

2. MERCURY

E.C. CONSTABLE

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INTRODUCTION

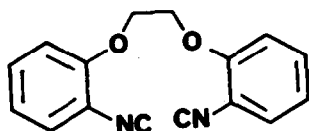
This review is a continuation of the 1982 Review of mercury coordination chemistry, published in this journal in 1984 [1]. The format and content is generally similar to that adopted in previous years; the section on ^{199}Hg NMR has been omitted, and that detailing compounds containing mercury-heterometal bonds is considerably expanded.

Once again, I must thank Drs. Olga Kennard, Sharon Bellard and Paul Raithby for their assistance in obtaining data from the Cambridge Crystallographic Data Centre.

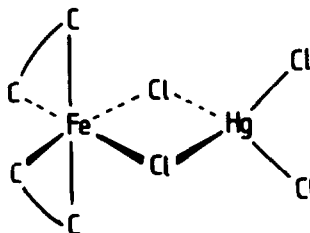
2.1 MERCURY(II)

2.1.1 Halide and pseudohalide complexes

Co-crystallisation of mercury(II) bromide and mercury(II) iodide from water gives a solid which is reported to be the mixed halide HgBrI [2]. Mercury(II) chloride reacts with *cis*- $[\text{FeCl}_2\text{L}_2]$ ($\text{L} = 1,2\text{-bis}(2'\text{-isocyanophenoxy})\text{ethane}$ (1) to give a chloro-bridged species thought to possess structure (2), *cis*- $[\text{L}_2\text{Fe}(\mu\text{-Cl})_2\text{HgCl}_2]$ [3]. Mercury(II) chloride is readily



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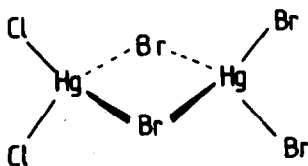


(2)

extracted from aqueous solution by *n*-butyl ethanoate (either alone or with a diluent such as chloroform, tetrachloromethane, cyclohexane, heptane, hexane or isooctane [4]. Di-*n*-pentylsulphoxide and di-*n*-octylsulphoxide have been used in the extraction of mercury(II) thiocyanate from aqueous medium; in each case the extracted species is of the stoichiometry $\text{Hg}(\text{SCN})_2 \cdot 3\text{S}$ [5].

Trihalomercurate complex ions continue to be of interest, and a number of spectroscopic and structural studies of these species have been recently reported. It is now well-established that a number of structural types give rise to an apparent stoichiometry $[\text{HgX}_3]^-$, with the two commonest (and simplest) being a mononuclear $[\text{HgX}_3]^-$ ion or a binuclear halogen bridged $[\text{X}_2\text{Hg}(\mu\text{-X})_2\text{HgX}_2]^{2-}$. It is common for the mononuclear anions to exhibit long range intermolecular interactions, and the precise description is frequently a matter of semantics. The complex $[\text{L}_2\text{H}][\text{HgI}_3]$ ($\text{L} = \text{quinoline}$) has been reported; the cation possesses the expected symmetrical hydrogen bridged structure [6]. The related mixed halide complex $[\text{L}_2\text{H}]_2[\text{I}_2\text{Hg}(\mu\text{-Br})_2\text{HgI}_2]$ has also been described [7]. Contreras and Seguel have reported Raman studies of a large number of trihalomercurate(II) complexes, and have further demonstrated

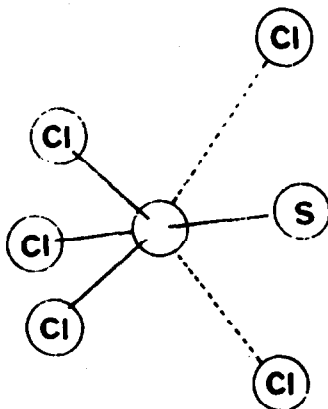
the use of this technique in determining the solution and solid state structures of these compounds [8,9]. Raman studies have indicated that the mixed halide complexes $[\text{Pr}_4\text{N}]_2[\text{Hg}_2\text{Br}_4\text{X}_2]$ ($\text{X} = \text{Cl}$ or I) possess the indicated dimeric structure; the dichlorotetrabromomercurate(II) was thought to possess C_{2v} symmetry, with the two chlorides coordinated to the same mercury atom (3)[8].



(3)

Brodersen has reported the crystal structural analyses of numerous mercurate(II) anions, including the magnesium salt $[\text{Mg}(\text{OH}_2)_6][\text{Hg}_2\text{X}_6]$ ($\text{X} = \text{Br}$ or I); in each case, a binuclear anion is present [10].

An X-ray analysis of the complex $[\text{NH}_4][\text{HgCl}_2(\text{SCN})]$ has also been described; the metal atoms are basically three-coordinate, forming chains with bridging chlorides ($\text{Hg}-\text{Cl}_{\text{terminal}}$ 2.339 Å, $\text{Hg}-\text{Cl}_{\text{bridging}}$ 2.785 Å), although there are two more distant mercury-chloride contacts at 3.5 Å (4) [11].



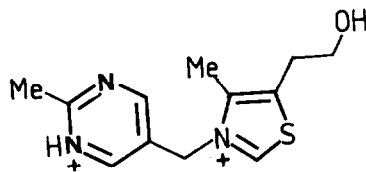
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A more unusual structure is found in $[\text{MeNH}_3][\text{HgCl}_3]$, in which the mercury

is in a four-coordinate distorted tetrahedral environment. Each mercury exhibits two short (2.32 - 2.37 Å) and two long (2.71 - 2.82 Å) contacts to chlorine, and the structure may be described in terms of chains constructed from edge-sharing tetrahedra. Once again, the structure is not simply described, since each mercury also has a fifth contact with a more distant chlorine at 3.21 Å [13]. A similar, basically tetrahedral environment is found in $[\text{Me}_2\text{NH}_2][\text{HgCl}_3]$; in this case there are three distinct and independent mercury environments, and, once again, longer contacts in the range 3.37 - 3.47 Å [14].

The tetrahalomercurate(II) ions are usually found to be tetrahedral, although a considerable degree of distortion may be present. These ions are frequently distorted in a sense to give two long Hg-X and two short Hg-X bonds. This is observed in the crystal structures of $[\text{M}(\text{OH}_2)_8][\text{HgI}_4]$ (M = Ca or Sr), both of which possess a distorted tetrahedral mononuclear anion [12]. In each case the Group IIA ion is in an eight-coordinate environment, although the compounds are not isostructural. The mercury-iodine bond lengths are in the range 2.74 - 2.85 Å [12]. A discrete tetrahedral anion is also found in $[\text{MeNH}_3]_2[\text{HgCl}_4]$, with mercury-chlorine distances in the range 2.464 - 2.478 Å [13]. A similar, distorted tetrahedral anion is present in $[\text{Me}_2\text{NH}_2]_2[\text{HgCl}_4]$ (Hg - Cl, 2.42 - 2.53 Å) [14]. A structural analysis of $\text{Cs}_2[\text{HgCl}_4]$ has revealed a slightly different pattern of distortion in the anion, which exhibits one short (2.386 Å) and three long (2.453 - 2.458 Å) mercury-chlorine bonds [15]. The bromo analogue, $\text{Cs}_2[\text{HgBr}_4]$ is isostructural [15]. The X-ray powder pattern of $[\text{MeNH}_3]_2[\text{HgBr}_4]$ has been described [16].

The multiplicity of structural modes open to halomercurate(II) ions is emphasised in the recent description of the crystal structure of N-ethylammonium tetrachloromercurate(II), in which the mercury is in a distorted octahedral environment (Hg - Cl, 2.437 - 2.842 Å [17]. The interaction of thiamine hydrochloride (5) with mercury(II) chloride has been investigated [27]. At pH = 3 the predominant species are $[\text{HL}][\text{HgCl}_4]$ and $[\text{HL}][\text{HgCl}_3]_2$, whereas at pH = 5, $[\text{L}][\text{Hg}_2\text{Cl}_5]$ is present. The solution species may be



(5)

detected by a combination of IR and NMR spectroscopy. A single crystal structural analysis of the complex $[\text{HL}][\text{HgCl}_4]$ has been reported; the mercury is in a distorted tetrahedral environment ($\text{Hg} - \text{Cl}$, 2.395 - 2.553 Å) [27].

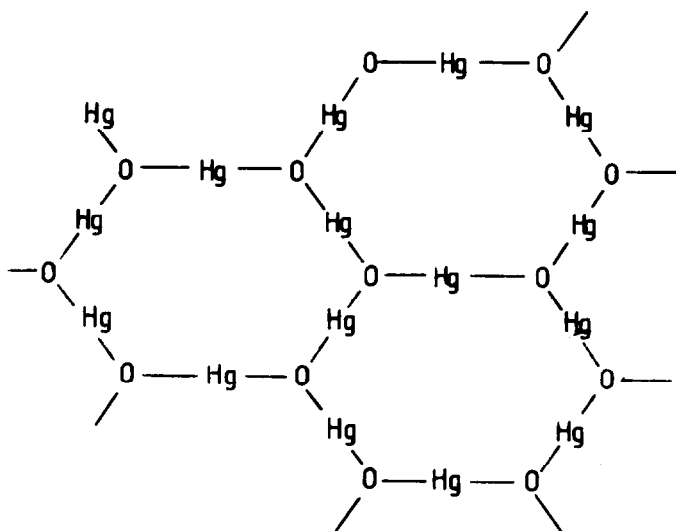
In aqueous dmf, in the presence of base, pentafluorobenzene reacts with tetrabromomercurate(II) or tetraiodomercurate(II) to give very high yields of bis(pentafluorophenyl)mercury(II) [18]. Numerous complex anions incorporating pseudohalides are known, although the structural chemistry is more complex, since the pseudohalides are prone to act as bridging ligands. This facet of the chemistry of these complex ions has been emphasised in the structural studies of Group IIA mercurates recently reported by Brodersen and co-workers. A layer type structure is observed in $\text{MgHg}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$; the mercury is in a distorted tetrahedral S_4 environment with the thiocyanate ions acting as bridges to the magnesium ions [19]. Each magnesium is in an octahedral N_4O_2 environment. A similar structure is observed in the calcium salt, $\text{CaHg}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$ [20]. In contrast, the trihydrate, $\text{CaHg}(\text{SCN})_4 \cdot 3\text{H}_2\text{O}$ adopts a diamond type structure [20]. The strontium complex, $\text{SrHg}(\text{SCN})_4 \cdot 3\text{H}_2\text{O}$ adopts a related structure, with the strontium in a tricapped trigonal prismatic N_4O_5 environment [21]. This nine-coordinate environment is found in other strontium mercurates [22].

Related studies of pseudohalide complexes have investigated the thermooptical properties of $\text{MHg}(\text{SCN})_4$ ($M = \text{Co}, \text{Cd}, \text{Cu}$ or Zn) [23], and the thermal decomposition of $[\text{Me}_3]_2[\text{Hg}(\text{CN})_4]$ [24]. The polynuclear complexes $\text{MHg}(\text{SCN})_4 \cdot L_n$ ($M = \text{Ni}$ or Cu , L_n = nitrogen heterocycle) have also been reported [25].

A number of compounds possessing an anion of apparent stoichiometry $[\text{Hg}_2\text{Cl}_5]^-$ are known, and possess an array of structural types. Recently described structures include $[\text{Me}_2\text{NH}_2][\text{Hg}_2\text{Cl}_5]$ [14] and $[\text{MeNH}_3][\text{Hg}_2\text{Cl}_5]$ [13]; in neither case is the anion simple. Just as the $[\text{Hg}_2\text{Cl}_5]^-$ ion may be regarded as being derived from $[\text{HgCl}_3]^-$ and HgCl_2 , the $[\text{Hg}_3\text{Cl}_8]^{2-}$ ion is formed from $[\text{Hg}_2\text{Cl}_6]^{2-}$ and HgCl_2 . This description appears to have some structural significance, and the recent structural analysis of $\text{MgHg}_3\text{Cl}_8 \cdot 6\text{H}_2\text{O}$ has revealed the presence of $[\text{Mg}(\text{OH}_2)_6]^{2+}$, $[\text{Hg}_2\text{Cl}_6]^{2-}$ and linear pseudo- HgCl_2 units [26].

