CHAPTER I

A SHORT REVIEW OF ORGANOMERCURY CHEMISTRY

IA. Introduction

Mercury was one of the first metals known to man. Aristotle mentioned mercury in his "Metereology" 320 BC and Theophrastus, 300 BC, spoke of liquid silver or quick silver as being obtained by rubbing cinnabar (HgS). Dioscorides stated in the first century that the metal was obtained by heating cinnabar with charcoal in an iron pot. In 1759 J.A. Brown demonstrated the metallic nature of mercury freezing it to a solid metal by cooling it with a mixture of snow and nitric acid.

According to the definition of organometallic compounds, organomercury compounds are substances which contain at least one Hg-C bond.

The known organomercury(II) compounds are of an enormous number and variety. They include the alkyls and aryls, the "salts" of the type RHgX and various polymercury compounds. Compounds having almost every kind of functional group in the organic part are known. In recent years a number of organomercury complexes have also been reported.

IB. Routes to organomercury compounds

Dialkyls and diaryls are conveniently prepared by the action of Grignard reagents on anhydrous metal halides. The alkyl and aryl mercury halides are obtained by a wide variety of routes. Generally the Grignard method is quite convenient.

$$RMgX + HgCl_2 \longrightarrow RHgX + MgCl_2$$

The reaction between mercury and methyl iodide in sunlight was discovered in 1853 by Frankland : it is still a very simple and effective way of making methyl mercury iodide.

The organomercury compounds may also be formed by the use of alkyl or aryl halides and sodium amalgam[1], diazo compounds, diazonium salts[2-4], decarboxylation reactions, mercuration of aromatic compounds and by the reaction between mercury halides (or acetates) and olefins or acetylenes.

IC. Organomercury(I) compounds

Organomercury(I) compounds are virtually unknown. Casanova et al claimed the preparation of di-n-hexyl-dimercury[5] by electrochemical reduction of 1,6-dibromohexane at a mercury cathode, but Avaca et al subsequently obtained polymeric Hg^{II} products from reactions of this type, and doubted whether Hg^{I} was present[6]. Butin et al have reported that RHgHgR species formed at a mercury surface during electrochemical reduction have short life time[7]. Blues, Bryce-Smith and Karimpour prepared organometallic ketenide derivatives of mercury(I), which they claim to be the first examples of stable organomercury(I) compounds[8].

II. Properties and structure of organomercury compounds

Although the chemistry of cadmium is essentially homologous to that of zinc, mercury is more different than similar to zinc and cadmium both in the properties of the element and in its compounds. Thus the organomercury compounds R_2Hg and RHgX are stable to air and water but the corresponding zinc and cadmium compounds are unstable to air and water. Some of the physical properties of organomercury compounds are summarised in Table I.

Table - I

Physical Properties of Organomercury Compounds
(From: Comprehensive Inorganic Chemistry, Vol.3,
edited by J.C.Bailar JR., H.J.Emeleus, R.Nyholm,
A.F.Trotman-Dickenson, Pergamon Press)

Compound	M.P. (°C)	B.P. (°C)	Density g cm^{-1}	R.I
$HgMe_2$	-	92.5	3.069	1.547
$HgEt_2$	-	159	2.466	1.548
$Hg^{n}Pr_2$	-	190	2.021	1.517
$Hg^{i}Pr_2$	-	65/10 mm	2.002	1.526
$Hg^{n}Bu_2$	-	105/7 mm	1.778	1.506
$Hg^{i}Bu_2$	Subl. > 100	206	1.768	1.497

Contd..

Table - I (Contd..)

Compound	M.P. (°C)	B.P. (°C)	Density g cm^{-1}	R.I.
Hg(n-pentyl)$_2$	-	133/10 mm	1.637	1.499
Hg(n-hexyl)$_2$	-	158/10 mm	1.536	1.497
Hg(Vinyl)$_2$	-	59.5/20 mm	-	-
HgPh$_2$	121.8 (Subl.)	204/10 mm	2.318	-
MeHgCl	170 (Subl. > 100)	-	4.063	-
EtHgCl	193 (Subl. > 40)	-	3.482	-
^{n}BuHgCl	130	-	-	-
PhHgCl	271	-	-	-

The RHgX compounds are crystalline solids whose properties depend on the nature of X. When X is an atom or group which can form covalent bonds to Hg, for example, Cl, Br, I, CN, SCN, OH, the compound is a covalent non polar substance more soluble in organic liquids than in water. When X is SO_4^{2-} or NO_3^-, the substance is salt like and presumably quite ionic, for instance, $[RHg]^+NO_3^-$. Acetates behave as weak electrolytes.

The equivalent conductivities of some methylmercury salts are shown in Table-2.

Table- 2

Equivalent Conductivity of Methylmercury Compounds ($Ohm^{-1} cm^{2}$)[9]

(0.1 N)

CH_3HgOH	CH_3HgOAc	$(CH_3Hg)_2SO_4$	CH_3HgNO_3
0.71	4.92	57.40	101.00

The dialkyls and diaryls are non polar, volatile, toxic liquids or low melting solids. All are thermally rather unstable and light sensitive, but can be kept for months without great loss.

Structural investigations of various kinds show that the organomercury compounds have a linear C-Hg-C or C-Hg-X skeleton; these include an electron diffraction study of $HgMe_2$[10], X-ray studies on $HgPh_2$[11-13], $Hg(p\text{-}Tolyl)_2$[14] and MeHgCN (also neutron diffraction)[15], and microwave spectra of MeHgX (X = Cl, Br)[16]. Vibrational spectra of MeHgX (X = Cl, Br, I, CN)[17,18] and rotation-vibration spectra of gaseous MeHgX and solid and gaseous deuterated analogues (Cl, Br, I)[19] are all consistent with a linear C-Hg-X skeleton. X-ray data for the phenylmercuric halides[20] and diphenyl mercury[11,21] also indicate the existence of linear CHgX and C-Hg-C skeletons and of a centre of symmetry in diphenyl mercury[13]. From an analysis of the vibrational spectra, both the phenylmercury halides and diphenylmercury can be considered as molecules with C_{2v} symmetry. The determination of the structure of diorthotolyl mercury by single crystal X-ray methods[22] shows that the crystal consists of individual molecular units with the mercury atom located on the crystallographic 2-fold axis of symmetry. The C-Hg-C fragment is nearly linear with an angle of 178.0(4°). The methyl groups lie on the same side of the molecule and the rings are twisted with respect to one another by 58.9°. The Hg-C bond distance is 2.09(1)Å. The structure of mercury(II) bis pentafluorophenyl has been determined by X-ray diffraction[23] and involves almost linear C-Hg-C bonds. These derivatives are appreciably better Lewis acids than the corresponding nonhalogenated species.

