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2. MERCURY

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CONTENTS

INTRODUCTION

This review is a continuation of the 1980 Review of mercury published in this journal in 1982 [1]. The format and content is similar to that adopted in the 1980 review, and also to that in the zinc and cadmium reviews in this series. An attempt to review the more important developments in the use of mercury in organic synthesis has been made. A large number of papers dealing with the physical and spectroscopic properties of mercury halides and related species have been ignored in this review as they were thought to be of little interest to the coordination chemist.

I should like to thank Dr. Olga Kennard and Dr. Sharon Bellard for their aid in obtaining structural data from the Cambridge Crystallographic Data Centre.

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2.1 MERCURY(II)

2.1.1 Halide and pseudohalide complexes

The single crystal structure of $HgCl_2$ has been redetermined, and the authors make comment on the problem of attack at the surface of the hygroscopic crystal by water. However, recrystallisation from toluene gave satisfactory crystals, from which an <Cl-Hg-Cl angle of 178.9° and an Hg-Cl distance of 2.291 Å were determined [2]. The solubility of $HgCl_2$ in perchloric acid has been investigated, and a value for ΔH°_{form}(crystalline $HgCl_2$) of -54.77 ± 0.13 kcal mol^{-1} calculated [3]. The formation of the mixed complexes HgXY continues to be of interest, and spectroscopic studies of HgX_2 and HgXY (X,Y = halide or pseudohalide) have been reported [4,5]. Russian workers have demonstrated that the solvation term, ΔG°_{solv} for the process:

$$HgX_2 + HgY_2 \rightleftharpoons 2HgXY$$

is near zero [4]. A series of HgXY species (X = CN; Y = SCN, Br, OH etc.) have been characterised in aqueous solution, and the thermodynamic parameters for their formation determined [6]. Although HgClBr is formed on dissolution of $Hg[ClO_4]_2$ in aqueous solutions containing sodium bromide and chloride ($\Delta G^\circ_{form} = -39.15\pm0.22$ kcal mol^{-1}, $\Delta H^\circ_{form} = -44.13\pm0.17$ kcal mol^{-1}, $\Delta S^\circ = 46.3\pm0.9$ e.u.) [7], there is no hard evidence for the formation of a stable solid HgICl species in the HgI_2-HgCl system at room temperature [8]. The formation of the mixed complexes HgXY (X = halide; Y = SCN) in dmso has been investigated [9].

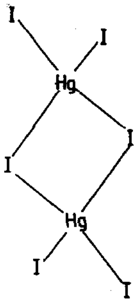
The pseudohalide complexes $[HgX_2L_2]$ (X = $N(CN)_2$, $C(CN)_3$, $ONC(CN)_2$, SCN; L = MeCN, dmf, dma, dmso) have been described, and it is proposed that the solvent molecules are coordinated to the metal through oxygen, to give a pseudo-tetrahedral geometry about the mercury [10-12]. The stability of these complexes is $Cl>Br>I>SCN>N(CN)_2>ONC(CN)_2 > C(CN)_3$ and MeCN>dma>dmf>dmso , the non-linear pseudohalide ions giving the least stable complexes. A combination of Raman spectroscopic and diffraction techniques have been applied to the study of solutions of $Hg(SCN)_2$ in dmso, and it is thought that a pseudo-octahedral structure, with four coordinated dmso molecules, is adopted, to give an S_2O_4 environment about the metal [13].

A number of workers have investigated the equilibrium:

$$HgX_2 + 2X^- \rightleftharpoons [HgX_3]^- + X^- \rightleftharpoons [HgX_4]^{2-}$$

and, as expected, the precise constitution of solutions containing HgX_2 and X^- depends on the concentration and nature of X, and the solvent. Studies of the HgI_2-I^- system in the presence of organic cations have shown that the predominant anionic species is

