	-181(23)	238(23)	45(23)
C(11)	101(12)	71(10)	77(10)	-18(8)	27(9)	-25(9)
C(12)	115(15)	113(15)	119(15)	-39(13)	34(13)	-38(13)
C(13)	318(36)	169(25)	178(24)	-77(20)	164(25)	-128(27)
C(21)	60(91)	93(11)	67(9)	-7(8)	17(7)	16(9)
C(22)	100(13)	77(11)	111(13)	20(10)	36(11)	5(10)
C(23)	129(16)	121(16)	102(14)	13(12)	22(12)	-5(13)
C(31)	110(13)	67(10)	73(10)	-21(8)	10(9)	19(10)
C(32)	86(11)	85(12)	82(11)	-13(9)	27(9)	9(10)
C(33)	103(14)	125(16)	124(15)	-17(13)	15(12)	26(14)
C(41)	75(11)	106(14)	134(15)	-12(13)	44(11)	15(10)
C(42)	119(16)	126(17)	109(14)	21(13)	61(12)	16(14)
C(43)	115(15)	159(20)	106(14)	49(14)	30(12)	3(14)
C(51)	181(23)	95(15)	122(17)	-13(13)	35(17)	48(16)
C(52)	132(19)	126(19)	147(21)	14(16)	12(16)	-7(16)
C(53)	227(31)	112(19)	220(28)	5(19)	-56(23)	72(20)
C(61)	98(15)	206(25)	196(22)	-114(20)	34(15)	-11(16)
C(62)	212(24)	210(25)	183(24)	-28(21)	46(19)	-31(20)
C(63)	165(23)	168(23)	174(21)	-23(17)	-9(18)	-78(20)

Table 16 Final Fractional and Thermal Parameters (x 10^4) for $[\alpha Pr_3PHgI_2]_n$ with Estimated Standard Deviations in Parentheses

Final Fractional Coordinates (Hg x 10^5, other atoms x 10^4)

	x	y	z
Hg	27729(4)	47693(2)	4650(2)
I1	4289(7)	6567(3)	392(3)
I2	573(6)	4308(4)	-1184(3)
P	3500(24)	3720(15)	1844(11)

Anisotropic Thermal Parameters ($Å^2$ x 10^4 for Hg, I; x 10^3 for P)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	1384(28)	1092(22)	941(19)	248(16)	37(17)	-308(20)
I1	1504(42)	963(30)	1077(31)	-156(23)	671(30)	-353(29)
I2	1061(34)	1267(38)	956(28)	-126(25)	92(24)	-147(29)
P	113(15)	122(15)	88(10)	7(10)	11(10)	27(12)

Table 17 Torsion Angles for the 2:1 Complex $[(NCCH_2CH_2)_3P]_2HgCl_2$

	Angle (°) with E.S.D's in Parenthesis	
	Dimer I	Dimer II
P1-C11-C12-C13	160.8(4.8)	178.4(1.3)
P1-C21-C22-C23	48.9(6.2)	176.9(3.2)
P1-C31-C32-C33	171.3(3.1)	85.7(10.9)
P2-C41-C42-C43	56.5(7.8)	158.3(3.3)
P2-C51-C52-C53	120.9(7.6)	173.9(5.1)
P2-C61-C62-C63	151.3(8.0)	178.7(2.4)

Table 18 Torsion angles for 1:1 $(R_3P)HgX_2$ complexes

(a) Pr_3PHgCl_2

	Angle (°) with E.S.D's in Parenthesis
Cl2-Hg1-P1-C11	25.8(0.7)
Cl2-Hg1-P1-C21	144.2(0.6)
Cl2-Hg1-P1-C31	96.3(0.8)
Cl2*-Hg1-P1-C11	65.2(0.6)
Cl2*-Hg1-P1-C21	53.3(0.6)
Cl2*-Hg1-P1-C31	172.8(0.8)
Cl1-Hg1-P1-C11	176.5(0.7)
Cl1-Hg1-P1-C21	65.1(0.7)
Cl1-Hg1-P1-C31	54.4(0.9)
Hg1-P1-C31-C32	0.7(24.1)
Hg1-P1-C21-C22	48.5(22.0)
Hg1-P1-C11-C12	69.4(1.6)
P1-C31-C32-C33	151.6(22.0)
P1-C21-C22-C23	179.5(1.7)
P1-C11-C12-C13	173.1(1.7)
C11-P1-C21-C22	170.6(1.4)
C11-P1-C31-C32	124.2(24.0)
C21-P1-C31-C32	122.2(24.0)

(b) Pr_3PHgBr_2

Br2-Hg1-P1-C11	143.4(0.6)
Br2-Hg1-P1-C21	24.2(0.6)
Br2-Hg1-P1-C31	97.5(0.6)
Br2*-Hg1-P1-C11	53.9(0.6)