The IR spectrum and general reactivity of $Hg(C_5H_5)_2$ led to its formulation[24] as a σ bonded derivative; several studies of its NMR spectrum show that it is stereochemically non rigid[25] with rapid changes in the point of attachment of mercury to each ring. The C_5H_5 ring can simultaneously form part of a π -cyclopentadienyl system, as evidenced by the recent preparation[26] of $(C_5H_5FeC_5H_4)_2Hg$ and $[(CO)_3Mn(C_5H_4)]_2Hg$. On the basis of IR and NMR investigations, dicyclopentadienylmercury, cyclopentadienylmercury halides and cyclopentadienyl methyl mercury studied in situ were assumed to be sandwitch π -complexes[27].

Dipole moments of $Hg(aryl)_2$ derivatives in benzene and decaline are non-zero but small[28]; this may reflect the easy deformability of the $C\widehat{Hg}C$ angle. Vibrational spectra confirm that low-lying bending modes are easily excited[29]. The magnitude of the dipole moment of ethylmercury halides indicates that the Hg-halogen bond is partly electrovalent[30].

In the dialkyls of mercury, the mean bond dissociation energies, $\bar{D}(Hg-R)$ are of the order of 20-30 KCal/mole, implying that Hg-C is normally rather a weak bond, and that mercury alkyls should decompose on heating. Although this is the case, it has transpired that Hg-C bonds are more stable to heat than indicated by the $\bar{D}$ values[31].

The oxides and sulfides, $(RHg)_2O$ and $(RHg)_2S$ are monomeric, while alkoxides such as PhHgOMe appear to be cyclic trimer[32]. In the solid state $MeHgOSiMe_3$ is tetrameric with a cubane like structure but it becomes monomeric in solution[33].

IB. Complexes of organomercury compounds

In the last decade there has been increasing interest in the co-ordination chemistry of organomercury compounds. Of the alkylmercury compounds, methyl mercury(II) has received extensive investigation presumably for the following reasons:

Methylmercury(II) is regarded as one of the simplest Lewis acids as its co-ordination geometry is restricted almost entirely to linear geometry[34,35]. As essentially unifunctional cation it has been studied extensively as a prototype soft acid[35,36], as a model spectroscopic probe for binding of metal ions to complex molecules[37] and has also received attention owing to its role as a toxic species and its use in studies of polynucleotides[35,38] and proteins[35].

The survey of literature reveals that the ability of two-coordinate mercury to form complexes with bases is very dependent upon the nature of the groups attached to mercury. Thus while mercury(II) chloride is well known to form a wide range of adducts with both mono-dentate and bidentate ligands[39] no complexes have been isolated for mercury dialkyls. The relative electronegativities of mercury and the adjoining groups, together with the resulting influence upon the formal charge on mercury, appear to play an important role in complex formation. Thus the inability of mercury dialkyls to form stable complexes may be due to the similar electronegativities of alkyl groups and mercury (Ca.2.3 and 1.9 respectively)[40], and hence the resulting low formal charge on mercury. Replacement of alkyl by more electronegative groups would be expected to enhance stable complex formation. Certainly the presence of a halogen in the organomercury halides, RHgX, does appear to increase the acceptor character of mercury as will be evident from the survey that follows. Substitution in R_2Hg by electron withdrawing substituents in R should also increase the formal charge on mercury, thereby enhancing the formation of stable addition compounds. Thus, bis (trinitromethyl) mercury[41] and bis (fluoroalkyl) mercurials[42,43] form a wide range of isolable complexes, in contrast to the mercury dialkyls themselves. Similarly, while diphenylmercury gives rise to weak complexes of the type $Ph_2Hg.2L$ (L = phen, dmp, 2,4,7,9 — tetramethyl-1, 10-phenanthroline[44,45], bis (penta fluorophenyl) mercury addition complexes are more numerous and stable[46-49].

Organomercury complexes reported so far can be conveniently discussed under the following heads.

(a) Complexes of organomercury salts with neutral donor molecules.

Generally adducts of organomercury salts with neutral ligands may be isolated when the neutral molecule is coordinated more strongly to the mercury atom than the counter ion. Under the circumstances, the ligand replaces the anion which is forced out into the outer sphere of the complex.

Coates and his coworkers[50,51] have isolated and identified a great number of complexes of the type (RHgL)X, where R may be Me, Et, Pr or Bu; X = Cl, Br, I, ClO_4 or BF_4; L = Me_3P, Et_3P, Me_2PhP, Et_3As or Ph_3As, which slowly disproportionate. They also observed it earlier that the reaction between MeHgI and Et_3P in EtOH gave a crystalline complex which slowly transformed to give the final products.

$$2RHgX + 2Et_3P \longrightarrow (\text{Complex}) \longrightarrow R_2Hg + (Et_3P)_2HgX_2$$

The formation of organomercury co-ordination complexes as intermediates was also supported by the observation[52] that addition of $(C_6H_5)_3P$ increases the conductance of dilute solution of C_6H_5HgCl in dioxane-water to an extent consistent with the formation of a 1:1 complex. However, phenylmercuric chloride was the only mercury compound isolated from the reaction mixture.

When X = ClO_4, the complex did not undergo immediate dismutation. Thus methylmercury perchlorate gave isolable complexes not only with phosphines, but also with triethyl and triphenyl arsine and with pyridine. With aromatic organomercury derivatives, only the phenylmercury nitrate/triphenylphosphine complex was isolated. NMR studies have shown that only 1:1 adduct is formed when MeHgCl reacts with PMe_3[53].

A variety of nitrate and tetrafluoroborate salts of complex organomercury cations, $[\mathrm{Me_3P - HgCH_3}]^+$, $[\mathrm{Me_3As - HgCH_3}]^+$, $[\mathrm{Me_2S - HgCH_3}]^+$, $[\mathrm{Py{-}HgCH_3}]^+$ has been prepared and studied by Raman, IR and NMR spectroscopy[54].

In ~~the~~ contrast to the lack of success in isolating an adduct of phenylmercuric chloride with triphenylphosphine, bidentate ligands such as 1,10-phenanthroline (phen) or 3,4,7,8-tetramethyl-1, 10-phenanthroline (tmp) readily added a phenylmercuric chloride molecule to give crystalline complexes[55,56].