[HgI$_3$]$^-$ [14], and, indeed, the solid salt [Pr$_4$N][HgI$_3$] has been isolated [15]. Raman and far infra-red spectroscopic studies, and a single crystal structural analysis, have demonstrated the anion to consist of dimeric [HgI$_3$]$^-$ units, with each mercury atom tetrahedrally coordinated to four iodine atoms, in such a way that the two tetrahedra are edge sharing (1) [15]. The interaction of HgI$_2$ with LiI in the solid state has also been investigated. A number of 1-alkylpyridinium salts with [HgX$_3$]$^-$ (X = Cl, Br or I) have been investigated [16], and the reaction of HgI$_2$ with [Ar$_2$HgREt]I shown to result in the formation of [Ar$_2$HgREt][HgI$_3$][17]. Among the species formed in the reaction of [SCN]$^-$ with Hg^{2+} in dmso is the pseudotetrahedral anion [Hg(SCN)$_3$(dmso)]$^-$ [13]. A crystal structural analysis of Cs[HgBr$_3$] has been reported, and the anion shown to consist of tetrahedrally coordinated mercury atoms, with the tetrahedra sharing vertices [18]. A crystal structural analysis of [PhCH$_2$NH$_3$][HgCl$_3$] has also been reported, and has revealed the anion to possess two short (2.3 Å) and two long (2.9 Å) Hg-Cl bonds, and to adopt a linear structure [19]. One of the mercury atoms has a fifth contact with a chlorine atom at 3.27 Å, and the cation is located between the Hg$_2$Cl$_5$ chains. The reaction of L-tryptophan with HgCl produces the complex [L$_2$H][HgCl$_3$](L$_2$H = 2), in which the anion has been demonstrated crystallographically to be a polymeric chain with HgCl$_3$ units [20].



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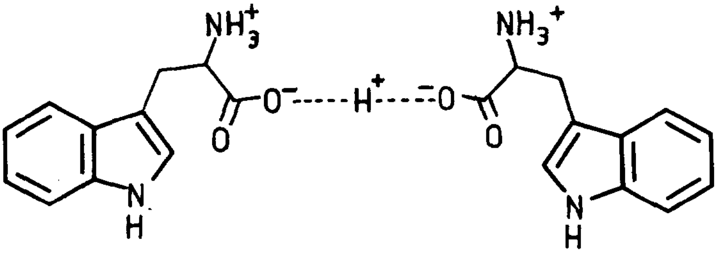

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The mixed anion $[Hg(CN)_2Cl]^-$ is formally present in the compounds $[MHg(CN)_2Cl].H_2O$ (M = Na or K), but a crystal structural analysis has demonstrated the existance of isolated $Hg(CN)_2$ units in an MCl lattice [21]. The cationic species $[Me_2N{=}CClNMe_2]^+$ (L^+) is known to act as a source of bis(dimethylamino)carbene, but on reaction with $HgCl_2$ the only isolated species were the complexes $L[HgCl_3]$, $L[HgCl_3].HgCl_2$ and $L_2[HgCl_4]$[22].

The tetrahedral anions $[HgX_4]^-$ (X = halide or pseudohalide) continue to be of interest, and Raman studies of $K_2[Hg(CN)_4]$ in the solid state [23] and in aqueous solution [24] have been reported. The solid state study suggests that the compound may exhibit a tetragonal distortion of the $[Hg(CN)_4]^{2-}$ ion at room temperature, which gives rise to a distortion from cubic symmetry. A crystal structure analysis of $L_2[HgBr_4]$(L = D,L-homocysteine thiolactonium), formed in the reaction of $HgBr_2$ with D,L-homocysteine, has been reported, and the anion shown to adopt a polymeric chain [20]. A crystal structure of $[Hg(SCN)_4Co(dmf)_2]$, which is formed from the reaction of $[Hg(SCN)_4Co]$ with dmf, has been reported [25]. The compound is polymeric, with four *S*-bonded thiocyanates coordinated tetrahedrally about the mercury atom (Hg-S 2.525 Å), and with the cobalt atom coordinated to one thiocyanate group of each of four $Hg(SCN)_4$ units and two dmf molecules, to give an octahedral *cis*-CoO_2N_4 unit. In dmso the $[Hg(SCN)_4]^{2-}$ ion appears to be tetrahedral [13]. A number of compounds of stoichiometry $[MHg(ECN)_4L_x]$ and $[MHg(SCN)_2(SeCN)_2L_x]$ (E = S or Se; M = Co or Ni; L = amide or thioamide; x = 2 or 4) have been reported, and structures have been proposed on the basis of spectroscopic studies [26].