	Angle (°) with E.S.D's in Parenthesis
Br2*-Hg1-P1-C21	65.3(0.5)
Br2*-Hg1-P1-C31	173.1(0.6)
Br1-Hg1-P1-C11	55.6(0.6)
Br1-Hg1-P1-C21	174.8(0.5)
Br1-Hg1-P1-C31	63.5(0.6)
Hg1-P1-C11-C12	59.0(1.3)
Hg1-P1-C -C22	65.0(1.2)
Hg1-P1-C31-C32	178.5(1.0)
P1-C11-C12-C13	179.8(1.4)
P1-C21-C22-C23	174.2(1.1)
P1-C31-C32-C33	178.5(1.2)
C11-P1-C21-C22	175.4(1.1)
C11-P1-C31-C32	58.9(1.3)
C21-P1-C31-C32	56.8(1.3)

(c) $\underline{Pr_3PHgI_2}$

I1-Hg1-P1-C11	167.1(1.5)
I1-Hg1-P1-C21	54.7(1.7)
I1-Hg1-P1-C31	36.8(2.6)
I2-Hg1-P1-C11	130.7(1.5)
I2-Hg1-P1-C21	7.5(1.7)
I2-Hg1-P1-C31	98.9(2.6)
P1-C11-C12-C13	170.8(5.6)
P1-C21-C22-C23	146.8(6.3)
P1-C31-C32-C33	178.3(4.4)
C11-P1-C21-C22	57.7(7.5)
C11-P1-C31-C32	35.1(3.9)

	Angle (°) with E.S.D's in Parenthesis
C21-P1-C31-C32	173.6(2.9)
Hg1-P1-C11-C12	170.4(4.6)
Hg1-P1-C21-C22	173.5(5.8)
Hg1-P1-C31-C32	79.9(2.7)
Hg1-P2-C41-C42	87.4(6.3)
Hg1-P2-C51-C52	27.7(6.7)
Hg1-P2-C61-C62	176.3(5.6)
P2-C41-C42-C43	163.5(8.1)
P2-C51-C52-C53	179.9(4.2)
P2-C61-C62-C63	167.1(5.6)

(d) $(NCCH_2CH_2)_3PHgCl_2$

P-C11-C12-C13	170.3(1.9)
P-C21-C22-C33	74.5(2.7)
P-C31-C32-C33	171.3(1.9)

A2. The Absorption Correction

Absorption corrections have been made for $[\beta\text{-Pr}_3\text{PHgI}_2]_2$ and $[(\text{NCCH}_2\text{CH}_2)_3\text{PHgCl}_2]_n$ using ABSCOR.[66] An outline of this method follows.

The intensity of the emergent X-ray beam may be reduced by the absorption of the X-rays by the crystal. The extent of the absorption is given by:

$$I = I_0 \exp(-\mu X) \qquad \underline{3}$$

Where I = measured intensity of emergent beam

I_0 = intensity of emergent beam at zero absorption

X = total path length of the X-ray through the crystal in cm

μ = linear absorption coefficient (cm^{-1}) and is given by

$$\mu = \frac{N}{V_c} \Sigma_{aj} (\mu_{aj}) \qquad \underline{4}$$

N = number of molecules per unit cell

V_c = volume of unit cell

μ_a = atomic absorption coefficient

j = the j^{th} atom

The transmission factor T is equal to I/I_0 and is obtained by integration over the volume of the crystal.

$$T = I/I_0 = \frac{1}{V} \int_V \exp[-\mu(X_1 + X_2)].dV \qquad \underline{5}$$

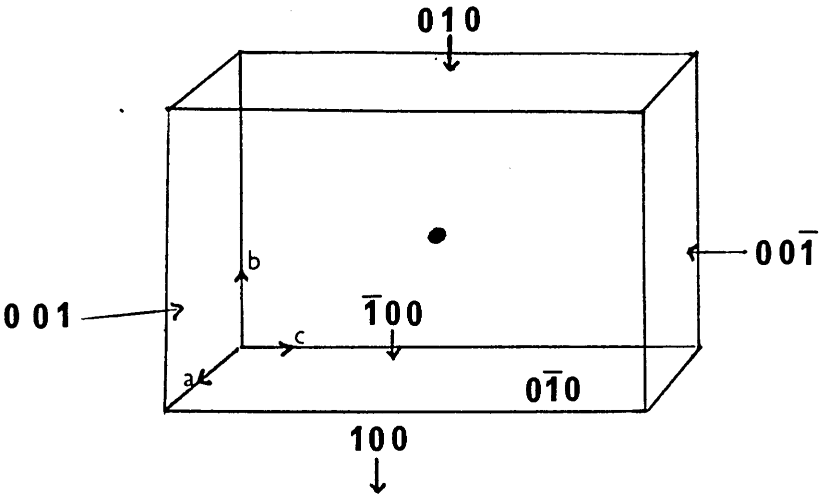
where X_1 = length of incident beam from point of entry to the element of volume dV.

X_2 = length of diffracted beam from the point of emergence from element dV, to the point of emergence from the crystal.

The crystal is considered as a convex polyhedron, for which every reflection may be divided into a number of tetrahedra. The absorption correction for one tetrahedron is calculated and the summation of the corrections for all tetrahedra gives the total absorption correction required by a particular reflection.