On the basis of IR data obtained for these complexes, the following structure has been suggested[55,56].

Conductivity and molecular weight measurements in acetone solutions of the complex PhHgCl.phen indicate that in this solvent the complex is completely dissociated. In boiling benzene, however, dissociation occurs[57]

$$\mathrm{2PhHgCl.phen} \longrightarrow \mathrm{phen.HgCl_2} + \mathrm{Ph_2Hg} + \mathrm{phen}\ .$$

However, no dissociation occurs for PhHgCl.tmp even after boiling for 8 hr. in benzene.

Complexes of RHgX are mostly ionic in nature having the structure $[RHgL]^{+}X^{-}$, (L = R_3P, R_3As). However, PhHg.L (L = phen & tmp) are apparently non ionic.

Organometallic compounds of mercury are soluble in pyridine and ethylenediamine, from which they are recovered unchanged[58]. Maynard and Howard observed that the conductivity of an aqueous solution of methylmercury acetate was increased by the addition of pyridine[59]. This suggests coordinate combination of the pyridine and the methylmercury group.

Chelate complexes of RHg^{+} cations (R = Me, Ph)[60,61] with 8-hydroxyquinoline have also been isolated and characterised.

Complex formation involving neutral ligands has been extensively studied by polarographic methods for phenylmercury cation in methylene chloride[62]. The effect of ligand concentrations on the half wave potentials of $PhHgClO_4$ solutions suggests the presence of 1:1 complexes. The method has been used to study complexation with tetrahydrothiophene, pyridine, hexamethyltriamidophosphate, tetramethylurea, dimethylsulfoxide, dimethylformamide, methanol, acetonitrile and tetrahydrofuran.

Complexes of CH_3Hg^{+} and $PhHg^{+}$ with a number of substituted quinolines, 2,2'-bipyridines and 1,10-phenanthrolines have also been investigated in water and in aqueous dioxane by pH and pHg methods[63]. Stability constants show that the phenylmercury complexes are more stable than the methylmercury species. Canty and Deacon[64] have synthesised the complex $[MeHg(2,2'\text{-bipy})]^+[NO_3]^-$, having a potentially bidentate ligand which was first reported by Coates and Lauder[50]. In view of the novelty of three-coordination in organomercury chemistry Canty et al[65] have studied complexes of this type by NMR spectroscopy and have also determined the crystal structure of the 2,2'-bipyridyl complex. They have also reported the isolation (eqn. 1) and preliminary study of a series of

$$MeHgNO_3 + L \rightarrow [MeHgL]NO_3 \qquad .. \quad (1)$$

complexes $[MeHgL][NO_3]$ (L = 2,2'-bipyridyl, 1,10-phenanthroline and related ligands) having three-coordinate mercury. The synthetic and spectroscopic studies of cationic complexes of methylmercury(II), $[MeHgL][NO_3]$ have also been reported by Canty & Marker[66]. The complexes $[MeHgL][NO_3]$ (L = pyridine; 2-methyl-, 3-methyl-, 4-methyl-, 2-benzyl-, 2,4-dimethyl-, and 2,6-dimethyl-pyridine; 2,2'-bipyridyl; 3,3'-dimethyl-, 4,4'- dimethyl-, 5,5'-dimethyl-, and 6,6'-dimethyl-2,2'-bipyridyl; 1,10-phenanthroline; 2,9-dimethyl-, 4,7-dimethyl-, and 5,6-dimethyl-1, 10-phenanthroline) are obtained from addition reactions in acetone. A complex of composition $MeHgNO_3 \cdot 2L$ is also formed with 3,3'-dimethyl-2,2'-bipyridyl. Evidence of coordination of ligands to the mercury atom has been obtained from the infrared studies. Proton magnetic resonance spectra indicate that the complexes of 2,2'-bipyridyls (except for those of 3,3'-dimethyl-2,2'-bipyridyl) and 1,10-phenanthrolines have three-coordinate mercury in solution.

Geier, Erni and Steiner[67] have investigated the interaction of methylmercuric hydroxide with 1,10-phenanthroline, as well as with 2,2'-bipyridine, terpyridine and pyridine-2-azo-4-dimethyl-aniline. They reported the formation of chelate complexes. Canty et al[68] reported the preparation of some new linear complexes of the formula $[MeHgL]NO_3$ (L = substituted pyridines, e.g., 2,3-dmpy; 3,4-dmpy; 3,5-dmpy; 2,4,6-tmpy; 2,3,6-tmpy; 5-Et,2-mpy; 3-Et,4-mpy). X-ray and ^1H NMR studies[69] of $[MeHgL]NO_3$ (L = 4,4',4"-triethyl-2,2':6',2"-terpyridyl and Di-2-pyridylmethane) show that Et_3-terpy acts as a tridentate ligand in the solid state but as a bidentate ligand in methanol, while Py_2CH_2 behaves as a bidentate ligand both in solution and in the solid state. The complexes were isolated as solids by the reaction of $MeHgNO_3$ with the appropriate ligand.

Raman studies[70] have shown the formation of CH_3HgPy^+ and $CH_3HgNH_3^+$ when $MeHgClO_4$ is dissolved in pyridine and liquid ammonia respectively. MeHgI also forms $[CH_3HgNH_3]^+$ in liquid ammonia, but when dissolved in pyridine, the neutral iodo complex is formed. Gardiner et al[71] observed that the Raman spectra for $[HgEt(Cl)]$, $[HgBr(Me)]$ and $[HgMe(I)]$ dissolved in liquid ammonia and liquid ND_3 were quite different to those reported earlier for solutions in weakly coordinating non-aqueous solvents. These authors have interpreted the Raman spectra of the chloro and bromo compounds in terms of the formation of $[HgR(NH_3)_3]^+$ cations. However, the iodo compounds appear to form different species as shown below:

$$[HgMe(I)] \xrightarrow{\text{liquid } NH_3} [HgMe(I)(NH_3)_2]$$

$$\rightleftharpoons [HgMe(NH_3)_3][I \text{ (solvated)}]$$

The simple amine complex $[CH_3HgNH_3]Cl$ was reported by Brodersen[72] and the related $[CH_3HgNH_3].ClO_4$ was prepared by Breitinger and Das[73]. The latter workers have collected infrared spectra for the crystalline perchlorate and fluoride and have carried out a normal coordinate analysis for CH_3HgNH_3[74].