Other complexes containing $[HgX_4]^{2-}$ ions reported this year include the $[Fe(cp)_2]^+$ salt, from the reaction of ferrocene with excess $HgCl_2$ [27] and a series of 1-alkylpyridinium salts $L_2[HgX_4]$ (X = Cl, Br, I, or SCN) [16]. The effect of γ-irradiation on solutions of $HgCl_2$ in hydrochloric acid has been investigated [28].

A detailed investigation of ^{199}Hg chemical shifts in a large range of $[HgX_4]^{2-}$, $[HgX_3Y]^{2-}$ and $[HgX_2Y_2]^{2-}$ species has been reported, and is discussed in further detail in section 2.5 [29].

Compounds formulated as $Pb[MHg(SeCN)_6]$ (M = Co or Ni) have been reported, and a number of their reactions with Lewis bases described [30]. Mass spectroscopy has been used to identify a species $[HgAlCl_5]$ formed in the reaction of $HgCl_2$ with $AlCl_3$ [31]. The systems $Cs_2[HgBr_4]$-$Cs_2[HgI_4]$ and $Cs[Hg_2Br_5]$-$Cs[Hg_2I_5]$ have been investigated thermochemically [32], and highly conducting solids of stoichiometry $L_{1.25}[Hg_2I_5]$ (L = tetrathiotetracene) or $L_3[Hg_2I_5]$ (L = tetraselenotetracene) from the reaction of a benzonitrile solution of the appropriate ligand with HgI_2 [33]. The compounds are probably of the cation-radical type.

2.1.2 Complexes with oxygen donor ligands

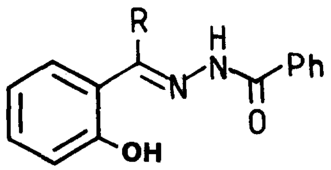
The crystal structure of mercury(II) sulphate has been redetermined, and the metal shown to be in a very distorted HgO_4 tetrahedron ($<$ O-Hg-O from 84.4° to 143.4°) [34].

A number of sulphoxide complexes have been investigated, and the oxidation of $[(Bu_2S)_2HgCl_2]$ by hydrogen peroxide has been shown to result in the formation of $[(Bu_2SO)HgCl_2]$ [35]. A crystal structure analysis has shown that the metal is in a tetragonal pyramidal Cl_4O environment, with the sulphoxide bonding to the metal through the oxygen atom. Although mercury(II) trifluoromethylsulphonate salts are of some considerable interest, they are inconvenient to handle, and the solid salts $[Hg(dmso)_6][F_3CSO_3]_2$ has been shown to possess attractive properties as a stable alternative. The ligands are coordinated *via* oxygen (ν Hg-O 405 cm^{-1}), and a ^{199}Hg n.m.r. study of a series of derivatives has been reported. The compound is very reactive, and interacts with Ph_2Hg and mercury to give $[PhHg(dmso)_2][F_3CSO_3]$ or $[Hg(F_3CSO_3)]$ respectively [36]. The electrochemistry of mercury(II) compounds in dmso solution, in which ions $[Hg(dmso)_x]^{n+}$ are presumably formed, has been investigated [37]. The metal is considerably less 'noble' in dmso than in water, as is demonstrated by the electrode potentials (E°, mV, Ag/AgCl = 0):

	dmso	H_2O
Hg/Hg^{2+}	-301	-51
Hg/Hg_2^{2+}	-342	-4
Hg_2^{2+}/Hg^{2+}	-261	106

A 1:1 complex with the tetrapod ligand *cis,cis,cis* -1,2,3,4-cyclopentanetetracarboxylic acid has been described [38].

The complex $[HgL_2]$ (HL = 3) has been described, and the ligand is thought to act as a tetradentate *N,N',O*-donor (4) [39].