To enable an absorption correction to be made the crystal shape must be defined. The faces of the crystal are defined in terms of their Miller indices. A point of origin within the crystal is chosen and the perpendicular distances from all the faces to this origin are measured. Having defined the crystal shape the value of T in equation 5 may be calculated using the Abscor computer program which will also give corrected intensities for each reflection. For example, this is illustrated below in Fig. A1 for $[(NCCH_2CH_2P)_3HgCl_2]_n$.

Fig. A1 Schematic Diagram of the $[(NCCH_2CH_2P)_3HgCl_2]_n$ crystal



A3. Preparative Methods

(a) Preparation of Ph_3PHgI_2

Equimolar portions of ligand and mercury(II) halide were dissolved separately in minimal quantities of warm ethanol. The solution of ligand was added dropwise to the mercury(II) halide solution, the resulting precipitate being filtered off and recrystallised from DMF/H_2O mixture as white crystals and dried *in vacuo*.

(b) Preparation of Pr_3PHgX_2 (where X =Cl or Br)

These were similarly prepared by the action of an alcoholic solution of the ligand (1 mole) on the alcoholic mercury(II) halide solution.[24] The product was recrystallised from ethanol as white needle shaped crystals.

(c) Preparation of Pr_3PHgI_2 (α- and β-forms)

The reaction of alcoholic solutions of the ligand and mercury(II) iodide gave a pale yellow mass. Recrystallisation of the product from alcohol/acetone (4:1 by vol.) gave white needle shaped crystals of the α-form of the product. The β-form is deposited from the mother-liquor as yellow crystals. The α-form of the iodide may also be formed by the rapid recrystallisation of the β-form.

(d) Preparation of $[(NCCH_2CH_2)_3P]_nHgX_2$ (when X = Cl n = 1 and 2 when X =Br n = 2)

These complexes were prepared by mixing alcoholic solutions of the ligand and the appropriate mercury(II) halide in the required mole ratio. The resultant precipitate were recrystallised from acetone as white crystals and dried *in vacuo*.

(e) Preparation of $[(2\text{-thienyl})_3P]_2HgCl_2$

A hot solution of the phosphine ligand in ethanol (2.5 mol) was added to a hot solution of the mercury(II) chloride. The solution was allowed to cool and the resulting precipitate was filtered off, washed with ethanol and dried. The product was recrystallised from hot ethanol as colourless needles.

(f) Preparation of $(Pr_3P)_2Hg(\mu\text{-}I)_2CdI_2$

This complex was prepared by the treatment of hot ethanolic $(Pr_3P)_2CdI_2$ solution with 1 mole solution of hot mercury(II) iodide. On standing a white crystalline product was formed,[41] which was recrystallised from ethanol as fine colourless needles.

A4. Analytical Data

Compound	% C		% H	
	Calculated	Found	Calculated	Found
‡Ph_3PHgI_2	30.16	30.25	2.10	2.02
*Pr_3PHgCl_2	25.04	25.07	4.90	4.92
*Pr_3PHgBr_2	20.76	20.97	4.07	4.04
‡Pr_3PHgI_2 (α-form)	17.58	17.77	3.44	3.38
‡Pr_3PHgI_2 (β-form)	17.58	17.77	3.44	3.34
*$(NCCH_2CH_2)_3PHgCl_2$	23.40	23.30	2.60	2.55
*$[(NCCH_2CH_2)_3P]_2HgCl_2$	32.85	32.95	3.65	3.60
*$[(NCCH_2CH_2)_3P]_2HgBr_2Me_2CO$	31.33	31.36	3.76	3.73
*$[(2\text{-thienyl})_3P]_2HgCl_2$	34.65	34.65	2.15	2.10
‡$(Pr_3P)_2HgI_2CdI_2$	18.94	18.89	3.70	3.61

*Analysis carried out by Elemental Micro-Analysis Ltd., Devon.

‡Analysis carried out by The City University Chemistry Department, London.