It is suggested that the symmetrization reaction by ammonia goes through an intermediate formation of a complex of the organomercury salt, for example:

$$RHgX + NH_3 \overset{\text{Fast}}{\rightleftharpoons} RHgX.NH_3$$

$$2RHgX.NH_3 \xrightarrow{\text{Slow}} R_2Hg + HgX_2(NH_3)_2$$

Intermediate formation of a complex is supported by the preparation of complexes of organomercury salts with ammonia[75].

Thermochemical studies on the adduct formation between arylmercuric halides (Ar = C_6H_5, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, o-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-ClC_6H_4, o-ClC_6H_4, C_6Cl_5) and 4-methylpyridine, 1,10-phenanthroline, N,N,N',N' — tetramethylethylene diamine and tertiary phosphines in benzene solution have also been reported[76]. The nitrogenous bases are shown to form 1:1 adducts in solution and as expected, the bidentate ligands form much stronger complexes than 4-methylpyridine. In both cases, however, the enthalpies of formation are low indicating Hg-N bond to be rather weak. Evidence obtained indicated that tertiary phosphines cause symmetrization of arylmercuric halides.

Thermodynamic studies[77] of the reaction of a variety of alkylmercuric halides (Me, Benzyl, Et, Pr, Bu, cyclohexyl) with Py, 4-mpy, phen, N,N,N',N"-tetramethyl-1, 2-diaminoethane (tmed) and Bu_3P indicate that the potentially bidentate bases, bipy and phen, form much more stable adducts with alkylmercury(II) halides than the unidentate heterocyclic bases suggesting chelation in the former. The enthalpies are however, smaller with bipy or phen, showing that only weak Hg-N bonds are formed. This appears to be a common feature in organomercury complexes[42,76,78,79] and according to Gradon et al[77] this probably arises from misfitting of the small chelate angle with the preferred near linear stereochemistry of the mercury leading to poor orbital overlap in these cases. PBu_3 forms dimeric adducts, $(RHgX.PBu_3)_2$ of higher stability.

n-Butylmercuric nitrate in benzene solution forms 1:1 adducts of type $n\text{-}C_4H_9HgL(NO_2)$ with pyridine, 4-methylpyridine, 2,2'-bipyridine, triethylamine, tri-n-butylamine, tri-n-butylphosphine, triphenylphosphine and diphos[80]. The stabilities and the enthalpies of formation have been determined. A 4-coordinate adduct is formed with tetramethyl ethylene diamine. On the other hand, in water, acetone and acetonitrile, these ligands form complexes of type $n\text{-}C_4H_9HgL^+NO_2^-$. Distribution of $n\text{-}C_4H_9HgNO_3$ between benzene and water as a function of added ligand have also been studied[80].

Complexes of unsymmetrical fluorinated organomercurials, $R_FHgX.L$ (where L is a neutral bidentate ligand) are difficult to study since they are apt to readily disproportionation. Canty and Deacon[55,81], however, have succeeded in isolating a number of complexes of the type $C_6F_5HgX.L$ (where X is Cl, Br; L is

2,2'-bipyridyl, 1,10-phenanthroline, 2-9-dimethyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline). IR data suggest that these complexes are four coordinate and tetrahedral. Nevertheless, conductivity and molecular weight measurements have shown that even the most stable of these complexes is dissociated in acetone solution. For the unsymmetrical compound C_6Cl_5HgCl, complexes with 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 2,4,7,8-tetramethyl-1,10-phenanthroline have been isolated[55]. The $C_6Cl_5HgX.L$ complexes obtained, unlike the analogous $C_6F_5HgX.L$ complexes, disproportionate much less readily.

The perchloro compounds, $(Cl_3C)_2Hg$ and Cl_3CHgBr, have been reported to form 1:1 adducts with bipy and pyridine respectively[82,83] and ^{35}Cl NQR spectra suggest that they form stable solvates when dissolved in ethers[84]. Trifluoromethylmercury compounds, CF_3HgX ($X = Cl$, I, O_2CCF_3) also form weak 1:1 and 1:2 complexes with donor solvents such as acetone, pyridine, DMF and DMSO, THF (1:2 stoichiometry in DMSO, DMF, THF and acetone, A 1:1 and 1:2 mixture in pyridine)[85].

Gradon et al[77] have investigated calorimetrically the reactions of trichloromethylmercurials, CCl_3HgCl and $(CCl_3)_2Hg$, with a wider range of bases (pyridine, 4-mpy, 2-mpy, bipy, phen, $BuNH_2$, Et_2NH, pip, tmed, Py-NO, C_4H_8S) in benzene solution.

It has been found that the perchlorocompound CCl_3HgCl forms stable adducts (compared to those formed by alkyl mercury halides) with N-bases and also with tetrahydrothiophene and pyridine N-oxide but is symmetrised by phosphines.

Methyl mercury(II) chloride is the extremely toxic form of the heavy metal which has caused numerous deaths and many cases of brain damage[86]. Recent work has reemphasised the inherent biological dangers in mercury pollution to human, animal, and plant life in view of the apparent ease of conversion of inorganic mercury to CH_3HgCl by biological methylation processes involving, for example, methyl group transfer from methyl corrinoids[87,88], present in microorganism. In order to understand and combat the inhibitory effects of MeHg, a number of workers have undertaken the investigation of complexes of $MeHg^+$ with proteins and enzymes.

Simpson[89] has determined association constants of methylmercuric ion with nucleosides. Methylmercury(II) also forms a 1:1 complexes with glutathione[90].

Proton NMR spectroscopy was used to determine formation constants of complexes of CH_3Hg^+ with a series of amines and aminoacids in aqueous solution[91]. The complexes with amines are formed only at intermediate pH since at low pH the amine is protonated and at high pH the complex dissociates to form MeHgOH. With aminoacids, the site of CH_3Hg^+ complexation is found to be pH dependent. At low pH CH_3Hg^+ binds to the carboxylate group, at higher pH, to the amino group. For example, the coordination of methylmercury(II) ion with 3-phenylalanine $[PhCH_2CH(NH_2)CO_2H]$ shows a pH dependent equilibrium (eqn. 2) between two complexes in which the ligand is bonded through either its amino or its carboxylate group

$$H^+ + [HgMe\{H_2NCH(CO_2)CH_2Ph\}] \rightleftharpoons [HgMe\{O_2CCH(NH_3)CH_2Ph\}]^+ \qquad \ldots (2)$$

As expected, the equilibrium lies to the left-hand side at high pH, and the concentration of the carboxylate-bound species increases as the pH is decreased. Equilibrium analogous to (2) have also been observed in the complexes with tyrosine [3-(p-hydroxyphenyl)-alanine, L-dopa [3-(3,4-dihydroxyphenyl) alanine][92] and with 2-amino-4-phenylbutanoic acid[93].