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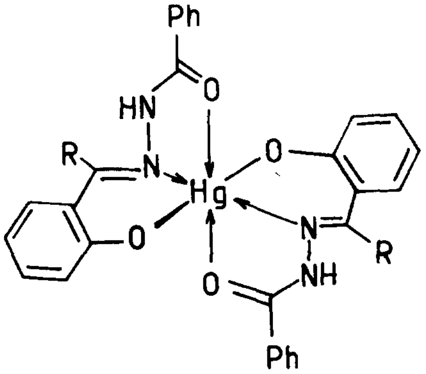
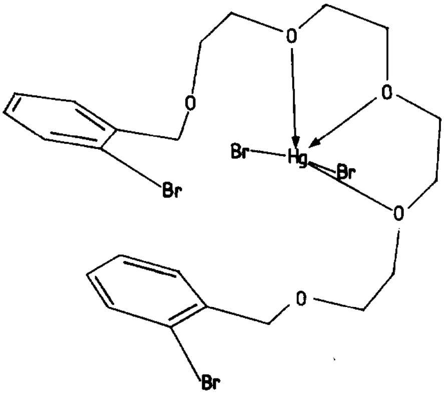


(4)

4-Aminobenzophenone has been shown to form mercury(II) complexes in which it is coordinated to the metal through oxygen rather than nitrogen[40]. The extraction of mercury from aqueous solution by salicylaldoxime in CCl_4 has been studied [41].

The crystal structure of [$HgLBr_2$] (L = 1,15-bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane) has been reported: the metal is seven coordinate, and bonds to the five oxygen atoms and the two ionic bromide ions (5). There is no evidence for any interaction between the metal and the bromo substituents on the aromatic rings [42].



(5)

A 1:1 complex of benzo[c]cinnoline *N,N'*-dioxide with $HgCl_2$ has been reported, and it is suggested that the compound is dimeric [43].

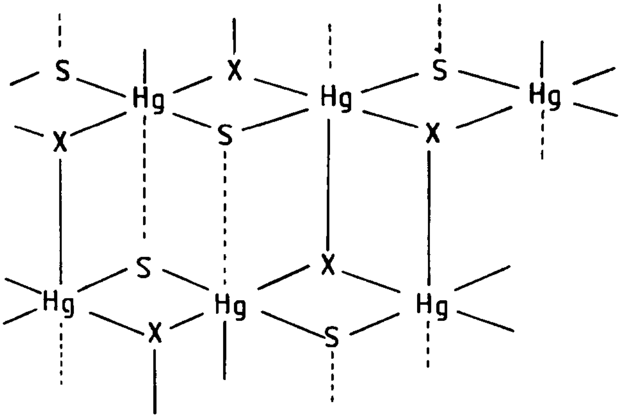
The complexes [$Hg(Ph_3EO)_4$][ClO_4]$_2$ (E = P or As) have been described [44], as have [$Hg(Et_3PO)_2Cl_2$] and [$Hg(Et_3PO)Cl_2$] [45]. The use of tri-n-octylphosphine oxide in benzene solution for the extraction of mercury(II) from aqueous chloride medium has been investigated [46].

2.1.3 *Complexes with sulphur and selenium donor ligands*

2.1.3.1 *Thiols*

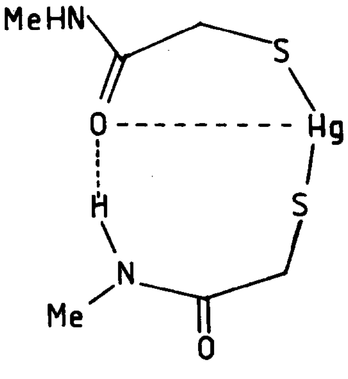
Two groups have reported studies of the vibrational spectra of [RSHgX] species (R = Me, Et, Pr, Bu; X = Cl, Br or I) [47,48]. Canty has investigated the [MeSHgX] (X = Cl or Br) system, and has proposed a polymeric structure in which the mercury is in a pseudo-octahedral environment (6), and advises caution in assigning structures on the basis of apparently simple vibrational spectra [48] . A study of the infra-red and Raman spectra of a series of [RSHgX] species has demonstrated the formation of a range of monomeric, dimeric and polymeric structures in the solid state, but has established the compounds to be monomeric in pyridine solution [47]. In pyridine solution the equilibrium:

$$2RSHgX \rightleftharpoons Hg(SR) + HgX$$



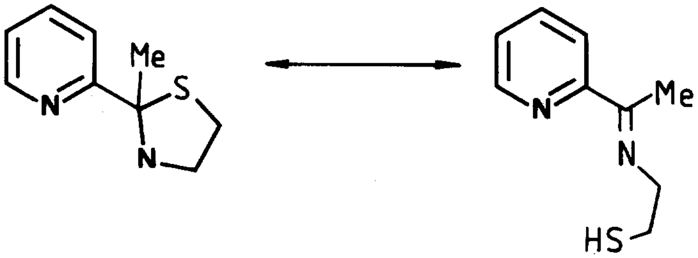
(6)