2.1.2 Complexes with oxygen donor ligands

The crystal structure of mercury(II) peroxide, $\alpha\text{-HgO}_2$ has been reported [28]. The compound $\text{Hg}_3\text{O}_2(\text{NO}_3)_2$ has also been structurally characterised [29]. This is the species formulated $3\text{HgO} \cdot \text{N}_2\text{O}_5$ in the $\text{HgO} - \text{H}_2\text{O} - \text{N}_2\text{O}_5$ system, and consists of a honeycombed net of Hg_3O_2 and isolated nitrate anions (6). An X-



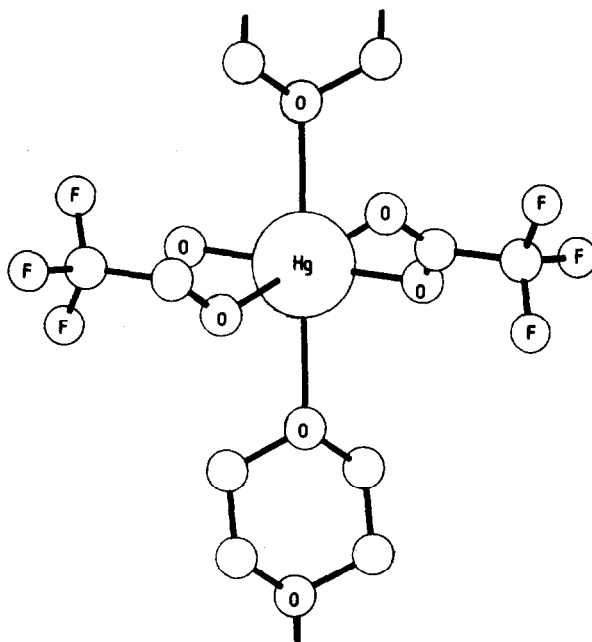
(6)

ray study of aqueous mercury(II) nitrate (1:40 and 1:25 solutions at 298.15 K) has demonstrated that the mercury is present in solution as an octahedral hexaaqua ion, with the nitrate ions in the second coordination sphere (*i.e.* a fairly tight ion-pair) [30].

Acetonitrile solutions of $[\text{Hg}(\text{O}_3\text{SCl})_2]$ react with pyridine to give mixtures of $[\text{Hg}(\text{py})_4(\text{O}_3\text{SCl})_2]$ and $[\text{Hg}(\text{MeCN})_4(\text{O}_3\text{SCl})_2]$; the chlorosulphate ligand is thought to be adopting a monodentate bonding mode [31]. The complex $[\text{Hg}(\text{O}_2\text{NCO}_2\text{Et})_2]$ has been prepared [32].

A crystal structural analysis of the unusual polymeric complex $[\text{Hg}(\text{O}_2\text{CCF}_3)_2\text{L}_2]$ ($\text{L} = 1,4\text{-dioxane}$) has been described; the metal is in a six-coordinate octahedral environment (7) [33]. The 1,4-dioxane acts as a bridging bidentate ligand, as does the trifluoroethanoate; each mercury atom is bound to one oxygen atom from each of four carboxylate groups, and there is considerable variation in the Hg - O bond lengths.

A number of mercury(II) complexes with carboxylic acids (RCO_2H , $\text{R} = \text{H}$, Me, Et or n-Pr) have been reported [34]. Good yields of 3-iodopyridine are obtained from the reaction of nitrobenzene solutions of iodine with $[\text{HgL}_2]$ ($\text{HL} = \text{pyridine-3-carboxylic acid}$); lower yields are obtained upon attempted bromination. The full extent of this Hunsdiecker type reaction has not been



(7)

established, although very poor yields were obtained with the corresponding pyridine-2-carboxylic acid and pyridine-4-carboxylic acid derivatives [35]

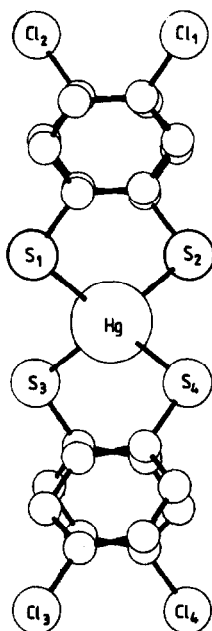
Ligand transfer reactions from tin(IV) to mercury(II) proceed readily, and $[\text{HgL}_2\text{Cl}_2]$ may be prepared by the reaction of mercury(II) chloride with $[\text{Ph}_2\text{SnLCl}_2]$ (L = pyridine *N*-oxide) [36].

2.1.3 Complexes with sulphur, selenium and tellurium ligands

2.1.3.1 Thiols

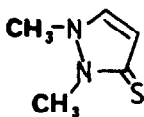
A crystal structural analysis of a tetra(thiophenolato)mercurate(II) salt has been reported; in $[\text{Me}_4\text{N}]_2[\text{HgL}_4]$ (L = 4-chlorothiophenol), the anion is approximately tetrahedral, although the ligand conformation results in an approximate overall D_{2d} symmetry (8) [37]. The mercury - sulphur distances are in the range 2.537 - 2.552 Å.

1,2-Dimethylpyrazoline-3-thione (9) forms a *S* bonded 1:1 complex with mercury(II) chloride; this complex was included in a study of the effects of

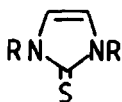


(8)

complexation on the thioamide stretching frequencies of this ligand and its derivatives [38]. The related complexes $[\text{HgL}_2\text{Cl}_2]$ ($\text{L} = \mathbf{10}$, $\text{R} = \text{H}$ or Me) have also been prepared, and are also thought to contain an *S*-bonded ligand [39].

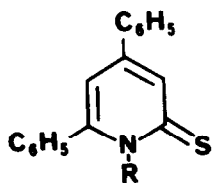


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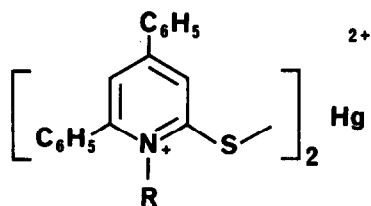


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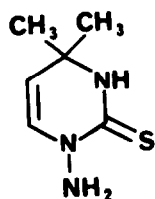
1-Alkyl-4,6-diphenylpyridine-2-thiones ($\mathbf{11}$) react with mercury(II) salts to form 2:1 adducts of the type ($\mathbf{12}$) [40]. These novel complexes, incorporating a positively charged ligand, are of some interest in organic synthesis. Complexes with 1-amino-1,4-dihydro-4,4,6-trimethylpyrimidine-2(1*H*)-thione ($\mathbf{13}$) have also been described [41].



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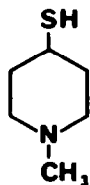


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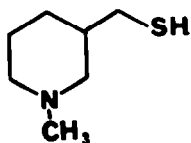


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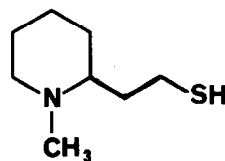
It is relatively recently that positively charged ligands have been widely investigated (see above), and further examples are found in the mercury(II) complexes of the Zwitterionic species, 1-methylpiperidine-4-thiol (**14**), 1-methyl-3-mercaptomethylpiperidine (**15**) and 1-methyl-2-(2-mercaptoethyl)piperidine (**16**) [42]. Among the complexes which have been



(14)



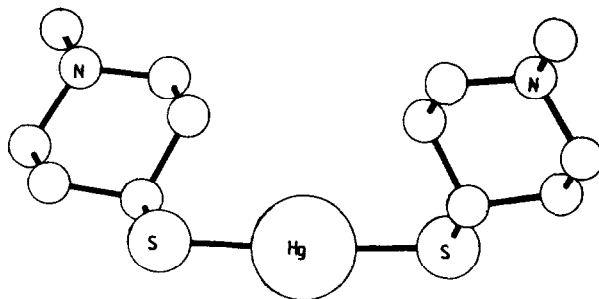
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(16)

described are $[\text{HgL}_n][\text{ClO}_4]_2 \cdot m\text{H}_2\text{O}$ ($\text{L} = \text{14}$, $n = 1$ or 2 , $m = 0$; $\text{L} = \text{15}$, $n = 1$, $m = 1$; $\text{L} = \text{16}$, $n = 1$, $m = 0.5$); a single crystal structural analysis of the 2:1 complex with **14** has been described (17) [42]. Thioglycollic acid, $\text{HSCH}_2\text{CO}_2\text{H}$,

can act as a bidentate dianionic ligand, and a number of salts of the tetrahedral complex ion $[\text{HgL}_2]^{2-}$ with sodium, potassium, cerium, praseodymium, lanthanum, neodymium, calcium, strontium and barium have been described [43].



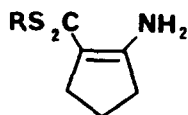
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2.1.3.2 Thioethers and sulfoxides

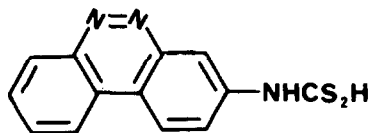
The extraction of mercury(II) from thiocyanate medium by sulfoxides has been mentioned earlier (Section 2.1.1) [5].

2.1.3.3 Thioamides, thio acids and related ligands

A tetrahedral mercury(II) complex, $[\text{HgL}_2]$ (HL = **18**, R = H) of 2-aminocyclohexenedithiocarboxylic acid has been reported [44]. The methyl ester of this acid also forms a mercury(II) complex $[\text{HgL}_2\text{X}_2]$ (HL = **18**, R = Me; X = halide) [44].

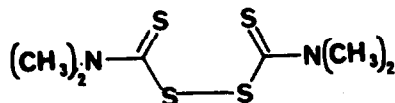


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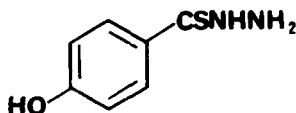
Dithiocarbamates continue to be of interest as ligands, and a series of complexes of the type HgML_4 ($M = \text{Co, Ni or Cu}$; $L = \text{Et}_2\text{NCS}_2\text{H}$) have been reported [45]. 4-Aminophenazone reacts with alkaline ethanolic carbon disulphide to form the dithiocarbamate (19), which forms a 2:1 mercury complex $[\text{HgL}_2]$ in which it acts as a bidentate S_2 donor [46]. A related ligand, N,N,N',N' -tetramethylthiuram disulphide (20) has been shown to form the complexes $[\text{HgLX}_2]$



(20)

($L = 20$; $X = \text{Cl, Br, I or SCN}$) and $[\text{HgL}(\text{NO}_3)_2]$ [47]. The nitrate acts as a monodentate ligand in the latter complex.

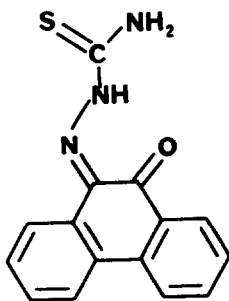
A range of complexes of mercury(II) chloride with thioamides has been described; a variety of bonding modes is exhibited [48]. The complexes $[\text{HgL}_2]$ and $[\text{Hg}(\text{HL})\text{Cl}_2]$ ($\text{HL} = 21$) have also been reported, in which the ligand is thought to act as a bidentate NS donor [49].



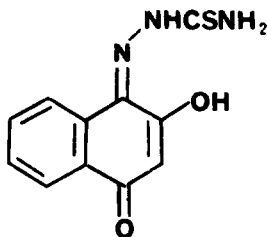
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N,N' -Diphenylthiourea, PhNHC(=S)NHPh , acts as a bidentate bridging NS donor in the polymeric complex $[\text{Hg}(\text{OH}_2)\text{LCl}]\text{Cl}$, which is prepared by the reaction of the thiourea with mercury(II) chloride in ethanol [50]. Complexes with a number of N -(2-pyridyl)thioureas have also been characterised [51]. Mercury(II) chloride forms a 1:1 complex ($\lg K$, 5.12) with 1-benzoyl-2-monothioibiuret, $\text{H}_2\text{NCONHC(=S)NHCOPh}$ [52]. The 2:1 complexes $[\text{HgL}_2]\text{Cl}_2$ with monothioibiuret imines, $\text{PhCONHC(=NH)NHC(=S)NHAr}$ or $\text{PhNHC(=NH)NHC(=S)NHAr}$, have been described; the mercury is in a tetrahedral NS environment [53].