X-ray crystal structures of methyl-L-cysteinatomercury(II) and methyl-DL-methioninemercury(II) have been determined[94]. It was found that the CH_3Hg moiety is bound via a deprotonated sulfhydryl group in the former and via an amino group in the latter. The L-cysteine complex $MeHgSCH_2CH(\overset{+}{N}H_3)CO_2$, H_2O was obtained from the reaction of MeHgOH with L-cysteine in aqueous ethanol[94,95].

The toxic pollutant methylmercury chloride forms 1:1 and 2:1 complexes with the sulfur aminoacid DL-penicillamine[96]. The mode of binding of the methylmercury by pencillamine has been established by a three-dimensional X-ray study of $[CH_3Hg]_2(SC(CH_3)_2CHNH_2COO)$. Organomercury complexes of penicillamine and some other sulfur containing ligands were further investigated by Sugiura et al[97]. They have studied the complex formation of phenylmercury and methylmercury with penicillamine and sulfur-or nitrogen-coordinating ligands by means of preparative, infrared and proton magnetic resonance and potentiometric titration. Penicillamine and phenylmercury reacted to form 1:1 dimer complex containing bridging S atoms. The formation of 2:1 complexes was observed in penicillamine, cysteine, glutathione and 2,3-dimercapto-1-propanol.

The binding of MeHg(II) with tryptophan, tryptamine and benzimidazole and their formation constants have been determined by Anderson et al[98]. Peringer Paul[99] reported the preparation of N-phenylmercuriadenine by treating PhHgOH or PhHgOAc with adenine in water at room temperature.

Organomercury(II) salts are found to react with dithizone (diphenylthiocarbazone, 3-mercapto-1,5-diphenylformazan, HDz) to give intensely colored 1:1 complexes of the general formula RHgDz, where R = Me, Et, $PhCH_2$, Ph, p-Me.C_6H_4, p-Cl.C_6H_4 or p-Br.C_6H_4[100]. The complexes may be extracted quantitatively into an organic phase. Other workers[101,102] also found that organomercury(II) salts react with dithizone.

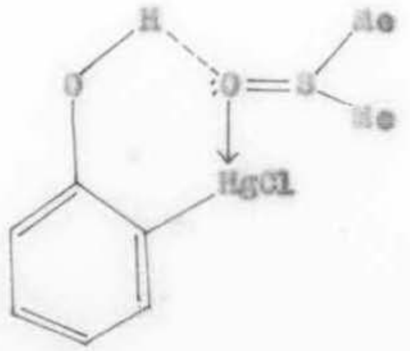
Irving and Kiwan[103] carried out a detailed investigation of the reactions of a number of organomercury compounds with dithizone. Kiwan and Fouda[104] reported that cyclohexyl-, and a variety of (2-alkoxy cycloalkyl) mercury ions, $ROC_nH_{2n-2}Hg^+$, form with dithizone yellow 1:1 complexes of the type $ROC_nH_{2n-2}HgHDz$ which can be extracted quantitatively into CCl_4 over a wide range of pH. At low pH and in the presence of excess of dithizone, cleavage of the C-Hg bond occurs resulting in anomalous pH extraction curves. In alkaline media and in the presence of excess of organomercurial, dithizone yields a series of secondary dithizonates which are less soluble in solvents than the corresponding primary complexes.

Toropova and Saikina reported the formation of thiourea complexes[105]. Organomercury selenocyanates have been prepared from diphenylmercury[106].

A crystalline complex is formed when trans-$ClCH = CHHgCl$ is treated with hexamethylphosphoramide in petroleum ether. This 1:1 adduct, trans-$ClCH = CHHgCl.OP(NMe_2)$ dissociated in solution (DMSO, dioxane, excess HMPA)[107]. Morell and Breitinger reported that methylmercuric cyanide can also function as ligand[108].

$$2MeHgBr + AgCN + AgNO_3 \xrightarrow{Et_2O} [MeHgC \equiv N \rightarrow HgMe]^+ NO_3^-$$

An IR study of o- and p- chloromercuriphenols in donor solvents (DMSO, HMPT) indicates the formation of complexes of the following type[109].



Organomercury(II) complexes of thiols and dithiols have also been reported[110].

Canty et al[111] reported the synthesis, spectroscopic and X-ray studies of methylmercury-selenourea complexes. Selennium bound selenourea complexes of methylmercury $[MeHgSeC(NH_2)_2]X$ (X = Cl, Br, NO_3, ClO_4) were prepared from MeHgX and $(H_2N)_2CSe$.

b. Complexes of organomercury compounds of the type $R_2Hg.L$.

The fact that the electronegativities of alkyl groups and mercury have similar values (Ca. 2.3 and 1.9 respectively on the Pauling Scale)[40] prevents the formation of strong coordinative mercury-ligand bonds. Consequently complexes of dialkylmercury compounds have not been isolated, contrasting sharply with mercury(II) halide systems, for which many complexes have been obtained[39]. For diphenylmercury, because the electronegativity of the phenyl group is greater (3.0)[40], complexes of the type $Ph_2Hg.2L$ (L = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 2,4,7,9-tetramethyl-1,10-phenanthroline) have been reported[44,45]. Even these are very weak complexes dissociating completely in benzene or chloroform solution. The solid state IR and UV spectra does not provide any evidence of covalent Hg-N bond formation in these systems. An X-ray diffraction study of the diphenylmercury complexes formed by the methyl substituted phenanthroline ligands did not unambiguously define the role of the phenanthroline ligands because of disorder problems, but is believed that interaction is only weak[112]. Calorimetric studies[113] indicated the formation of $Ph_2Hg.C_5H_5N$ in CCl_4 solution. Unsuccessful attempt to prepare complexes between diphenylmercury and 2,2'-bipyridine[46] or ethylenediamine[56] have been reported. Lagowski and coworkers[114] using oscillometric titration techniques, have found that diphenylmercury forms very weak 1:1 and 1:2 adducts with neutral donors, such as pyridine, piperidine, triphenylphosphine, triphenylarsine, pyridine N-oxide, dimethylsulfoxide in benzene solution. Another report, however, contradicts the formation of any complex by diphenylmercury with triphenylphosphine[56]. PMR data suggest that solvation of dimethylmercury and dibenzylmercury by polar solvents may involve a weak donor-acceptor interaction[115]. Dialkynylmercury compounds, $(RC \equiv C)_2Hg$, ($R = CH_3$, $ClCH_2$, $BrCH_2$, C_6H_5) also form isolable complexes with both phen and dmp[116,117].