Structure Factors for [(2-thienyl)$_3$P]$_2$HgCl$_2$

3	1	16	40	-19
4	1	16	50	49
-8	2	16	32	26
-6	2	16	24	28
-5	2	16	59	69
-3	2	16	71	96
-1	2	16	127	72
0	2	16	29	-32
1	2	16	37	12
3	2	16	36	-41
4	2	16	33	-16
-8	3	16	24	3
-7	3	16	60	-77
-6	3	16	36	-10
-5	3	16	50	-58
-3	3	16	37	2
-2	3	16	27	-21
-1	3	16	70	66
0	3	16	46	-10
1	3	16	75	91
2	3	16	33	4
3	3	16	72	67
-8	4	16	37	51
-6	4	16	36	54
-5	4	16	26	-49
-4	4	16	42	23
-3	4	16	77	-68
-2	4	16	62	-27
-1	4	16	74	-51
0	4	16	71	-63
1	4	16	26	-9
2	4	16	50	-62
3	4	16	22	29
4	4	16	29	-32
-7	5	16	19	11
-6	5	16	62	42
-4	5	16	83	89
-3	5	16	32	0
-2	5	16	101	91
-1	5	16	27	-10
0	5	16	49	44
2	5	16	30	-19
3	5	16	23	-10
4	5	16	47	-55
-7	6	16	12	-6
-6	6	16	64	-63
-5	6	16	34	-30
-4	6	16	37	-27
-3	6	16	50	-41
-1	6	16	26	-31
0	6	16	86	74
2	6	16	71	73
3	6	16	36	18
-7	7	16	75	62
-5	7	16	19	46
-4	7	16	49	-42
-3	7	16	21	-2
-2	7	16	52	-43
-1	7	16	65	-53
0	7	16	29	-21
1	7	16	65	-73
3	7	16	47	-54
-7	8	16	21	13
-5	8	16	43	63
-3	8	16	112	96
-2	8	16	20	3
-1	8	16	41	60
0	8	16	27	6
1	8	16	21	11
2	8	16	24	6
3	8	16	39	-11
-6	9	16	34	-23
-5	9	16	54	-13
-4	9	16	86	-49
-2	9	16	41	-50
-1	9	16	24	44
1	9	16	71	61
-6	10	16	77	67
-3	10	16	24	-24
-2	10	16	46	-29
-1	10	16	24	-19
0	10	16	51	-46
1	10	16	19	-3
2	10	16	57	-56
-5	11	16	40	-13
-4	11	16	79	67
-2	11	16	65	60
1	11	16	37	21
-3	12	16	52	-57
-2	12	16	20	17
-1	12	16	65	-42
-7	0	17	25	11
-3	0	17	95	96
-1	0	17	68	72
1	0	17	30	14
3	0	17	22	-38
-7	1	17	61	-61
-6	1	17	30	-22
-5	1	17	53	-47
-4	1	17	55	-48
-2	1	17	35	-50
-1	1	17	31	50
0	1	17	51	-25
1	1	17	52	70
2	1	17	18	8
3	1	17	40	52
-6	2	17	50	66
-5	2	17	17	-24
-4	2	17	48	30
-3	2	17	29	-34
-2	2	17	23	-30
-1	2	17	17	-26
0	2	17	50	-73
2	2	17	55	-73
-6	3	17	47	38
-5	3	17	32	-12
-4	3	17	57	42
-3	3	17	25	0
-2	3	17	75	85
-1	3	17	44	13
0	3	17	52	42
-6	4	17	32	-47
-5	4	17	66	-47
-3	4	17	79	-66
-2	4	17	19	21
-1	4	17	67	-51
0	4	17	40	52
2	4	17	33	52
3	4	17	36	27
-7	5	17	75	69
-6	5	17	23	-5
-5	5	17	57	53
-3	5	17	41	1
-1	5	17	85	-56
1	5	17	57	-79
3	5	17	34	-59
-6	6	17	44	-28
-5	6	17	33	54
-3	6	17	86	77
-1	6	17	52	59
0	6	17	26	31
2	6	17	23	32
3	6	17	26	-31
-6	7	17	39	-30
-5	7	17	19	-25
-4	7	17	53	-66
-2	7	17	80	-68
0	7	17	29	-35
1	7	17	44	38
-6	8	17	72	61
-3	8	17	23	6
-2	8	17	19	-27
0	8	17	64	-67
2	8	17	80	-68
-5	9	17	53	-29
-4	9	17	49	54
-2	9	17	36	57
-1	9	17	25	31
1	9	17	51	44
-5	10	17	70	-49
-4	10	17	22	-7
-3	10	17	77	-70
-1	10	17	45	-53
-3	11	17	25	1
-6	0	18	68	66
-4	0	18	18	31
0	0	18	69	-69
2	0	18	37	-71
-6	1	18	43	28
-5	1	18	29	-30
-4	1	18	60	63
-2	1	18	37	67
-1	1	18	21	29
0	1	18	35	35
1	1	18	35	43
2	1	18	17	-9
-5	2	18	62	-54
-3	2	18	47	-78
-1	2	18	31	-61
1	2	18	22	-14
-6	3	18	20	7
-5	3	18	49	51
-4	3	18	41	17
-3	3	18	19	3
-1	3	18	59	-50
0	3	18	22	9
1	3	18	60	-72
-5	4	18	29	38
-4	4	18	44	-22
-3	4	18	49	55
-2	4	18	27	19
-1	4	18	42	43
0	4	18	74	49
-5	5	18	18	-7
-4	5	18	64	-71
-3	5	18	18	0
-2	5	18	98	-75
0	5	18	19	-40
-5	6	18	29	23
-3	6	18	19	34
-2	6	18	36	-22
-1	6	18	29	26
0	6	18	64	-57
-4	7	18	56	34
-2	7	18	36	36
-1	7	18	39	40
-3	8	18	68	-72
0	8	18	13	-5
-5	0	19	60	-51
-1	0	19	46	-60
-5	1	19	26	41
-4	1	19	41	38
-2	1	19	19	41
-1	1	19	50	-37
0	1	19	20	22
-5	2	19	41	18
-3	2	19	19	27
-1	2	19	22	22
0	2	19	66	56
-4	3	19	65	-64
-2	3	19	50	-70
-1	3	19	24	-10
0	3	19	20	-38
-3	4	19	55	53
-2	4	19	39	-14
-1	4	19	39	42
0	6	19	24	-24