The thiosemicarbazide derivative, $\text{PhNHCSNHNHCOCH}_2\text{CHMe}_2$, forms a mercury(II) complex $[\text{HgLCl}_2]$ [54]. A related, positively charged, ligand is found in $[\text{PhNHCSNHNHCOCH}_2\text{NMe}_3]^+$, which forms a range of complexes of the type $[\text{HgLX}_2]\text{Cl}\cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{O}_2\text{CMe}, \text{NO}_3$ or 0.5SO_4) [55]. Mercury(II) complexes of the mono(thiocarbazones) of phenanthraquinone (22) and 2-hydroxynaphthoquinone (23) have been reported; in each case, the sulphur is not coordinated to the metal, which is in a tetrahedral environment, bonded to the imino nitrogen and the *ortho* oxygen atom [56].



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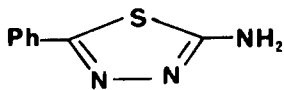


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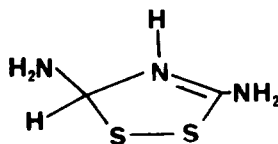
Other complexes which have been described include $[\text{HgL}_2]$ ($\text{HL} = \text{PhC}(\text{NH}_2)=\text{NHNHCSNH}_2$) [57], $[\text{HgLCl}]$ ($\text{HL} = \text{benzoin thiosemicarbazone}, \text{PhCHOHC}(\text{Ph})=\text{NHNHCSNH}_2$) [58] and $[\text{HgLCl}_2]$ ($\text{L} = \text{biacetyl monooxime } 1\text{-benzoylthiocarbazone}, \text{MeC}=\text{NOHC}(\text{Me})=\text{NHNHCSNHNHCOPh}$) [59].

2.1.3.3 Sulphur heterocycles

A 1:1 complex between mercury(II) chloride and 2-amino-5-phenyl-1,3,4-thiadiazole (24) has been described [60]. Thiouret salts (25) result from the oxidation of dithiobiuret, and form further examples of positively charged ligands which give mercury(II) complexes. Spectroscopic investigations indicate six-coordinate structures for the complexes $[\text{HgL}_2\text{X}_4]$ ($\text{X} = \text{Cl}, \text{Br}$ or I), with the halide in the equatorial plane, and a tetrahedral structure for $[\text{HgLX}_3]$ ($\text{X} = \text{Br}$ or I) [61]. A number of, probably, polymeric complexes of mercury(II) salts with 2-aminobenzothiazole (26) have been described [62]. 2-Arylimino- Δ^4 -thiazolines (27) form complexes with mercury(II) ethanoate,

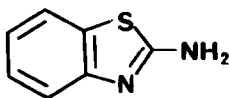


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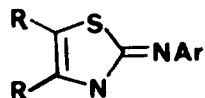


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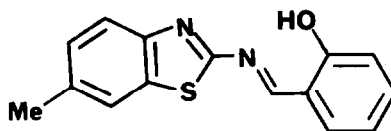
which are formulated arylmercury derivatives [63]. Complexes with the Schiff base derived from the reaction of 2-aminobenzothiazole with salicylaldehyde (28) have also been described [64].



(26)



(27)



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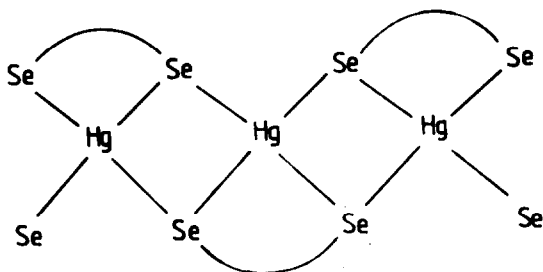
2.1.3.5 Phosphine sulphides and selenides

A number of complexes with triphenylphosphine sulphide or selenide and tri-*p*-tolylphosphine sulphide or selenide have been characterised; isolated compounds include $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{Ph}_3\text{PS}$, $3\text{Hg}(\text{NO}_3)_2 \cdot 4\text{Ph}_3\text{PSe}$ and $\text{HgX}_2 \cdot \text{Tol}_3\text{PSe}$ [65]. All these complexes are thought to possess polymeric structures. A series of complexes with the disulphides of potentially chelating diphosphines have also been investigated [66]. In the complexes with small diphosphines, $[\text{HgBr}_2\text{L}]$ ($\text{L} = \text{Me}_2\text{PSPSMe}_2$) and $[\text{Hg}(\text{NO}_3)_2\text{L}]$ ($\text{L} = \text{Ph}_2\text{PSCH}_2\text{PSPH}_2$), the ligands are thought to

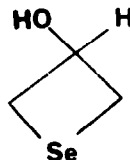
acts as chelating bidentates, whereas polymeric structures are proposed for the complexes with more flexible ligands, $[\text{Hg}(\text{NO}_3)_2\text{L}]$ ($\text{L} = \text{Ph}_2\text{PS}(\text{CH}_2)_n\text{PPh}_2$; $n = 2, 3$ or 4) [66].

2.1.3.6 Complexes with selenium and tellurium compounds

The mercury(II) complex, $[\text{HgL}_2]$, of the novel diselenol ligand $\text{HSeCH}_2\text{CHOHCH}_2\text{SeH}$ is thought to possess the polymeric structure (29) [67]. This complex is of interest since, upon demetallation with hydrogen sulphide, it yields the novel selenium heterocycle 30.



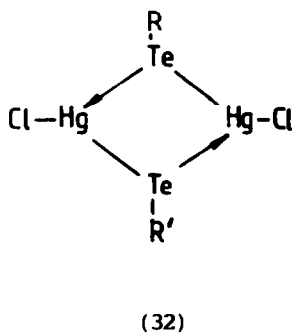
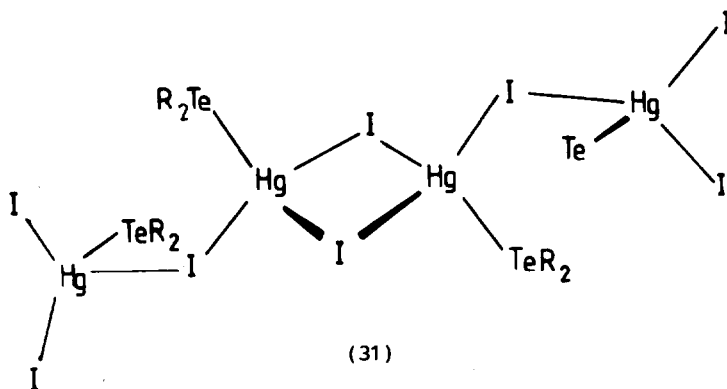
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A crystal structural analysis of the complex $[\text{Ph}_2\text{TeHgI}_2]$ has revealed an unusual tetrameric structure, in which two types of bridging iodine are present (31) [68]. The structure is reminiscent of those recently determined for some apparently simple phosphine complexes of mercury(II), and serves as a warning that mercury(II) complexes with soft ligands frequently possess structures considerably more complex than their stoichiometry might suggest.

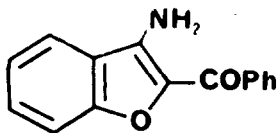
McWhinnie has presented evidence for the formation of complexes of mixed diaryl ditellurides on treating mercury(II) halides with mixtures of diphenyl ditelluride and bis(4-ethoxyphenyl) ditelluride [69]. In propionitrile, it is proposed that the products may be the unsymmetrical ditelluride complexes, $[\text{X}_2\text{HgPhTeTeArHgX}_2]$ ($\text{Ar} = 4\text{-ethoxyphenyl}$). If the reaction is conducted in ethanol, telluride complexes of the type 32 are thought to form [69].



2.1.4 Complexes with amine, amide and related ligands

2.1.4.1 Complexes with amines

The Raman spectra of the complexes $[\text{HgL}_2\text{X}_2]$ ($\text{L} = \text{NH}_3$ or ND_3 ; $\text{X} = \text{Cl}$ or Br) have been investigated [70]. A tetrahedral complex, $[\text{HgLCl}_2] \cdot n\text{H}_2\text{O}$ ($\text{L} = 3\text{-amino-2-benzoylbenzofuran}$, **33**) has been described [71], as have mixed metal complexes derived from the interaction of mercury(II) chloride with cadmium chloride and triethanolamine, $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ [72]. Stability constants for mercury(II) complexes with $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ have been determined [73]. The interaction of mercury(I) chloride with 1,4-diazabicyclo[2.2.2]octane (dabco, triethylenediamine, **34**) in the presence of hydrochloric acid leads to mercury(II) derivatives rather than the expected mercury(I) complexes [74]. A crystal structural analysis of the product has



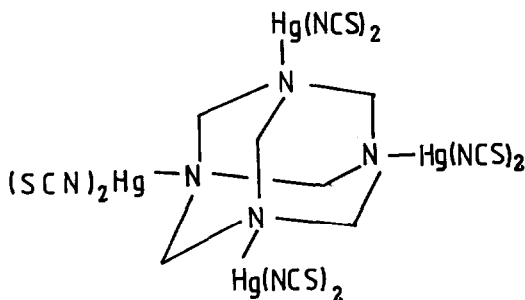
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(34)

revealed it to be the tetrachloromercurate(II) salt of the diamine diacation, $[\text{LH}_2][\text{HgCl}_4] \cdot \text{H}_2\text{O}$. The anion adopts the distorted tetrahedral configuration discussed earlier, with two short (2.438, 2.444 Å) and two long (2.529, 2.531 Å) mercury - chlorine distances [74].

The 4:1 complex between hexamethylenetetramine and mercury(II) thiocyanate has been further investigated [75,76]. There is some evidence that the thiocyanate ligands are bonded to the metal *via* the nitrogen atom (35); this would be the first example of an *N*-bonded thiocyanate at mercury(II), and a crystal structural analysis would provide valuable conformation.

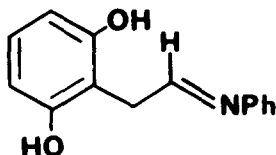


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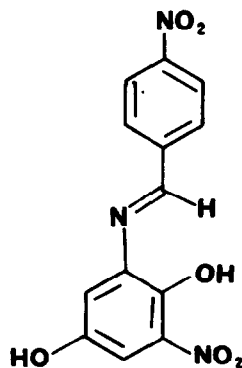
The useful reagent $[\text{Hg}(\text{N}(\text{SF}_5)_2)_2]$ is prepared by the reaction of mercury(II) fluoride with F_5SNSF_4 ; treatment with iodomethane or trifluoromethylsulphenyl chloride leads to the formation of $\text{MeN}(\text{SF}_5)_2$ or $\text{CF}_3\text{SN}(\text{SF}_5)_2$ respectively [77]. Enthalpies of formation for the complexes $[\text{HgL}_n\text{X}_2]$ ($\text{L} = \text{MeNHCONHMe}$; $n = 1$ or 2 ; $\text{X} = \text{Cl}$ or Br) have been reported [78]. A similar study of the *N*-methylurea complexes $[\text{HgLX}_2]$ ($\text{L} = \text{MeNHCONH}_2$; $\text{X} = \text{Cl}$ or Br) has also been described [79].