Diorganomercurials, R_2Hg, in which the organic group contains electron withdrawing substituents are capable of forming complexes with a variety of ligands because the electron withdrawing substituents in R increases the formal charge on mercury. For example, the bis(phenylethynyl) mercury complex with 1,10-phenanthroline may be isolated[118] while stable 1:1 phenanthroline complexes are also formed with carborane mercury derivatives[119].

A number of complexes containing neutral ligands have been synthesised for bis(trinitromethyl) mercury i.e., $[(NO_2)_3C]_2Hg \cdot L$, where L is THF, dioxane, tetrahydrothiophene, Me_2SO_4, tetrahydrothiophene sulfone, 3-methylpyridine N-oxide, Me_2NO, $Me_2C{:}NOH$[41].

Because of the high electronegativity of the perfluorinated groups, the perfluorinated organomercurials show much greater tendency towards complexation and have therefore been studied most extensively.

Emeleus and Lagowski[120] showed by conductometric titration of the system $(CF_3)_2Hg$-KX ($X = Cl$, Br, I) that bis(trifluoromethyl) mercury forms complex ions with halide ions.

Oscillometric titration in benzene[114] have demonstrated the formation of complexes of types $(R_F)_2HgL$ and $(R_F)_2HgL_2$, where R_F = CF_3, C_2F_5, $(CF_3)_2CF$, CF_3CFH, CF_3CH_2 and L = $C_5H_{11}N$, C_5H_5N, C_5H_5NO, $(C_6H_5)_3P$, $(CH_3)_2CO$, $(CH_3)_2SO$, C_2H_5OH and $(CH_3)_2S$.

IR data suggest that $(R_F)_2Hg$ compounds [where R_F = CF_3, $(CF_3)_2CF$, C_2F_5, CF_3CHF, CF_3CH_2] form complexes with pyridine N-oxide, tetramethylene sulfoxide, piperidine and ethylenediamine in CCl_4[43].

Bis(pentafluorophenyl) mercury reacts with bipyridyl and with 1,2-bis(diphenylphosphinoethane) to form the complexes, $(C_6F_5)_2Hg$ (bipy) and $(C_6F_5)_2Hg$ (diphos) with melting points of 122°C and 158°C respectively[46]. Complexes of bis(tetrafluoro-4-pyridyl)- and bis(tetrafluoro-2-pyridyl)mercury with 2,2'-bipyridyl have also been isolated.

Canty et al[64] reported the formation of a number of complexes of the type $(C_6F_5)_2Hg.L$, where L = 4,4'-Me_2-2,2'-bipyridyl, 2,2'-biquinolyl, 2,2' : 6,2''-terpyridyl, 2,4,7,9-Me_4-1,10-phenanthroline, ethylenediamine, o-phenylenediamine, diphenylamine, pyridine, 4-cyanopyridine, triphenylphosphine and its oxide, 1,2-bisdiphenylarsinoethane. They have also reported the complexes of the types $(C_6F_5)_2Hg.2L$ (where L = di-2-pyridylamine) and $[(C_6F_5)_2Hg]_2L$, where L = bisdiphenylphosphinomethane and bisdiphenylarsinomethane.

Thermodynamic studies[121] also revealed the formation in benzene solution of 1:1 adducts of $Hg(C_6F_5)_2$ with pyridine, 4-methylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, 1,2-diaminoethane, N,N'-tetramethyl-1,2-diaminoethane, -propane and -butane. The diamines probably all behave as bidentates, but in the pyridine adducts the Hg-N bonds are usually weak, 1,10-phenanthroline adduct is highly stable in which the ligand is believed to be bidentate. However, no evidence for complex formation in solution between bis(pentafluorophenyl)mercury and tri-*n*-butyl-amine, tri-*n*-butylphosphine, $Ph_2PCH_2CH_2PPh_2$ or tetrahydrofuran or between diphenylmercury and 1,10-phenanthroline could be obtained.

Crystalline 1:1 complexes of $Hg[CF(NO_2)_2]_2$ with 1:2-dimethoxyethane, diglyme and sulfolane and 1:2 complexes with $(Me_2N)_3PO$, 1,4-dioxane and DMSO have been reported[122]. IR spectra indicated these to be covalent adducts. Complexes of the same organomercury compound with pyridine, Et_3N and TMED were found to be unstable. Liquid, water-insoluble products were formed when $Hg[CF(NO_2)_2]_2$ was treated with THF, MeCN, $Me_2NCONMe_2$, DMF and 2-methyl-pyridine.

Use of NMR techniques showed that weak 1:1 and 1:2 complexes are formed when $(PhCH_2)_2Hg$ and $PhCH_2HgCF_3$ are dissolved in donor solvents such as acetone, pyridine, DMF and DMSO[123,124]. ^{19}F NMR studies of carbon tetrachloride solutions of polyfluoroalkylmercurials [$(CF_3)_2Hg$, $(C_2F_5)_2Hg$, $[(CF_3)_2CF]_2Hg$, $(CF_3CH_2)_2Hg$] containing Lewis bases (pyridine, butylamine, ethylenediamine, THF, DMF, dioxane) demonstrated the presence of 1:2 R_2Hg/Lewis base solvates (or 1:1 if the Lewis base was bidentate)[125]. Similarly ^{31}P NMR spectroscopy served to show that such polyfluoroalkylmercurials coordinate two tertiary phosphine molecules (or one bidentate diphosphine) in dichloromethane solution[126].

Bis(pentachlorophenyl)mercury, in contrast to its fluorinated analogue, gives no complexes with 2,2'-bipyridyl and 1,10-phenanthroline. Only a very unstable complex with 3,4,7,8-tetramethyl-1,10-phenanthroline has been reported[127]. Bell et al[128] have reported five complexes of bis(trichlorovinyl)mercury.