Structure Factors for $[(NCCH_2CH_2)_3P]_2HgCl_2$

[illegible]

0	1	0	300	342
5	1	0	72	-73
10	1	0	265	-257
14	1	0	155	155
16	1	0	77	-65
18	1	0	103	-97
-22	2	0	121	-123
-21	2	0	80	-71
-20	2	0	91	76
-19	2	0	63	-70
-18	2	0	116	120
-17	2	0	102	108
-16	2	0	231	-219
-13	2	0	62	-56
-12	2	0	230	250
-11	2	0	110	120
-10	2	0	336	-305
-7	2	0	80	-63
-6	2	0	351	340
-5	2	0	90	83
-4	2	0	390	-370
-2	2	0	137	-142
-1	2	0	136	-126
0	2	0	362	361
1	2	0	60	51
4	2	0	138	-109
5	2	0	159	-189
6	2	0	220	235
7	2	0	89	-83
8	2	0	100	-106
10	2	0	165	-150
-1	3	0	55	-60
0	3	0	50	-51
1	3	0	60	68
2	3	0	135	-170
4	3	0	409	455
5	3	0	139	-140
7	3	0	60	76
8	3	0	209	-210
9	3	0	82	75
10	3	0	100	109
12	3	0	53	20
14	3	0	137	-130
16	3	0	63	79
-19	4	0	69	61
-17	4	0	65	-67
-16	4	0	130	124
-14	4	0	60	-62
-13	4	0	71	70
-10	4	0	75	75
-9	4	0	73	-75
-8	4	0	67	59
-7	4	0	100	103
-6	4	0	240	-249
-4	4	0	151	160
-3	4	0	101	-132
-2	4	0	67	70
-1	4	0	86	91
0	4	0	240	-216
1	4	0	50	43
2	4	0	150	160
3	4	0	107	-108