is established. The compounds $[(MeNHCOCH_2S)_2Hg]$, $[(MeCONHCH_2CH_2S)_2Hg]$ and $[MeNHCOCH_2CH_2SHgCl]$ have been described, and show the expected S_2, S_2 and SCl coordination respectively [49]. Evidence from the vibrational spectrum of $[(MeNHCOCH_2S) Hg]$ suggests that a hydrogen bonded ten-membered ring is formed, and that there is a weak Hg-O interaction (7). The ligand 2-methyl-2-(2'-pyridyl)thiazolidine could exist as (8) or the ring-opened Schiff base tautomer (9). A 400 MHz ^1H and



(7)

^{13}C n.m.r. study has demonstrated that the favoured tautomer is (9), although opening of the thiazolidine ring occurs readily upon coordination to a metal. Thus, although the mercury(II) bis complex is correctly described as $[Hg(8)_2]^{2+}$, the 1:1 complex exists primarily as the thiolate (10) [50].



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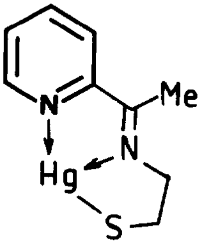
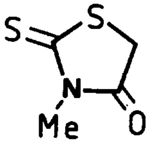


(10)

Although azaheterocycles bearing directly-bonded sulphur containing substituents are frequently described in the inorganic literature as mercapto derivatives, there is considerable evidence that a thione or thioamide structure is more realistic, and this nomenclature will be adopted in this review. It must be stressed that although a free ligand may favour one tautomeric form over others, the coordinated ligand need not necessarily show the same tautomeric behaviour (*vide supra*).

The complex $[HgLCl(H_2O)]$ (HL = 1-phenyltetrazoline-5-thione) has been shown to be polymeric, with the ligand acting as a bridging bidentate *S*,*N*-donor [51]. In contrast, 3-methylrhodanine (11) acts as an *S* donor in the complexes $[Hg_3L_2Cl_6]$ and $[HgLBr_2]$ [52]. A number of complexes of mercury(II) with 3-alkyl-4-(2'-pyridyl)-1,2,4(4*H*)-tetrazole-5-thione have been described [53]. The complexes $[HgCl_2L]$ and



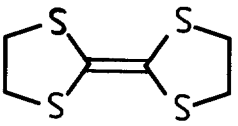
(11)

$[HgCl_2L_2]$ (HL = quinoline-8-thiol) were prepared as part of an investigation into the nature of the heteropolynuclear complex $[HgCl_2L_2Cu].2H_2O$ [54].

2.1.3.2 *Thioethers*

The compound [(EtSMe)HgCl$_2$] has been investigated by infra-red and Raman spectroscopy, and the structure confirmed by a single crystal structural determination [55]. Crystal structures have also been reported for the complexes $[HgLBr_2]$ and $[HgL(SCN)_2]$ (L = $HO_2CCH_2SCH_2CH_2SCH_2CO_2H$) [56]. In the first compound, the mercury is in a tetrahedral S_2Br_2 environment, but the thiocyanate complex is polymeric, with the metal adopting an octahedral configuration, and the ligand acting as a bridging tetradentate S_2O_2 donor [56]. A potentiometric investigation of the formation of the mercury(II) complexes of this same ligand indicates a value for lg K_1 of 18.99, and a value of 19.05 for the closely related ligand $HO_2CCH_2SCH_2CH_2SCH_2CH_2SCH_2CO_2H$ [57]. Although the zinc and cadmium complexes of $HO_2CCH_2CH_2SCH_2CH_2CO_2H$ are polymeric, the mercury(II) 1:1 complex is monomeric, with the ligand acting as an SO_3 donor [58].