Esquirol et al[129] have reported 1:1 adducts of 1, 10-phenanthroline with $PhHgC \equiv CH$, $PhHgC \equiv CMe$, $Hg(C \equiv CMe)_2$, $PhHgC \equiv CCH_2Cl$, $Hg(C \equiv CCH_2Cl)_2$, $PhHgC \equiv CPh$ and $Hg(C \equiv CPh)_2$.

Bell et al[130] have isolated four complexes, $(C_4H_3X)_2HgL$ (X = O, L = 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline; X = O, S, L = 2,9-dimethyl-1,10-phenanthroline). They claimed these to be the first reported examples of complexes formed by heterocyclic organomercury compounds.

As a Lewis acid $Hg(CN)_2$, which has a simple molecular structure with linear, $N \equiv C-Hg-C \equiv N$ molecules[131], is comparable to $Hg(CCl_3)_2$ and reacts with a variety of Lewis bases giving addition compounds in which the coordination number of the mercury is increased.

Adducts with O-donors (dioxan, hexamethylphosphoramide, dimethylsulfoxide) are generally of low stability[132-134].

N-donors form much more stable addition compounds. Simple aliphatic amines form 2:1 adducts in the homologous series $(RNH_2)_2Hg(CN)_2$[135] and the piperidine adduct $(pip)_2Hg(CN)_2$[136]. Bases with two nitrogen atoms, however, form only 1:1 adducts and are presumably chelate, giving the mercury a coordination number of four[134,137]. Heterocyclic bases also form stable addition compounds. These include $Hg(CN)_2$(3-cyanopyridine)$_2$, which is completely dissociated in THF[134] and several 1:1 adducts with quinoline derivative, which are only slightly dissociated in ethanol and are thus thought to contain 3-coordinate mercury[138]. The 1:1 adducts with 2,2'-bipyridine, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline have also been isolated[139,140]. Addition compounds have also been isolated with phosphines, for example $(Ph_3P)_2Hg(CN)_2$[139] and some 1:1 adducts with diphosphines and diarsines in which the bases are bidentate[141]. Calorimetric titration by Gradon et al[142] in acetonitrile demonstrated the formation of 1:1 adducts of

$Hg(CN)_2$ with a wide variety of N-donors, including uni- and bi-dentate heterocyclic bases, primary and secondary amines and uni and bidentate tertiary amines.

c. Anionic complexes of Organomercuric Compounds.

The coordinating ability of organomercury acceptors, such as, RHgX, R_FHgX, RHg^+ and R_FHg^+(R = alkyl or aryl groups, R_F = perfluoroalkyl or aryl group, X = halide ion) are markedly affected by the nature of organic substitutents. The ability to form complexes has been extensively investigated for the cationic species. On the other hand, the anionic species have received much less attention[120,143,144]. Moreover, the conclusions drawn from the several studies on the ability of organomercury(II) compounds to form anionic complexes with halides or pseudohalides are conflicting in a number of instances.

Anionic $RHgX_2^-$ and $RHgX_3^{2-}$, etc. complexes have been studied by Barbieri and coworkers[145-147] and by Toropova and Saikina[105] by means of solubility measurements, anion exchange paper chromatography and paper electrophoresis and polarography. In the $EtHg^+/SCN^-$ system evidence was presented for the existence of complexes, $EtHg(SCN)_n^{1-n}$ (n = 1 to 3)[146]. Iodide ion and thiocyanate complexes were much stronger than chloride or bromide complexes and , in fact no evidence was found for $RHgX_2^-$ (X = Cl or Br) at X^- concentration of 1M[145]. The stability[105] of such complexes depends on R increasing in the order:

Me < Et < n-Pr < i-Pr < n-Bu < i-Bu

The formation of the anionic complexes[144,148] of the type: $EtHgBr_2^-$, $EtHgBr_3^{2-}$ $(R_f)_2HgI^-$, $(R_f)_2HgI_2^{2-}$ where R_f is a fluoroalkyl ligand have also been reported. The existence of these complexes has been, however, questioned by Downs[149]. Studies on $[HgEt(Cl)]$[150] and $[HgEt(Br)]$[144] using ion-exchange paper chromatography suggested some complex formation but with much lower stability constants than for iodide.

Plassogna et al[151] made a spectrophotometric investigation of the interaction between RHgCl (R = Me, Et, Pr, Ph) and Ph_3CCl as a Cl^- donor in acetonitrile, this solvent provides a suitable medium for the formation of anionic complexes. Stability constants of the halo-complexes $RHgCl_2^-$ have been determined, and are discussed. They concluded that higher complexes, $[HgRX_3]^{2-}$ were not formed, although for inorganic mercury $(HgX_3)^-$ and HgX_4^{2-} species are known. Incidentally, this conflicts with the results obtained from studies in aqueous system[150]. The $(HgX_3)^-$ species are considerably more stable[152] than the corresponding $(RHgX_2)^-$ and this indicates a reluctance of organomercury acceptors to reach a coordination number higher than two. They also found that, whilst complex formation occurred when R = Me or Et, while Pr or Ph compounds do not show any complexation, though an earlier report[105] indicated that the complex formation was more complete when R = Pr than for Et or Me.

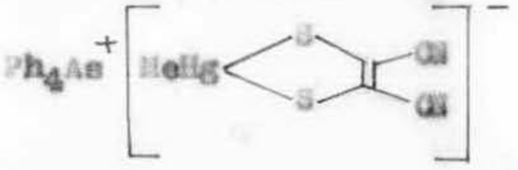
Anion exchange studies on CH_3HgCl in aqueous HCl and LiCl suggested the retention in the resin phase of the complex anion $CH_3HgCl_3^{2-}$. Stability constants for this species and for $CH_3HgCl_2^{-}$ were determined[153]. Laser, Raman, IR and NMR studies have established the formation of $CH_3Hg(SCN)_3^{2-}$ in the CH_3HgSCN/SCN^{-} system. These studies suggested an ion-dipole interaction in these complexes rather than a predominantly covalent one[154].

It is reported that bromide ion complexes of cyclopentadienylmercuric bromide are readily formed in aqueous solution[155].

$$C_5H_5HgBr + Br^{-} \longrightarrow C_5H_5HgBr_2^{-}$$

$$C_5H_5HgBr_2^{-} + Br^{-} \longrightarrow C_5H_5HgBr_3^{2-}$$

Evidence was obtained even for the formation of $C_5H_5HgBr_4^{3-}$. Cyclopentadienylmercuric bromide thus appears to be a stronger Lewis acid with respect to bromide ion than any other RHgBr or mercuric bromide. This may be due to the pronounced anionic character of the cyclopentadienyl substituent. Stocco[156] reported the characterisation of an anionic MeHg(II) complex of the cis -1,2-dicyanoethylene dithiolate ion A.