2.1.4.2 Complexes with imine ligands

Mercury(II) complexes of the Schiff base derived from aniline and 2,6-dihydroxybenzaldehyde (**36**) have been shown to possess useful fungicidal properties [80]. Other complexes with ligands related to salicylaldehyde imines which have been reported include $[\text{HgL}_2] \cdot 2\text{H}_2\text{O}$ ($\text{HL} = \text{37}$) [81] and $[\text{HgLCI}_2]$



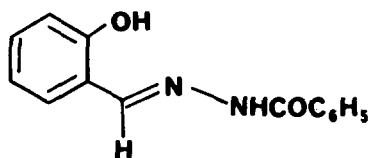
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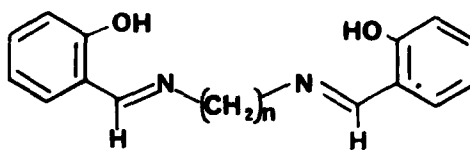
(37)

($\text{L} = \text{ArN}=\text{C}(\text{Me})\text{CH}_2\text{CONHNHPh}$; $\text{Ar} = 2\text{- or } 4\text{-ethoxyphenyl}$) [82]. The hydrazones **38** ($\text{Ar} = \text{phenyl, 2-pyridyl, 2-quinolyl or 8-quinolyl}$) appear to act as terdentate ligands in their mercury(II) complexes [83]. The Schiff base resulting from the condensation of 2 equivalents of salicylaldehyde with 1,2-diaminoethane is well known (Salen, **39**, $n = 2$) is well known. The mercury(II) complexes, $[\text{Hg}(\text{H}_2\text{L})\text{X}_2]$ ($\text{X} = \text{Cl, Br, I, NO}_3$) and $[\text{HgL}_2]$ ($\text{H}_2\text{L} = \text{39, } n = 2$) have been described; evidence has been presented for the ligand acting as an *O* donor, in the tautomeric form shown in **40** [84]. Similar arguments have been presented for the dimeric complexes derived from the related ligand derived from 1,3-diaminopropane (**39**, $n = 3$) [85].

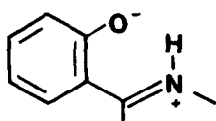
The mercury(II) complexes $[\text{HgL}]$ ($\text{H}_2\text{L} = \text{41}$; $\text{R} = \text{Me or Ph}$) are readily prepared by the template condensation of ethanolamine with the appropriate 1,3-dicarbonyl compound [86]. This constitutes one of the few template condensations about mercury(II) which have yet been reported. The related complexes $[\text{HgL}]$ ($\text{H}_2\text{L} = \text{42}$) [87] and $[\text{HgL}]\text{X}_2$ ($\text{H}_2\text{L} = \text{43}$) [88] have also been described.



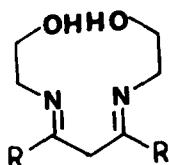
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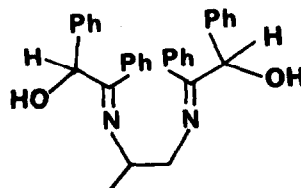
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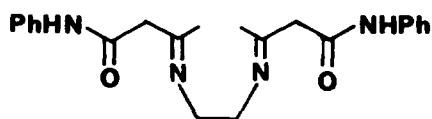
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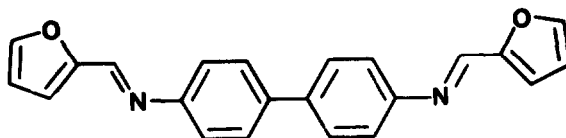
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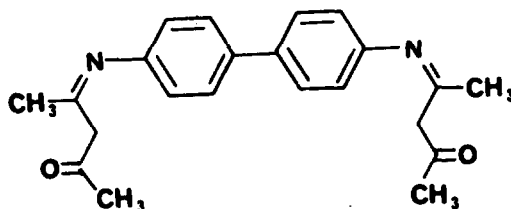
(43)

The Schiff base formed from the condensation of 4,4'-diaminobiphenyl (benzidine) with furfuraldehyde gives a binuclear mercury(II) complex, $[\text{Hg}_2\text{LCl}_4]$ ($\text{L} = 44$), which is an active antibacterial agent [89].

Another complex incorporating a ligand derived from benzidine is seen in $[\text{Hg}(\text{LCl}_2)]$ ($\text{L} = 45$); the compound is a non-electrolyte, and is thought to possess a dimeric structure in which the Schiff base acts as a bridging bidentate [90].



(44)

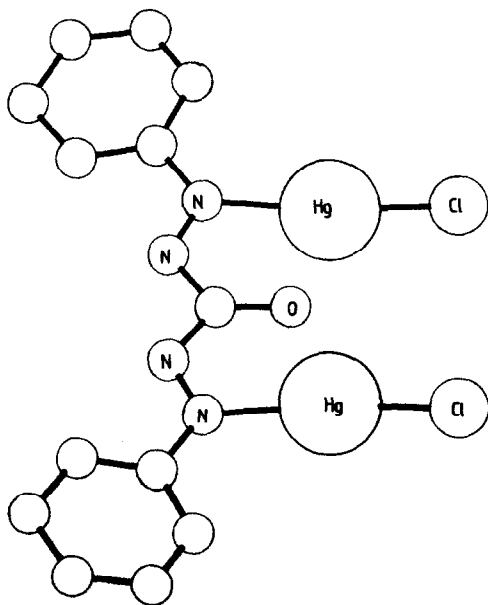


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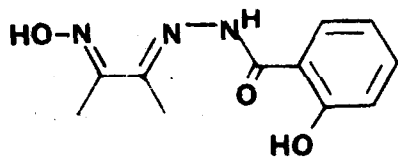
The complex $[(\text{PhN}=\text{NCON}=\text{NPh})\text{Hg}_2\text{Cl}_2]$ has been shown to possess the structure 46; each mercury atom is sandwiched between two phenyl rings of adjacent molecules, presumably representing some degree of π interaction [91]

Mercury(II) chloride forms complexes with the imines derived from the condensation of biacetyl monooxime with 2-hydroxybenzoylhydrazide (47) or $\text{Me}_2\text{NCH}_2\text{CONHNH}_2$ ($\text{Me}_2\text{NCH}_2\text{CONHN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NOH}$) [92,93]. The latter ligand forms the complex $[\text{Hg}(\text{HL})\text{Cl}_2]\text{Cl}$, in which the terminal amino group is protonated; this complex is thought to possess the structure 48 [93],

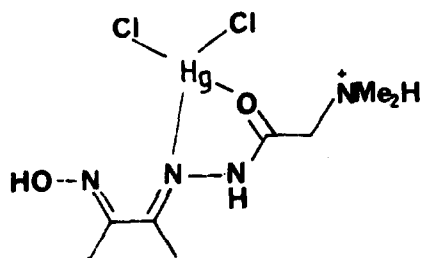
The 2:1 adducts of mercury(II) chloride with $\text{PhCONHC}(=\text{NH})\text{NHCONHPh}$ and $\text{PhNHCONHC}(=\text{NPh})\text{NHPH}$ have been prepared, and are thought to exhibit a tetrahedral N_2O_2 geometry about the metal [53]. The condensation of 2 equivalents of carbazide with 2,6-diacetylpyridine gives the pentadentate ligand 49; mercury(II) complexes of this ligand, and similar compounds derived from 2,5-diacetylpyridine have been described [94].



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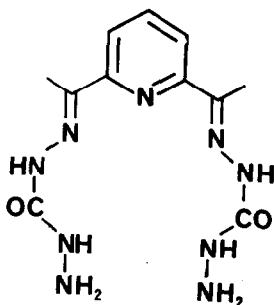


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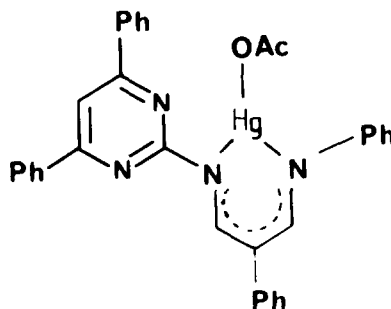


(48)

A number of complexes of formazans have been described recently, and the interaction of $\text{ArNHN}=\text{CPhN}=\text{NAr}'$ ($\text{Ar} = 4,6\text{-diphenyl-2-pyrimidinyl}$; $\text{Ar}' = \text{various}$) with mercury(II) ethanoate has been shown to result in the complexes $[\text{HgL}(\text{O}_2\text{CMe})]$ (50) [95].



(49)



(50)

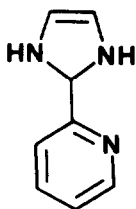
2.1.4.3 Complexes with amino acids

The stability constants for a series of mercury(II) complexes with amino acids have been determined [96]. Lysine is thought to act as a bidentate ligand, with the water present in the lattice, in the complex $[\text{HgL}_2] \cdot \text{H}_2\text{O}$ (HL = L-lysine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$) [97,98]. Mercury(II) complexes of the novel ligand $D,L-(\text{HO}_2\text{C})_2\text{CHNHCHMeCH}_2\text{NHCH}(\text{CO}_2\text{H})_2$ have also been reported [99]. Exchange reactions between the cobalt(II) and mercury(II) complexes of nitrilotriacetic acid, $\text{N}(\text{CH}_2\text{CO}_2\text{H})_3$ have been investigated [100].

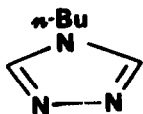
2.1.5 Complexes with nitrogen heterocycles

The binding of mercury(II) ions to imidazole, 1-methylimidazole and the 1,3-dimethylimidazolium cation has been studied by ^1H NMR methods [101]. The complexes $[\text{HgLX}_2]$ (L = 2-(2-pyridyl)imidazoline, **51**; X = Cl or Br) have been reported [102]. Complexes with a range of other five-membered ring heterocycles have been described, and are thought to possess polymeric structures; examples of these complexes include $\text{HgLI}_2 \cdot 1.5\text{HgI}_2$ (L = bis(methylaminoantipyril)ethane) [103], HgL_6Cl_2 (L = 4-*n*-butyl-1,2,4-triazole, **52**) [104] and $\text{HgL}_2(\text{NO}_3)_2$ (L = 5-aminotetrazole, **53**) [105].

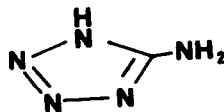
A number of complexes of benzimidazoles have been described in which the ligand may act as a neutral or anionic species; typical examples include $[\text{HgL}_2]$ and $[\text{Hg}(\text{HL})\text{Cl}_2]$ (HL = **54**; X = H, R = H or Me; X = NO_2 , R = H) [106,107].



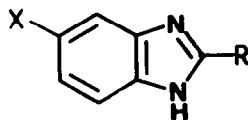
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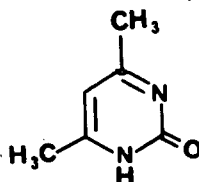
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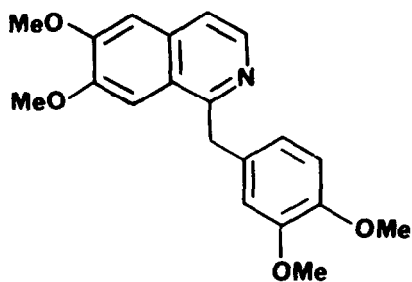


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The preparation of the complex $\text{Hg}(\text{py})_4(\text{O}_3\text{SCl})_2$ has been discussed in Section 2.1.2 [31]. Mercury(II) thiocyanate has been shown to form 1:1 complexes with 3- and 4-benzoylpyridines, in which the ligand is coordinated to the metal through the heterocyclic nitrogen only [108]. No complex with 2-benzoylpyridine could be isolated. Complexes with *N*-(2-pyridylmethyl) methanesulphonamide and *N*-(2-pyridylmethyl) trifluoromethanesulphonamide have been reported [109].

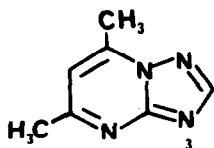
Studies of the vibrational spectra of a number of mercury(II) 2,2'-bipyridine complexes have been described [110]. The ligand transfer reactions discussed earlier (Section 2.1.2) have been used for the preparation of mercury(II) chloride adducts with 2,2'-bipyridine, 6,6'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 2,2':6',2''-terpyridine from the corresponding diphenyltin(IV) derivatives [36].

4,6-Dimethylpyrimidin-2(1*H*)-one (55) forms a number of complexes with mercury(II) halides; none appear to possess simple ionic structures [111]. Papaverine (56) reacts with mercury(II) chloride to give the complex $[\text{HgLCl}_2] \cdot \text{HCl}$, with the mercury interacting with the heterocyclic nitrogen atom [112].