It is well known that tetrathiafulvene forms metal complexes of the radical cation, radical or charge-transfer types, and the coordination chemistry of its tetrahydro derivative (12) has now been investigated. A crystal structural determination of the complex $[L(HgCl_2)_2]$ has been reported, and the metal shown to be in a distorted octahedral environment, with the ligand acting as a tetradentate S_2S_2 donor (13)[59]. In the complexes $[HgLX_2]$ (L = bis(2-pyridyl)disulphide; X = CN or SCN) the ligand is thought to be coordinated through sulphur [60].



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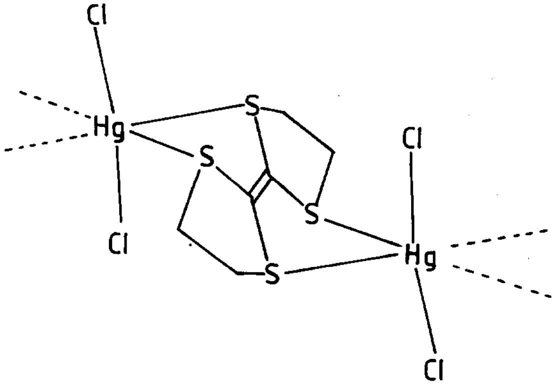

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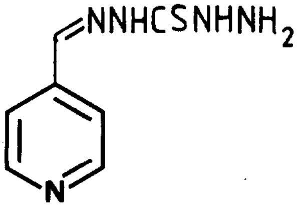
2.1.3.3 *Thioamide and related ligands*

The only simple thioamide complexes to have been described are $[HgL_2X_2]$ (X = Cl or SCN; L = $H_2NCSCSNH_2$), and it is proposed that the ligand is bonded to the metal through both the sulphur and nitrogen atoms [61]. There has been some interest in complexes of thiocarbamic acid derivatives, although the mode of coordination which is adopted is not always evident. The complexes $[HgL_2]$ (HL = *N*-ethyl-*N*(*m*-tolyl)-dithiocarbamic acid [62], $[HgL_2X_2]$ and $[HgLX_2]$ (L = *O*-ethyl *N*-methylthiocarbamate; X = Cl, Br or I) [63], $[HgL_2]$ (HL = $PhCONHNHCSNHNH_2$) [64], $[HgLCl_2]$ (L = 14) [65] and $[HgL_2L'_2]$ (L = 15, L' = 2-methylbenzimidazole) [66].



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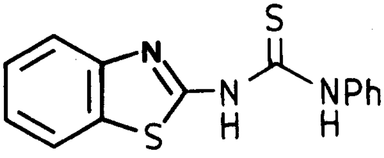

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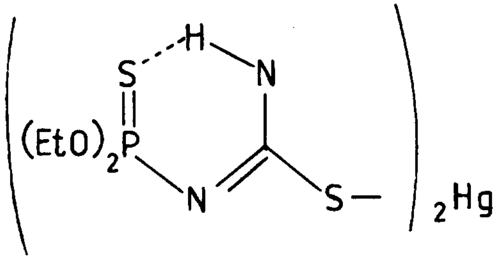
2.1.3.4 *Phosphine sulphides and phosphine selenides*

The coordination chemistry of phosphine sulphides and phosphine selenides has been investigated intensively in the last few years, and a number of studies of mercury(II) complexes have been reported. Preparative details for the complexes $[HgLX_2]$ (L = *p*-tolylphosphine selenide; X = Cl, Br or I), $Hg(NO_3)_2.2Ph_3PS$ and $3Hg(NO_3)_2.4Ph_3PSe$ have been reported and the structures of the products discussed [67]. A series of complexes $[Hg(R_3PE)_2X_2]$ (E = Se or S; X = Cl, Br or I) and $[Hg_2I_4(R_3PSe)_2]$ have been described and their ^{31}P n.m.r. spectra reported. An attempt was made to correlate the coupling constant $^1J_{^{31}P-^{77}Se}$ with the structures of the complexes [68]. A number of tritolylphosphine sulphide complexes of mercury(II) have been described [69]. Two intensive and elegant n.m.r. studies of tributylphosphine selenide complexes have been made, utilising ^{31}P, ^{199}Hg and ^{77}Se n.m.r. techniques [70,71].

Thiophosphorylthioureas react with HgO in acetone to give complexes of the type (16), in which the ligand is bonded to the metal *via* the thioamide, and not the phosphine sulphide sulphur atoms [72].