A

It is, however, possible that the two Hg-S bonds are not equal in length as in $MeHgS_2CNEt_2$.

The formation of alkylmercuric halide complex anions was studied using vibrational and nuclear magnetic spectroscopy[157]. Complex anions of type $[RHgX_2]^-$ were found to be formed with RHgCl (R = Me, Et, *n*-Pr, *n*-Bu), RHgBr (R = Me, Et, *n*-Pr, *n*-Bu), RHgI (R = Me, Et) and MeHgSCN in benzene, chloroform, dichloromethane, THF and acetonitrile, but not in methanol and water.

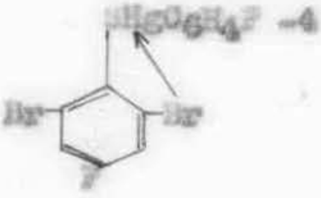
$$RHgX + n\text{-}Bu_4\overset{+}{N}X^- \longrightarrow [n\text{-}Bu_4N^+][RHgX_2^-]$$

Attempts to isolate such complexes have so far failed.

d. Intramolecular Coordination Compounds.

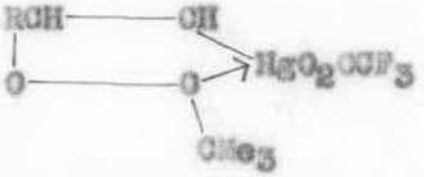
NMR investigations[158] of a series of γ-arylpropylmercury compounds suggested that π-electrons of a benzene ring are involved in coordinate bonding with the mercury atom. Kiefer et al[159] carried out an analysis of the NMR spectra of several compounds with the general structure $XCH_2C(CH_3)(OCH_3)CH_2HgY$ with variation of X,Y, solvent, concentration, and temperature. Chemical shift and spin coupling data were interpreted in terms of intramolecular donor-acceptor interaction between the electron pair donor atom X and the mercury atom. Both chloro and bromo substituents were found to form weak coordinate bonds with mercury.

A ^{19}F NMR study[160] in organomercury derivatives of 2,6-Dimethyl-4-fluorothiophenol and 2,6-Dibromo-4-fluorothiophenol supports the presence of intramolecular coordination.



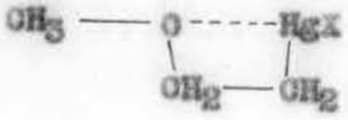
X-ray crystal structure determination of methyl-L-cysteinatomercury(II) and methyl-DL-methioninemercury(II)[94] and X-ray crystal structure and vibrational spectra of L-cysteinato(methyl)mercury(II) monohydrate[95] indicate that there may be a weak intramolecular Hg-O bond to a carboxylate oxygen atom.

Proton NMR studies provided evidence for intramolecular O →Hg coordination in β-peroxymercurials[161]

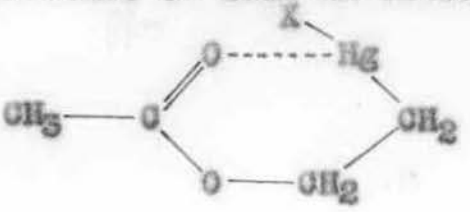


An IR spectroscopic study of bis (2,3,4,5-tetrachloro-6-nitrophenyl)-mercury suggested that intramolecular O →Hg coordination, as shown below, is a possibility[162]

Data obtained from a dipole moment study[163] has been interpreted in terms of weak intramolecular coordination between mercury and oxygen functionality in B and C in benzene medium. In ethyl acetate, only C gave evidence of such an interaction.



B



C

Evidence for intramolecular coordination between mercury and the C = O group in mercurated ortho-formylphenols has been obtained from infrared studies[164].

e. Arene complexes

Dean, Ibott and Stothers[165] reported the preparation of arene complexes of the mercurous ion by the action of arenes on SO_2 solutions of mercury(I) hexafluoroarsenate. 1:1 complexes with benzene, biphenyl, naphthalene, m-dinitro-benzene and 2:1 and 1:3 complexes with 9,10-benzophenanthrene have been observed.

$$mHg_2(AsF_6)_2 + nArH \xrightarrow{SO_2} mHg_2(AsF_6)_2 \cdot nArH$$

Raman spectroscopy showed that the Hg-Hg bond was retained in the complexes and the fact that the position of this bond was dependent on the arene confirmed the arene-Hg^{2+} interaction. They[166] have further reported the preparation of a wide range of arene complexes from mercurous hexafluoroarsenate and the appropriate arene in liquid SO_2. 1:1 complexes were obtained between $Hg_2(AsF_6)_2$ and benzene, biphenyl, naphthalene, 2-methyl-and 2,6-dimethylnaphthalene, acenaphthene, fluoranthene, fluorene, phenanthrene, anthracene, 9,10-dimethylanthracene and m-dinitrobenzene. Raman spectroscopy confirmed the existence of the dimeric Hg_2^{2+} cation in these complexes. ^{13}C NMR spectroscopy showed that Hg_2^{2+}-arene complexes exist in SO_2 solution.

Mercuric halides also form stable solid molecular complexes with aromatic hydrocarbons[167]. In dichloromethane solution 1:1 complexes are formed. Among the solid complexes which were isolated were the following: $2HgX_2$.toluene (X = Br, I); $2HgBr_2$.EtPh; $3HgI_2$.2EtPh; $HgBr_2$.acenaphthene; HgI_2.pyrene; HgI_2.2 anthracene. But these complexes were too unstable to be isolated.

$Hg(SbF_6)_2$.2 arene (arene = C_6HMe_5, durene, mesitylene, p-xylene, PhMe, C_6H_6, $C_{10}H_8$) and $Hg(AsF_6)_2$.2 arene (arene = C_6HMe_5, durene) were prepared from $Hg(SbF_6)_2$ and $HgF(AsF_6)$ respectively by treatment with excess arene in SO_2[168]. The complexes are stable to short exposure to moist air. Stability constants for some of the complexes were also reported. Low-temperature, slow-exchange (except when Arene = C_6H_6), ^1H and ^{13}C NMR spectra of the systems $Hg(SbF_6)_2$-Arene-SO_2 have provided evidence for very stable $Hg(Arene)^{2+}$ and $Hg(Arene)_2^{2+}$ complexes[169].

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