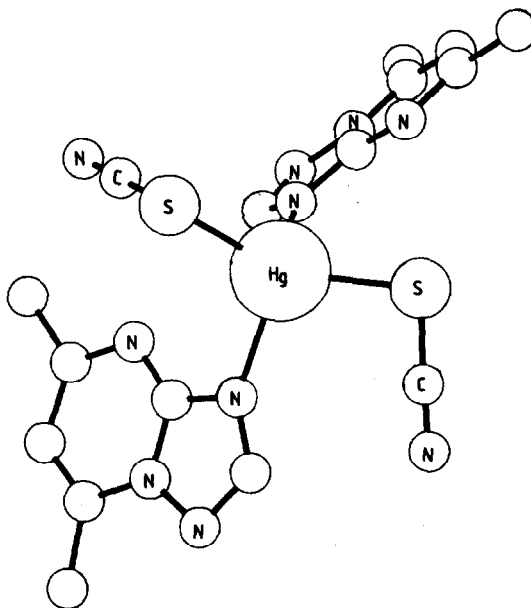


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A crystal structural analysis of the 1:2 complex of mercury(II) thiocyanate with 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (57) has been reported; the metal is in a distorted tetrahedral N_2S_2 environment, coordinated to N(3) of the heterocycle (58) [113]. The interaction of mercury(II) with 1-methylthymine has been investigated spectroscopically [114]. Complexes of

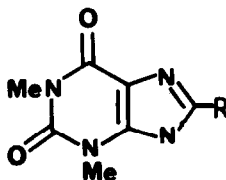


(57)



(58)

mercury(II) chloride with 4-alkoxybenzofuro[3,2-d]pyrimidines have been described [115]. A number of mercury(II) mediated reactions of **59** have been reported, and are discussed further in Section 2.5 [116]. The interaction of thiamine with mercury(II) chloride has been discussed earlier [27].



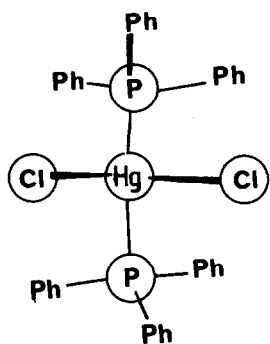
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2.1.5 Complexes with phosphorus and Group V donor ligands

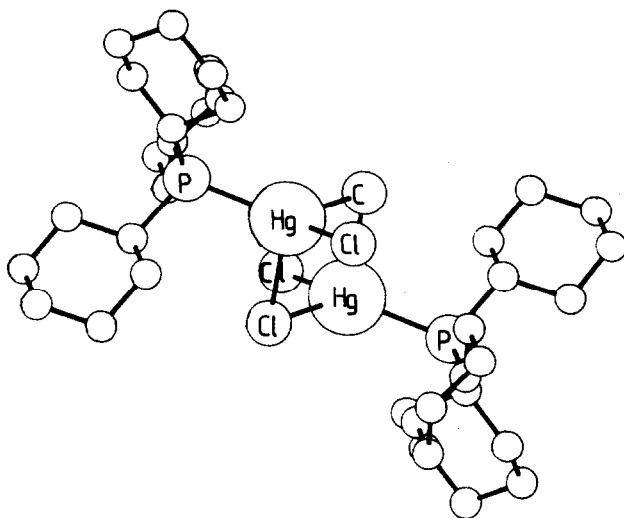
A single crystal structural analysis of the complex $[\text{HgCl}_2(\text{PPh}_3)_2]$ has been reported; the complex exists as discrete monomeric molecules with a distorted tetrahedral geometry about the mercury (**60**) [117]. The structure of $[(\text{cyc}_3\text{P})\text{Hg}(\mu\text{-Cl})_2\text{Cl}_2\text{Hg}(\text{cyc}_3\text{P})]$ has also been determined (**61**) [118]. Bell and his co-workers have surveyed the structural data available for 1:1 adducts of mercury(II) halides with tertiary phosphines [119]. They have also demonstrated that the vibrational spectra of these complexes are not usually characteristic, and that there is frequently little variation in the spectra with major changes in structure. The reaction of dichloro(ethyl)phosphine with ethoxycarbonylmethylzinc bromide results in the formation of the functionalised phosphine, $\text{EtP}(\text{CH}_2\text{CO}_2\text{Et})_2$, which forms mercury(II) complexes [120].

The complex $[\text{Hg}(\text{CN})_2(\text{dippe})]$ has been structurally characterised; infinite chains are formed with the diphosphine acting as a bridging bidentate ligand (**62**) [121]. The geometry about each mercury atom approximates to tetrahedral, although two mercury - phosphorus bond lengths (2.606, 2.534 Å) are observed. Shaw has previously described the formation of heterobinuclear complexes (**63**) from the reaction of $[\text{Pt}(\text{dppm})_2]\text{Cl}_2$ with $[\text{Hg}(\text{C CR})_2]$; further examples of these reactions [122] and the preparation of the palladium analogues [123] have now been reported.

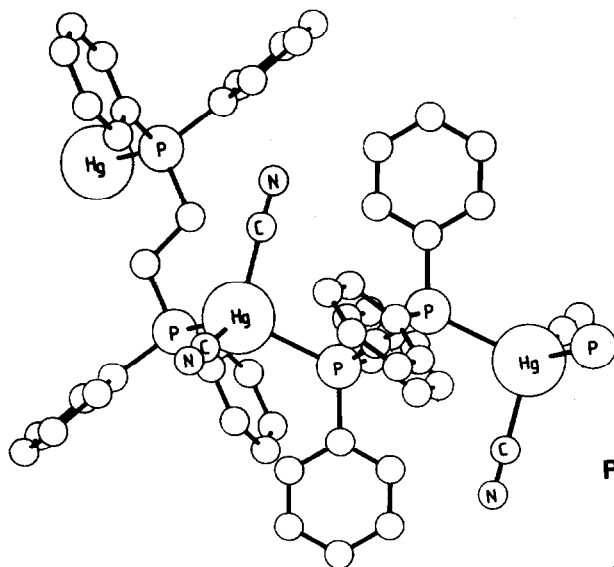
Mercury(II) trifluoromethanesulphonate forms 1:1 and 1:2 complexes with trimethyl and triethyl phosphites; the 1:2 complexes react with excess phosphite to give transient 1:3 complexes, which disproportionate to give



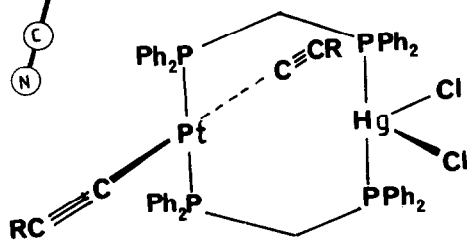
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(61)



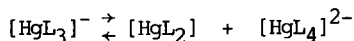
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(63)

$[\text{HgL}_2]^{2+}$ and $[\text{HgL}_4]^{2+}$ [124]. This behaviour is in contrast to that observed with phosphines.

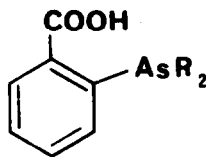
^{199}Hg NMR Spectroscopy has demonstrated the presence of two diastereoisomers of $[\text{HgL}_2]$ ($\text{HL} = \text{PhHP}(=\text{O})(\text{OBu})$) in solution; ligand redistribution reactions occur sufficiently rapidly to prevent isolation of the two diastereoisomers [125]. The disproportionation of 1:3 complexes is not limited to phosphites, and it has been shown that the equilibrium:



is also of importance when $\text{HL} = (\text{EtO})_2\text{HP}=\text{O}$ [126].

The reaction of $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CONEt}_2$ with aqueous acidic mercury(II) nitrate results in the formation of $\{(\text{EtO})_2\text{P}(\text{O})\text{CHCONEt}_2\text{Hg}(\text{NO}_3)\}$; the crystal structure of this complex has been reported [127]. The compound is dimeric, but the mercury is not bonded to the phosphorus of the ligand, instead it is bonded to the carbanionic carbon atom (64). The coordination number is brought up to five by interactions with two oxygen atoms of the nitrate anion, and two oxygen atoms of the phosphoryl and carbonyl groups of the other half of the dimer [127].

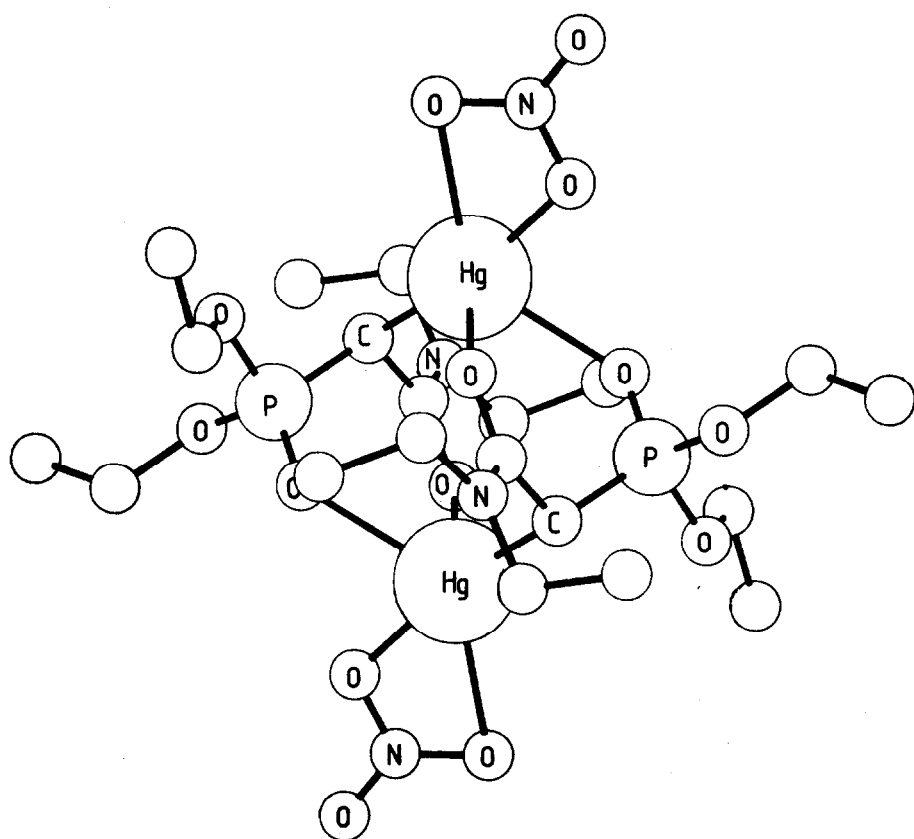
Mercury(II) complexes with a range of tertiary arsines have been reported [128], as has the compound $[\text{HgX}_2\text{L}]$ ($\text{L} = 65$) [129].



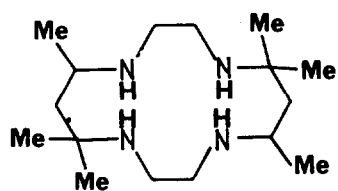
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2.1.7 Complexes with macrocyclic ligands

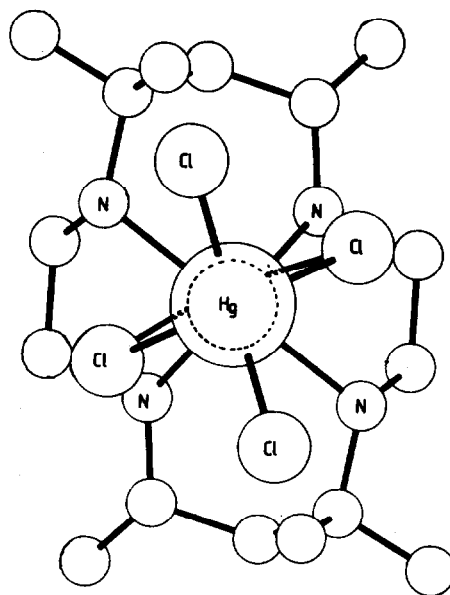
The crystal structure of the complex $2\text{HgCl}_2 \cdot \text{L}$ ($\text{L} = \text{rac}-5,5,7,12,12,14\text{-Me}_4\text{-}1,4,8,11\text{-[14]ane-N}_4$, 66) has been determined [130]. One mercury atom is slightly out of the N_4 plane, and connected to the second mercury by two bridging chlorines (67). The relative configuration at each chiral centre is $S(R), 4S(R), 7R(S), 8S(R), 11S(R), 14R(S)$ [130].