-2	1	13	157	-144
1	1	13	57	-53
-20	2	13	94	-93
-19	2	13	65	-55
-17	2	13	64	75
-13	2	13	92	-84
-11	2	13	135	134
-10	2	13	106	110
-8	2	13	77	-86
-7	2	13	96	-96
-5	2	13	55	38
-4	2	13	152	154
-2	2	13	97	-103
-1	2	13	77	-82
1	2	13	88	81
2	2	13	53	57
3	2	13	75	-95
7	2	13	69	58
8	2	13	73	70
-22	3	13	59	-53
-18	3	13	90	94
-17	3	13	69	68
-16	3	13	77	-68
-15	3	13	109	-110
-13	3	13	60	52
-12	3	13	82	84
-9	3	13	133	-131
-8	3	13	95	-94
-7	3	13	72	72
-6	3	13	137	145
-3	3	13	78	-68
-2	3	13	90	-96
-1	3	13	55	36
0	3	13	93	102
3	3	13	116	-122
4	3	13	67	-59
9	3	13	62	-61
10	3	13	60	-58
-20	4	13	75	67
-16	4	13	93	-93
-14	4	13	77	83
-11	4	13	71	-70
-10	4	13	103	-110
-8	4	13	77	69
-7	4	13	74	68
-5	4	13	51	-41
-4	4	13	144	-151
1	4	13	56	-54
2	4	13	75	-78
3	4	13	57	-50
4	4	13	71	67
5	4	13	76	78
8	4	13	80	-81
-18	5	13	79	-71
-14	5	13	63	60
-12	5	13	106	-112
-9	5	13	90	84
-6	5	13	169	-131
-2	5	13	79	93
0	5	13	84	-92
3	5	13	92	84
6	5	13	63	-64
-11	6	13	75	58
-10	6	13	56	48
-8	6	13	61	-51
-4	6	13	50	86
1	6	13	49	59
2	6	13	67	57
-26	0	14	185	-107
-25	0	14	60	66
-24	0	14	96	91
-22	0	14	75	67
-21	0	14	55	-51
-20	0	14	155	-148
-19	0	14	61	66
-18	0	14	133	141
-17	0	14	63	-63
-16	0	14	68	74
-15	0	14	90	-102
-14	0	14	184	-185
-13	0	14	88	83
-11	0	14	154	146
-10	0	14	244	238
-9	0	14	235	-212
-8	0	14	284	-273
-7	0	14	143	139
-5	0	14	53	75
-4	0	14	240	233
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-2	0	14	169	-188
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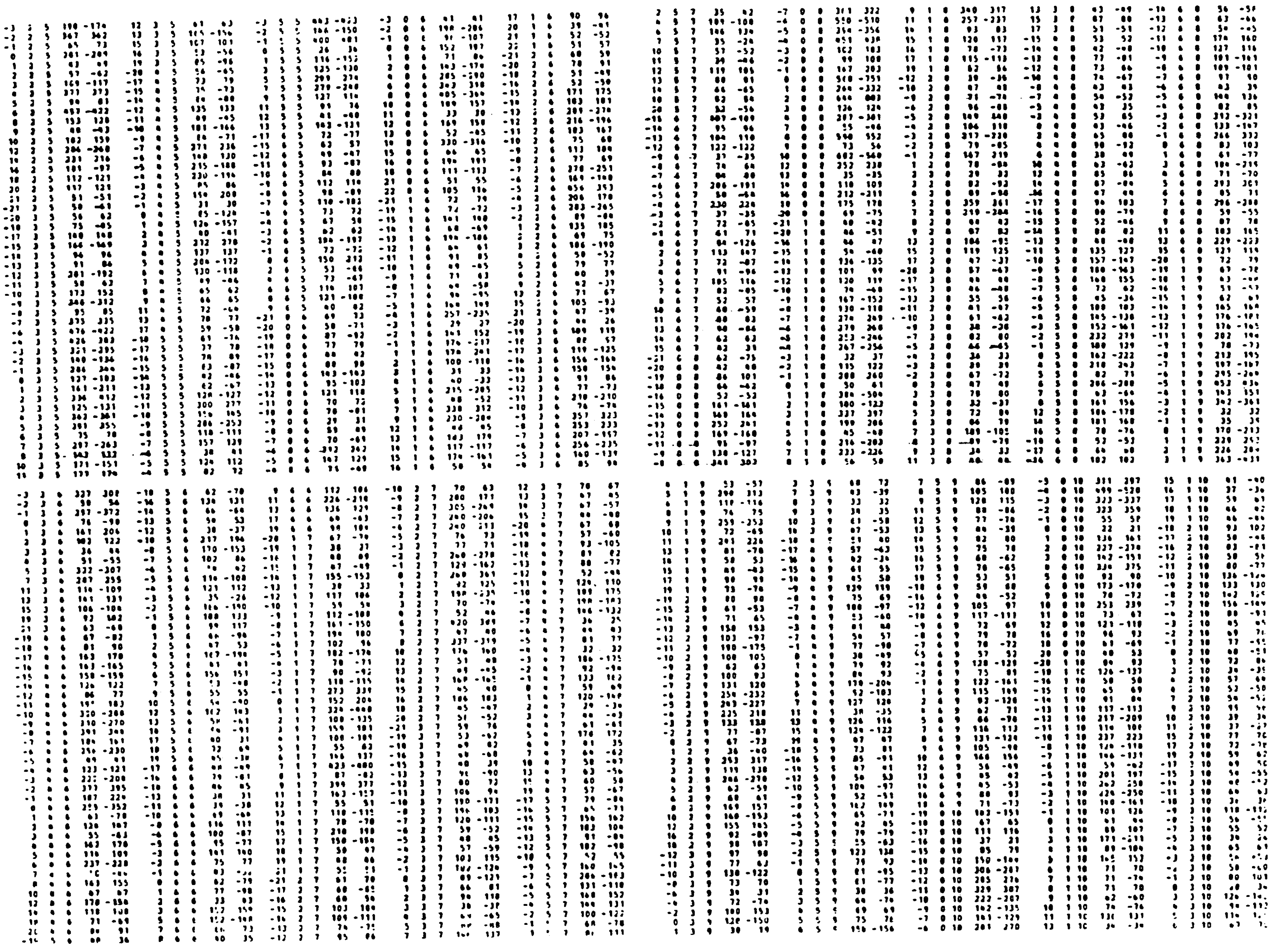