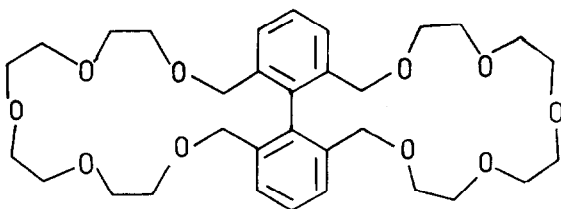
(64)



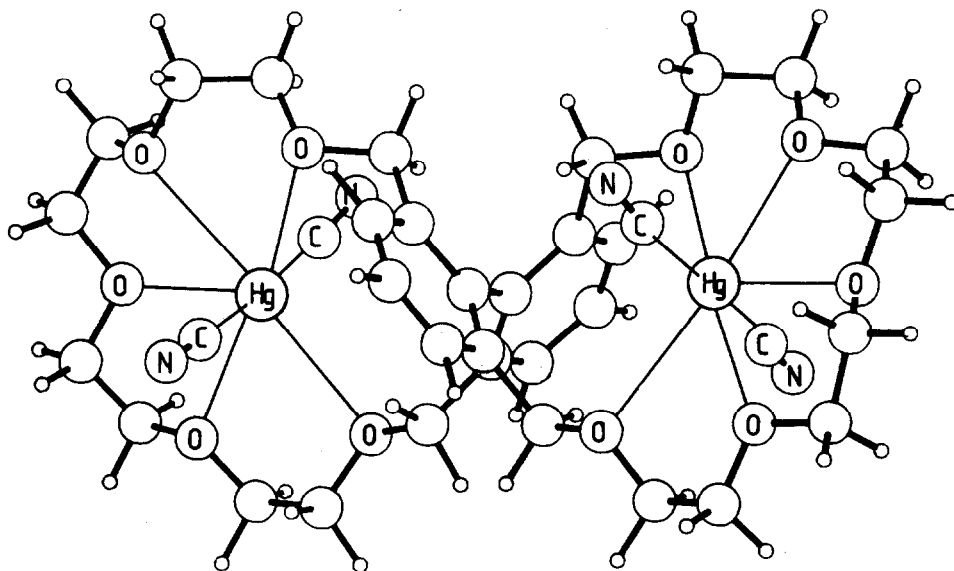
(66)



(67)



(68)



(69)

The unusual bismacrocycle (68) forms a 2:1 complex with mercury(II) cyanide, $[(\text{NC})_2\text{Hg}(\text{CN})_2]$ [131]. The crystal structure of the complex reveals each mercury to be in a slightly distorted pentagonal bipyramidal seven-coordinate environment (69) [131].

2.1.8 Aqueous solution chemistry of mercury(II)

Aqueous solutions of mercury(II) nitrate have been investigated by X-ray methods, and it is suggested that there are six water molecules in the first coordination sphere [30].

Interest continues in the mercury(II) assisted solvolysis of transition metal halo complexes. The thermal and photochemical behaviour of the binuclear species, $\text{trans}-[(\text{H}_3\text{N})_4(\text{H}_2\text{O})\text{Cr}(\text{NCS})\text{Hg}]^{4+}$, has been investigated [132]. Photochemical aquation gives $\text{cis}-[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$, whereas the thermal reaction gives rise to the *trans* isomer [132]. The aquation of a series of cobalt(III) complexes, $\text{cis}-[\text{CoCl}(\text{en})_2\text{L}]^{2+}$ ($\text{L} = \text{MeNH}_2$, $\text{HOCH}_2\text{CH}_2\text{NH}_2$, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, PrNH_2 , NH_3 , EtNH_2 or PhNH_2) has been investigated [133]. The release of thiocyanate from $\text{H}[\text{CoL}_2(\text{SCN})_2]$ ($\text{HL} = \text{dimethylglyoxime}$) is enhanced by aqueous mercury(II) salts. The release of both thiocyanate ions shows a linear dependence on the mercury(II) concentration, and mechanistic studies are compatible with an $\text{S}_{\text{E}}2$ route [134]. The aquation of $\text{cis}-[\text{CoCl}(\text{en})_2\text{L}]^{2+}$ ($\text{L} = \text{pyridine}$, 4-methylpyridine, 4-aminopyridine or 4-dimethylaminopyridine) has also been investigated [135].

Aquation reactions of organic halides are also accelerated by mercury(II) salts, and a number of studies of these reactions have been recently reported. The mercury(II) chloride catalysed solvolysis of a series of primary, tertiary and vinyl chlorides in aqueous dmsO, acetonitrile or ethanol has been studied [136, 137]. Mixtures of propan-1-ol and propan-2-ol result from the hydrolysis of 1-iodopropane in the presence of mercury(II) and magnesium(II) salts [138]. The isomerisation is favoured by high concentrations of Mg^{2+} ; the high concentrations of Mg^{2+} result in a decrease in the activity of the water, which in turn reduces the rate of hydrolysis of the intermediate ionic species, and hence favours the isomerisation [138]. Similar results are observed with 1-bromopropane and 1-iodobutane [138].

The oxidation of azide by *N*-bromosuccinimide in the presence of mercury(II) ethanoate has been investigated [139].

2.2 MERCURY(I)

2.2.1 Halide and pseudohalide complexes

A Raman spectroscopic study of the mercury(I) halides, Hg_2Cl_2 , Hg_2ClBr and Hg_2Br_2 , has been reported [140].

2.2.2 Complexes with oxygen donor ligands

A series of 1:1 complexes with the thioethers, $\text{RS}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SR}$ ($\text{R} = n\text{-propyl}$, $n\text{-butyl}$ or tert-butyl ; $n = 1, 2, 3$ or 5) [141]. The stability of the complexes decreases with increasing n , and as R becomes larger.

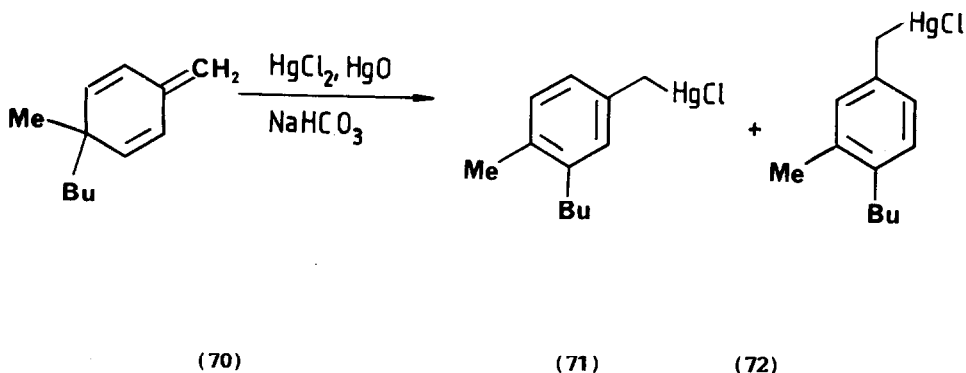
2.2.3 Complexes with nitrogen donor ligands

No complexes of mercury(I) in this category appear to have been described this year. The formation of tetrachloromercurate(II) salts in the reaction of Hg_2Cl_2 with 1,4-diazabicyclo[2.2.2]octane has already been discussed [74].

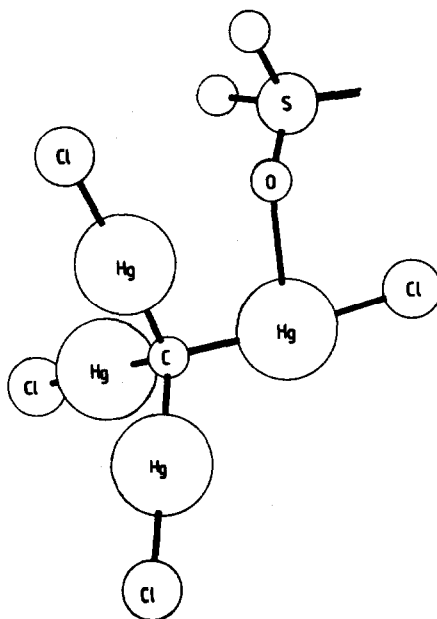
2.3 ORGANOMERCURY(II)

2.3.1 Halide and pseudohalide complexes

An attempt to correlate the spectroscopic properties of arylmercury(II) halides with Hammett σ_p parameters has been reported [142]. Pentabromobenzylmercury(II) bromide may be prepared in a direct synthesis, by the reaction of $\text{C}_6\text{Br}_5\text{CH}_2\text{Br}$ with metallic mercury in benzene at room temperature [143]. In dmf solution, in the presence of tetraethylammonium bromide, the reaction proceeds further, to give $[\text{Hg}(\text{C}_6\text{Br}_5\text{CH}_2)_2]$. A number of substitution and isomerisation reactions of 2-chlorovinylmercury(II) compounds have been described [144]. Benzylmercury(II) chlorides (71) and (72) are obtained in an oxidative rearrangement, when (70) is treated with a basic mixture of mercury(II) chloride and mercury(II) oxide in thf [145].

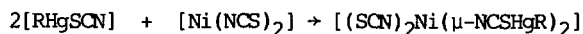
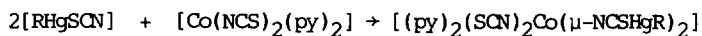


A crystal structural analysis of the complex $\text{C}(\text{HgCl})_4 \cdot \text{dmsO}$ has been reported; the complex is dimeric, and possesses a complex structure (73) [146].



(73)

A range of polynuclear complexes derived from organomercury(II) thiocyanates have been reported [147-151]. The characteristic feature of these complexes is a bridging thiocyanate, *S*-bonded to mercury and *N*-bonded to the other transition metal. Typical examples of these complexes are shown below:

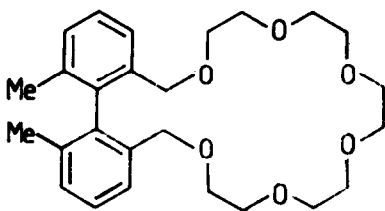


The complexes readily undergo substitution reactions, although the products are not always those expected. Thus, reaction with 2,2'-bipyridine or 1,10-phenanthroline gives the coordination isomers, $[\text{M}(\text{bipy})_3][\text{Hg}(\text{SCN})_4]$.

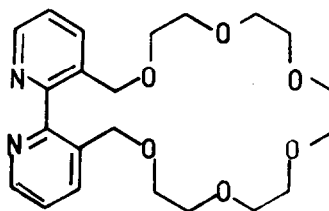
2.3.2 Complexes with oxygen donor ligands

The biphenyl derivatised crown ether (74) forms a 1:1 complex with $[\text{Hg}(\text{CF}_3)_2]$; the crystal structure of this complex has been reported, and it is seen that the metal is bound to only five of the ether oxygen atoms, and is in

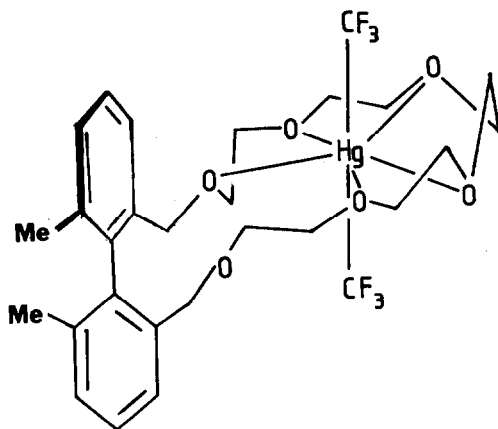
a distorted pentagonal bipyramidal environment [131]. The related ligand, 75, also forms a 1:1 complex with $[\text{Hg}(\text{CF}_3)_2]$ [152]. This complex is of particular interest as it provides a working model for allosteric effects, in which metal binding at one site has a consequence at a remote binding site. The rate of mercury loss from the 1:1 complex previously mentioned is retarded approximately seven times in the presence of palladium(II). This is compatible with palladium binding to the 2,2'-bipyridine and forcing it into a near planar configuration. This has a consequence on the conformation of the crown ether macrocyclic ring, such that it is more difficult for the bulky trifluoromethyl groups to pass through.



(74)



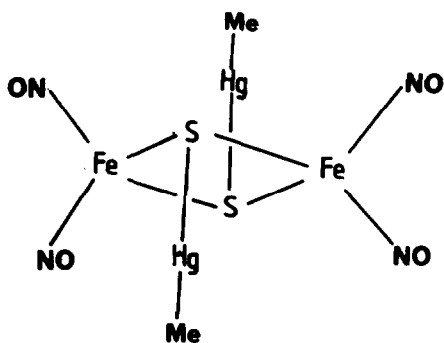
(76)



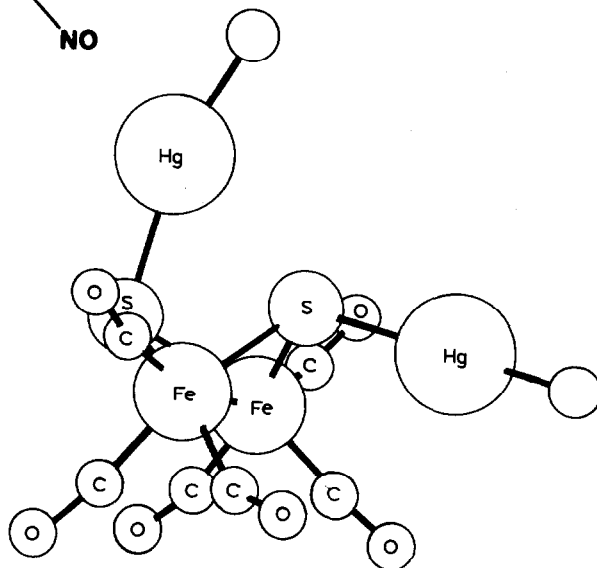
(75)

2.3.3 Complexes with sulphur donor ligands

The vibrational spectra of a series of phenylmercury(II) compounds, $[\text{PhHgSR}]$ ($\text{R} = \text{phenyl, 1-naphthyl, 2- or 4-pyridyl or 8-quinolyl}$) have been studied [153]. Fluorinated derivatives of these complexes have been investigated by ^{19}F NMR spectroscopic methods [154]. The reaction of methylmercury(II) chloride with the cluster anion, $[(\text{NO})_4\text{Fe}_2(\mu\text{-S})_2]^{2-}$, has been investigated [155]. The product of the reaction is the novel cluster, $[\text{Fe}_2(\text{NO})_4(\mu\text{-SHgMe})_2]$, in which the linear MeHgS units are mutually *trans* (77) [155]. The crystal structure of the carbonyl cluster, $[\text{Fe}_2(\text{CO})_6(\mu\text{-SHgMe})_2]$ (78) has also been determined [155].



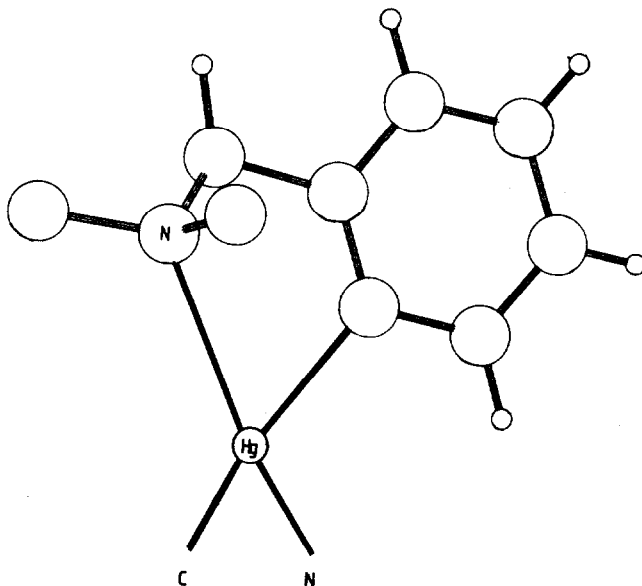
(77)



(78)

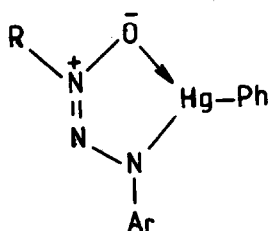
2.3.4 Complexes with nitrogen donor ligands

Mercury(II) chloride reacts with 2-dimethylaminomethylphenyllithium to give the expected cyclometallated complex, $[\text{HgL}_2]$ (HL = dimethylaminobenzene) [156]. A crystallographic investigation of this complex has shown the mercury to be in a near planar coordination geometry, with a linear *trans* C - Hg - C system (79).

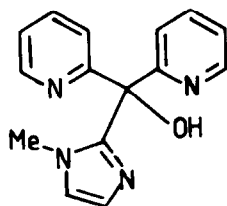


(79)

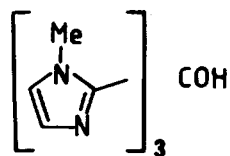
A number of arylmercury(II) complexes with 4-arylazobenzoic acids have been reported, and a number of different bonding modes and tautomeric forms postulated [157]. The reaction of triazene-1-oxides, $\text{ArNHN}=\text{NR}$, with phenylmercury(II) ethanoate has been investigated [158]. The product, $[\text{PhHgL}]$ (HL = $\text{ArNHN}=\text{NR}$), behaves as a monomer in benzene solution, and is thought to have the structure indicated in (80). The interaction of methylmercury(II) with imidazole, 1-methylimidazole and the 1,3-dimethylimidazolium cation has been studied using ^1H NMR techniques [101]. The binding site varies amongst these substrates; imidazole binds at N(1) and N(3), 1-methylimidazole at N(3) and C(2), and the 1,3-dimethylimidazolium cation at C(2). The ligands (81) and (82) are potentially chelating or bridging species, and their interaction with methylmercury(II) has been investigated [159]. Both ligands form complexes of



(80)

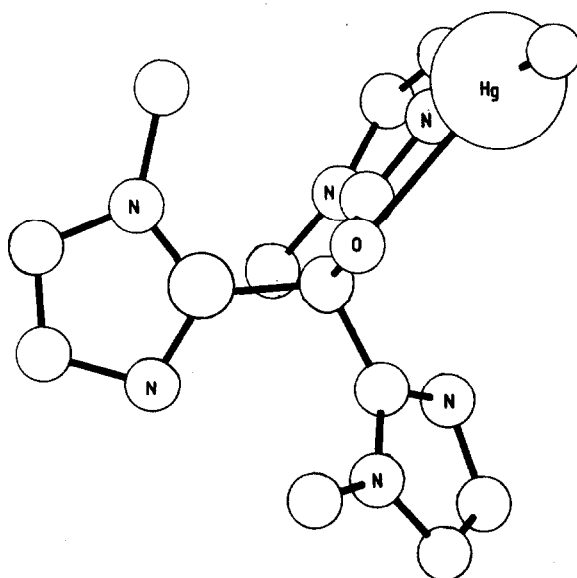


(81)



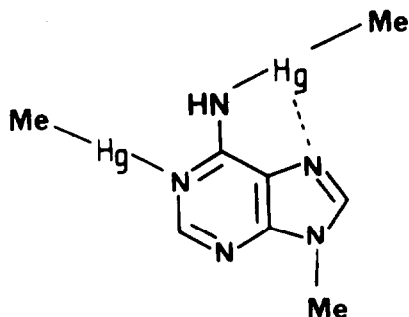
(82)

the type $[\text{MeHgL}][\text{NO}_3]$ ($\text{L} = \mathbf{81}$ or $\mathbf{82}$), and a structural study of the complex with $\mathbf{82}$ has been reported. The mercury is bonded to the heterocyclic nitrogen, and also shows a weak interaction with the hydroxyl group, to give a T-shaped trigonal coordination about the metal ($\mathbf{83}$).



(83)

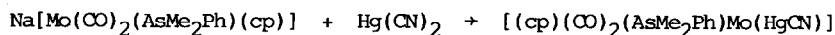
A crystal structural analysis of the complex $[(\text{MeHg})_2\text{L}]$ ($\text{HL} = 9\text{-methyladenine}$) has been described; the structure is as shown in **84**, with one methylmercury bonded to the deprotonated amine group [161]. A study of the vibrational spectra of methylmercury(II) complexes with 1-methylthymine has also been described [114].



(84)

2.4 COMPOUNDS WITH MERCURY-HETEROMETAL BONDS

A large number of complexes of the type $[(\text{cp})(\text{CO})_2\text{Mo}(\text{L})(\text{HgX})]$ ($\text{L} = \text{CO}$, $\text{P}(\text{OMe})_3$, PPh_3 or AsMe_2Ph ; $\text{X} = \text{Cl}$, Br , I , S_2COEt , $\text{S}_2\text{P}(\text{OEt})_2$, S_2CNET_2 , CN or $\{\text{Mo}(\text{CO})_3(\text{cp})\}$) have been described [162,164]. Typical preparations involve the treatment of mercury(II) salts with $\text{Na}[\text{Mo}(\text{CO})_2\text{L}(\text{cp})]$:



Crystal structural analyses have been reported for the complexes $[(\text{cp})(\text{CO})_3\text{Mo}(\text{S}_2\text{CNET}_2)]$ [162] (**85**) and $[(\text{cp})(\text{CO})_2(\text{AsMe}_2\text{Ph})\text{Mo}(\text{HgCN})]$ (**86**) [164]. The dithiocarbamate is bonded to **85** in an unsymmetrical manner, with bond lengths of 2.51 and 2.737 Å. The weakly bonded sulphur also exhibits another contact with a second mercury atom at 3.064 Å.

The related complexes, $[\text{Hg}(\mu\text{-PPh}_2\text{M}(\text{CO})_5)_2\text{L}_n]$ ($\text{M} = \text{Cr}$, Mo or W ; $\text{L} = \text{bipy}$ or phen), have been investigated by ^{31}P NMR spectroscopy [163].

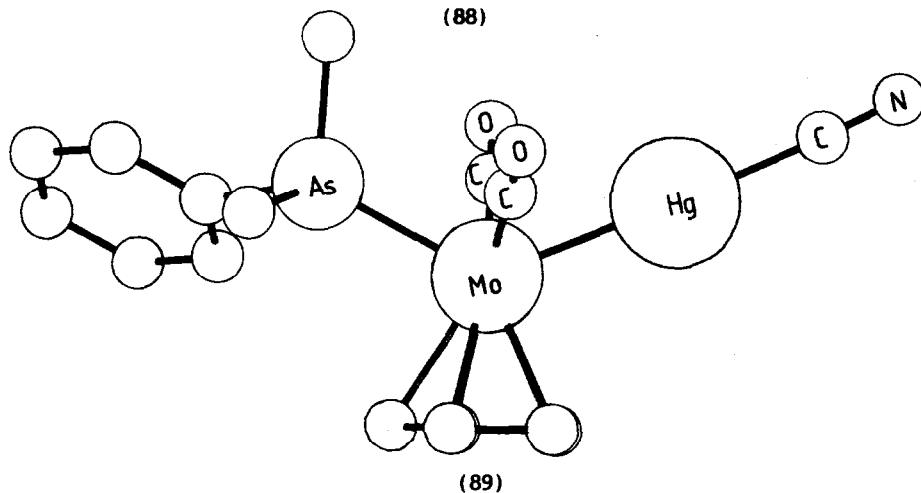
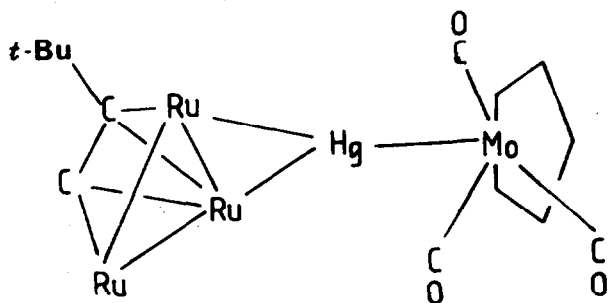
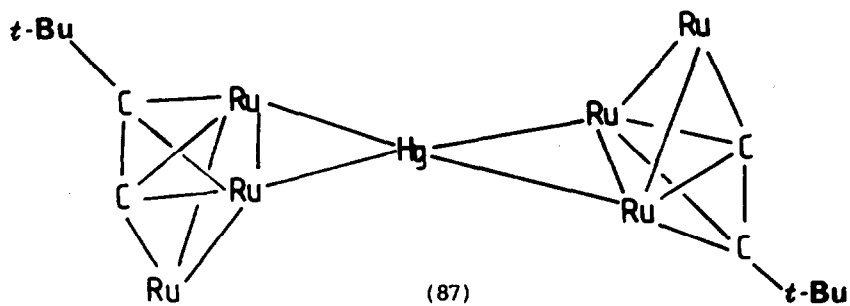
Mercury-metal bonded species result from the reaction of $[(\text{cp})\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mn}$ or Re) or $[(\text{C}_6\text{H}_6)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr}$, Mo or W) with mercury(II) ethanoate or