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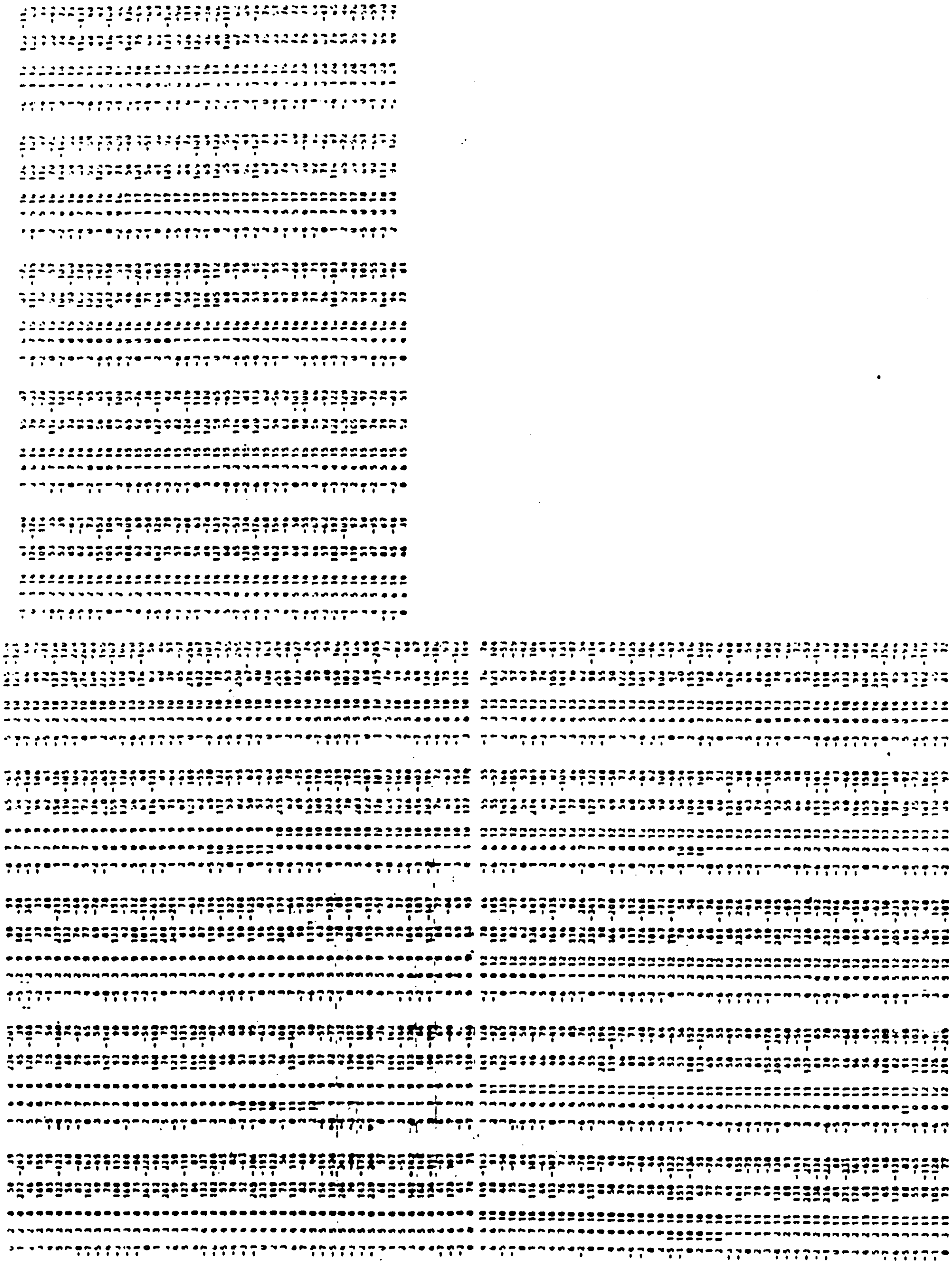

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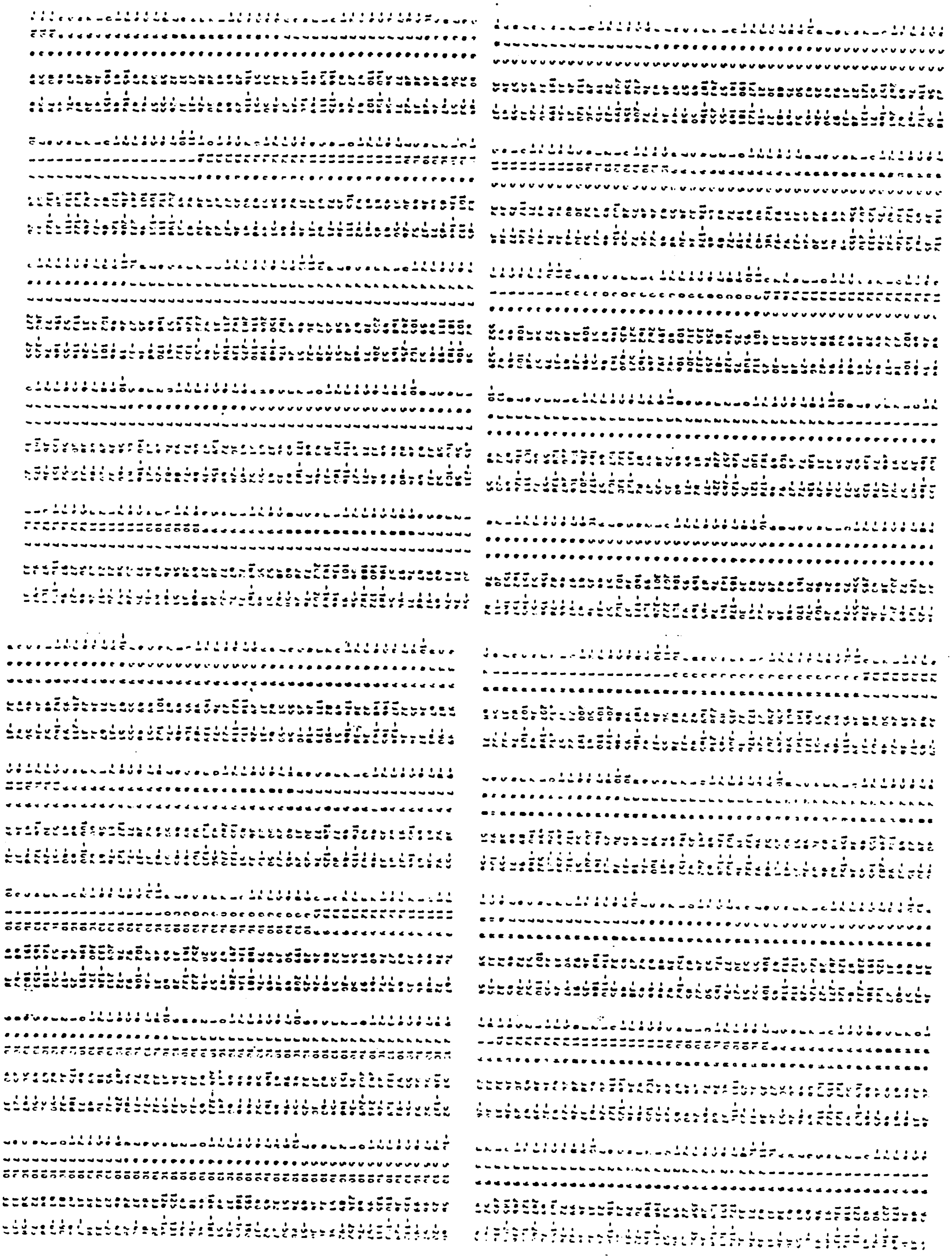

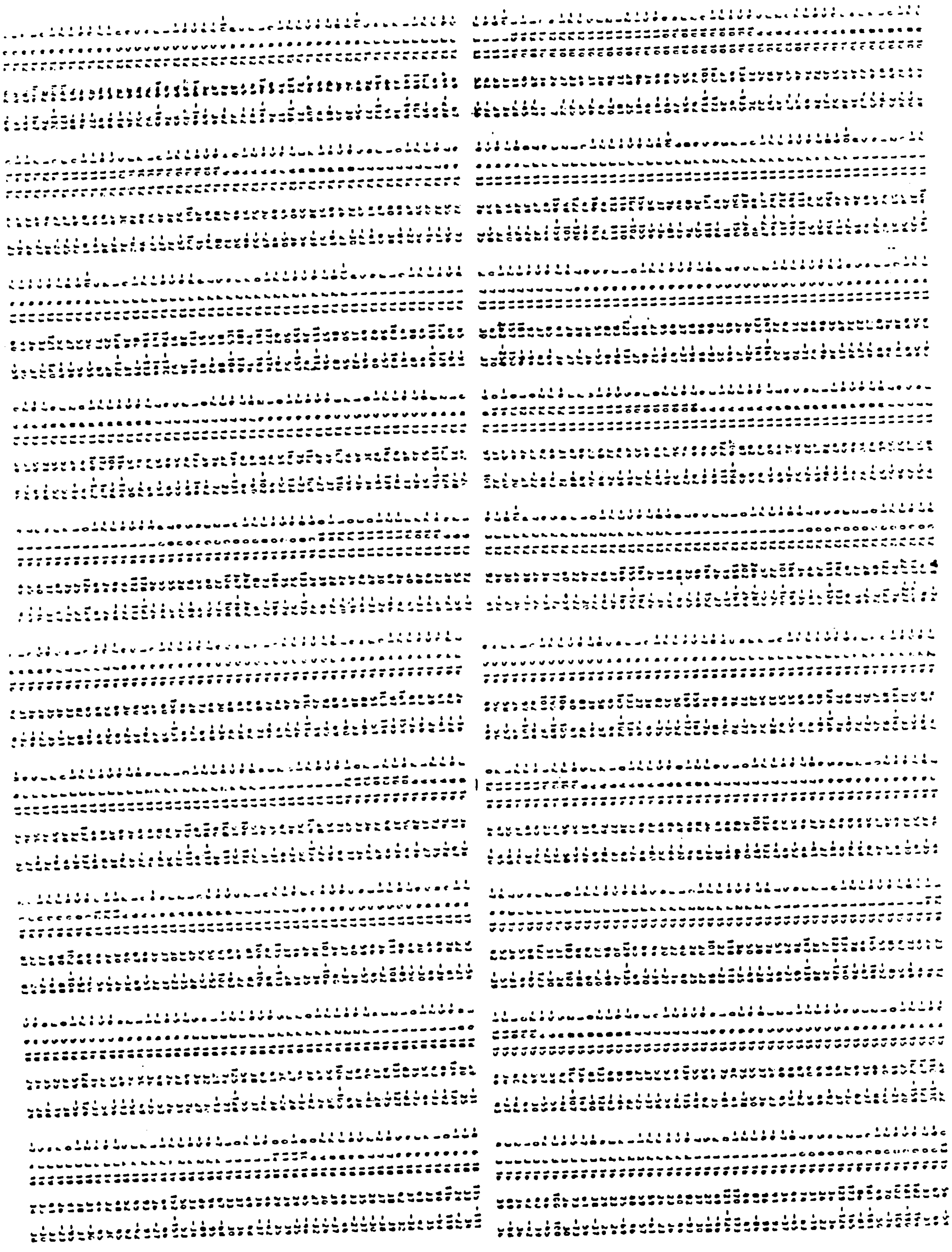

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