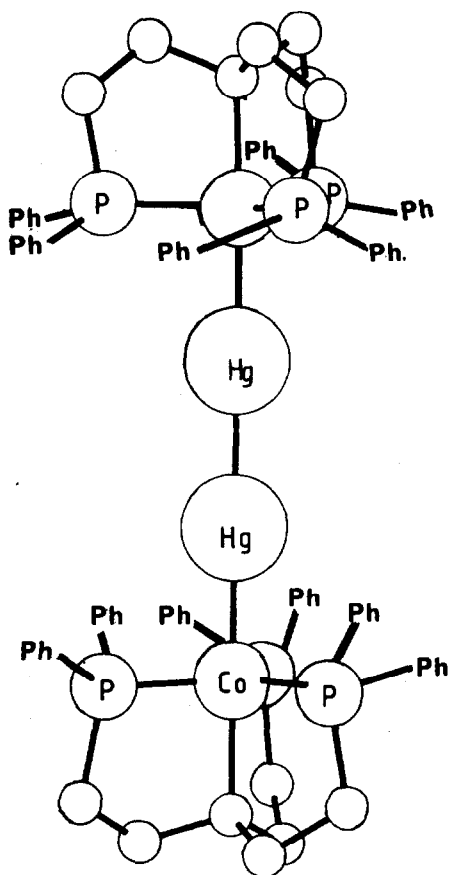
trifluoroethanoate [165].

A number of fluorinated iron-mercury derivatives have been prepared by the reaction of $[(\eta^3\text{-C}_3\text{F}_7)\text{Fe}(\text{CO})_4\text{I}]$ with HgFX ($\text{X} = \text{F}$, Ph or HgF); the products are $[(\eta^3\text{-C}_3\text{F}_7)\text{Fe}(\text{CO})_4]$, $[(\eta^3\text{-C}_3\text{F}_7)\text{Fe}(\text{CO})_4]_2\text{Hg}$ and $[(\eta^3\text{-C}_3\text{F}_7)\text{Fe}(\text{CO})_4\text{Hg}(\eta^3\text{-C}_3\text{F}_7)]$ [166]. The latter compound is also prepared by the direct reaction of metallic mercury with $[(\eta^3\text{-C}_3\text{F}_7)\text{Fe}(\text{CO})_4\text{I}]$. A number of mixed-metal triruthenium cluster compounds have been reported [167]; crystal structural analyses have been described for the compounds $[\text{Hg}\{\text{Ru}_3(\text{CO})_9(\text{CC}^t\text{Bu})\}_2]$ (87) and $[\text{Ru}_3(\text{CO})_9(\text{CC}^t\text{Bu})\text{HgMo}(\text{CO})_3(\text{cp})]$ (88). The complex $[\text{Ru}(\text{CF}_3)(\text{HgCF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (89) results from the reaction of $[\text{Hg}(\text{CF}_3)_2]$ with $[\text{Ru}(\text{CO})_n(\text{PPh}_3)_m]$ (n or $m = 2$ or 3) [168]. The complex is octahedral with *trans* phosphine groups, and the mercury *trans* to a carbonyl group [168].

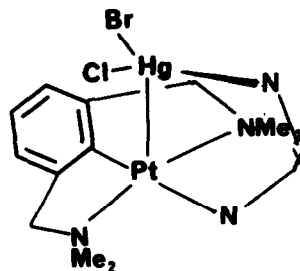
A spectroscopic investigation of the complexes $[\text{Hg}(\text{vwwv}_v\text{v}_2)]$ ($\text{L} = \text{PR}_3$) has been described [169]. The above trinuclear complex ($\text{L} = \text{CO}$) reacts with sodium amalgam or metallic mercury to give a series of products; amongst the characterised products are $[\text{Hg}\{\text{Co}(\text{CO})_4\}_3]^-$ and $[\text{Hg}\{\text{Co}(\text{CO})_4\}_2\text{Cl}]^-$ [170]. Cobalt-mercury bonded complexes also result from the sodium amalgam reduction of $[\text{CoL}(\text{Cl})]^+$ ($\text{L} = \text{E}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$; $\text{E} = \text{N}$ or P); a crystal structural analysis of the unusual bridged compound, $[\text{LCo}(\mu\text{-Hg})_2\text{CoL}]$ (90), has also been reported



[171]. Tetrakis(triphenylphosphine)nickel(0) reacts with a range of mercury(II) complexes to form nickel-mercury bonded species [160]. The

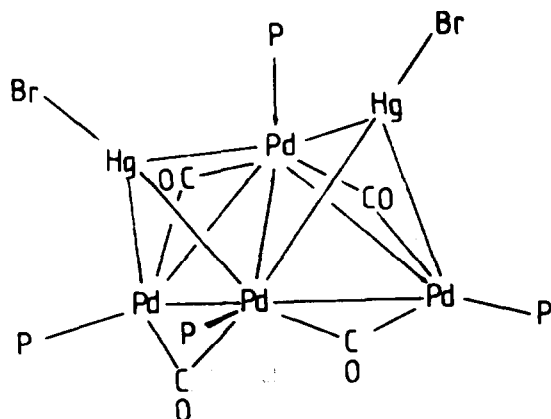


(90)

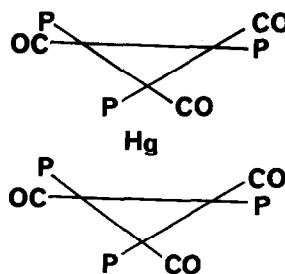


(91)

cyclometallated square-planar complex $[\text{LPtBr}]$ ($\text{HL} = 1,3\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$) reacts with $[\text{ClHg}(\text{ArNXNR})]$ ($\text{X} = \text{CH}$ or N) to give $[\text{LPtHg}(\text{ArNXNR})\text{ClBr}]$, which is thought to have the structure (91) [172]. Another platinum-mercury bonded complex, $[(\text{PPh}_3)_2\text{ArPtHgAr}']$, is prepared by the reaction of $[\text{HgAr}_2]$ with $[\text{Pt}(\text{PPh}_3)_3]$ [173]. The hexanuclear cluster, $[\text{Pd}_4(\text{CO})_4(\text{PET}_3)_4(\text{HgBr})_2]$, has been structurally characterised, and shown to possess a bis-face-capped butterfly structure (92) [174]. Metallic mercury reacts with $[\text{Pd}_4(\text{CO})_5(\text{PET}_3)_4]$ to give a heptanuclear cluster, $[\text{Hg}(\text{Pd}_3(\text{CO})_3(\text{PET}_3)_3)_2]$, which is thought to possess the structure (93) [175].



(92)

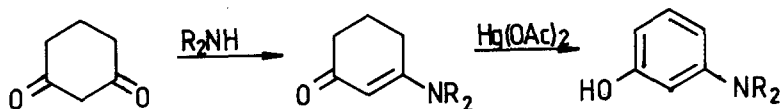


(93)

The complexes $[R(HgYb)I.(thf)_4]$ are prepared by the reaction of metallic ytterbium with $[RHgI]$ ($R = cp, CF_3$) [176].

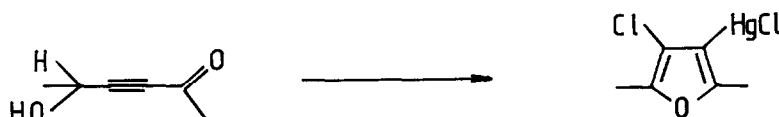
2.5 MERCURY IN ORGANIC SYNTHESIS

The use of mercury(II) compounds as oxidising agents has been investigated by a number of groups. Mercury(II) acetate oxidises acid hydrazides, $ArCONHNH_2$; a kinetic study has shown that two mechanisms for the oxidation are operative. Either the terminal amino group may coordinate to the metal ion, followed by cleavage of the C-N bond to give an acylium ion, $[ArCO]^+$, and a hydrazyl radical, $[H_2NNH^\bullet]$, coordinated to mercury(I), or a four electron transfer may occur, *via* $ArCON=NH$ [177]. The oxidation of 1,4-dihydroxybenzene to 1,4-benzoquinone by mercury(II) perchlorate in perchloric acid has also been studied [178]. A new route to 3-aminophenols, in which the key step is mercury(II) acetate oxidation of a 3-aminocyclohex-2-enone, has been described (Scheme 1) [179].



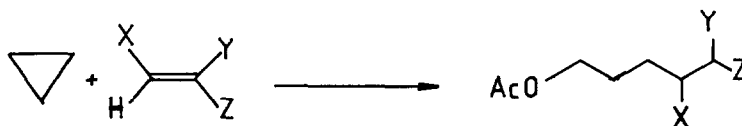
Scheme 1

Reactions of acetylenes with mercury(II) complexes have been known for many years, and continue to be of interest. A mechanistic study of the mercury(II) acetate catalysed hydration of acetylene has been reported; in acetic acid, the products are vinyl acetate and $\text{MeCH}(\text{O}_2\text{CCH}_3)_2$ which arise from a common intermediate, $\text{CH}_3\text{CO}_2\text{HgCH}=\text{CH}(\text{O}_2\text{CCH}_3)$ [180]. Acetylenic alcohols undergo hydration and/or isomerisation reactions upon treatment with aqueous perchloric acid solutions of mercury(II); the products are enones or hydroxyketones [181]. The normal addition of mercury(II) compounds to acetylenes is anti, although evidence is presented for syn addition to 4-hydroxy-2-alkyn-1-ones. Dehydration of the addition products gives 3-furylmercury(II) derivatives (Scheme 2) [182].



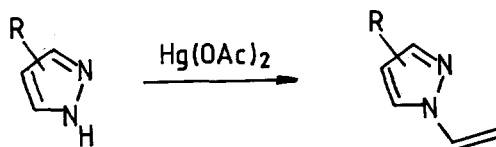
Scheme 2

Mercury(II) catalysed reactions of olefins continue to be of interest, and a number of such reactions have been reported this year. A useful three-carbon chain lengthening process involving the reaction of olefins with cyclopropanes in the presence of acetic acid solutions of mercury(II) acetate followed by demetallation (Scheme 3) has been described [183]. Pyrazoles and tetrazoles



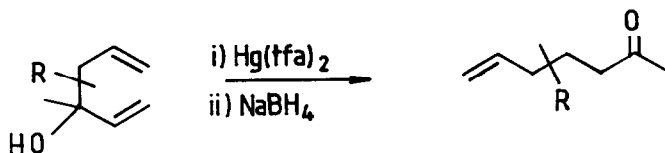
Scheme 3

react with vinyl n-butyl ether in the presence of 1,4-dihydroxybenzene and mercury(II) acetate to give N-vinyl compounds (Scheme 4) [184]. Rearrangement



Scheme 4

to enones occurs when 1,5-hexadiene-3-ols are treated with mercury(II) trifluoroacetate followed by borohydride demetallation (Scheme 5) [185].



Scheme 5

Divinyl sulphide undergoes desulphurisation upon treatment with mercury(II) chloride, to yield $\text{CH}_3\text{CH}(\text{OEt})_2$ [186].

The bromination of phenols by iodine monobromide in the presence of mercury(II) acetate and acetic acid has been studied; the first step is thought to be mercuriation of the aromatic ring, which is supported by the observed rate equation which is first order in the phenol and mercury(II) acetate, and zeroth order in iodine bromide [187].

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