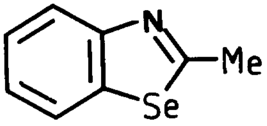
(16)

If the reaction is conducted in benzene or toluene the complex decomposes to give $(EtO)_2PSN{=}C{=}NPh$ or $(EtO)_2PSN{=}C{=}S$ respectively. Decomposition of the pure complex results in the formation of $(EtO)_2PSN{=}C(NHPh)_2$ [72].

Tetraallyldiphosphine disulphide $(CH_2{=}CHCH_2)_2PSPS(CH_2CH{=}CH_2)_2$, L, reacts with $HgCl_2$ to give $[HgLCl_2]$, which has been investigated by infra-red and Raman spectroscopic methods [73]. There is little evidence for the participation of the allyl groups in bonding to the metal.

2.1.3.5 *Sulphur and selenium heterocycles*

Interest in the coordination chemistry of sulphur and selenium heterocycles appears to have lapsed, and the only complexes to have been described are the benzoselenazole derivatives $[HgLX_2]$ (L =17 ; X = Cl, Br or I) and $[HgL_{1.5}X_2]$ (L = 17; X = ClO_4, NO_3) [74].



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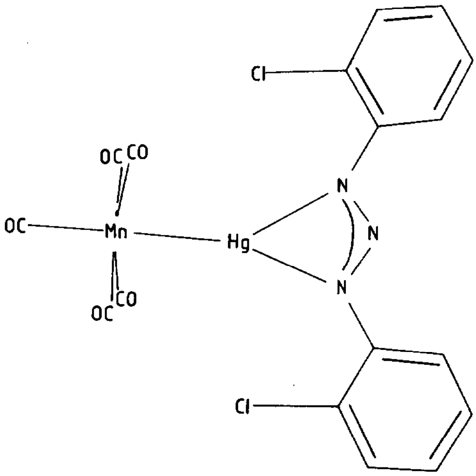
2.1.4 *Complexes with amine, amide and related ligands*

Few complexes of mercury(II) with simple monodentate amines have been reported this year, although the extraction of Hg^{2+} from aqueous iodide medium by Aliquat 336/$CHCl_3$ has been investigated [75]. A potentiometric study of the HgI_2-NH_2OH system in 50% ethanolic acetone has been reported, ($\beta_1 = 8.6 \times 10^{10}$, $\beta_2 = 7.6 \times 10^{12}$, $\beta_3 = 7.3 \times 10^{14}$, $\beta_4 = 6 \times 10^{15}$) [76].

Mercury(II) complexes of 1,3-pn [77], en, hexamethylenediamine and hexamethyleneimine [78] have been reported. The complexes $[HgL]^{2+}$, $[HgLCl_2]$ and $[HgLCl]^+$ (L = diamines) have been shown to be catalytically active in the hydrochlorination of alkynes [78]. In the polymeric complexes $[\{HgLX_2\}_n]$ (L = hexamethylenetetramine; X = Cl, Br or CN) the ligand is bidentate, and the mercury is in a tetrahedral environment [79].

The complex $[HgLCl_2]$ (L = tetramethyl ethylenediaminetetraacetate) has been described, and is a non-electrolyte in methanolic solution [80]. On the basis of this observation it was proposed that the metal is in a tetrahedral N_2Cl_2 environment. The complexes $[HgLX_2]$ (L = MeCONHCOMe; X = Cl or Br) are formed in the reaction of the ligand, diacetamide, with HgX_2 , and the thermochemistry of this process has been investigated [81]. Oxamic acid, H_2NCOCO_2H, may act as a bidentate *NO* or O_2 donor, and the first complexes of this ligand have been described. The mercury complex $K_2[HgL_2]$ ($LH_2 = H_2NCOCO_2H$) behaves as a 2:1 electrolyte in water, and a four coordinate N_2O_2 or O_4 environment about the metal is proposed [82].

Triazenato complexes have been of some interest, and a series of compounds $[HgL_2]$ ($L = ArN_3Ar$) have been prepared and investigated by multinuclear n.m.r. techniques [83,84]. The reaction of bis(1,3-di(2-chlorophenyl)-1-triazenato-*N1*,*N3*)mercury(II) with $[Hg\{Mn(CO)_5\}_2]$ in benzene leads to the formation of $[HgL\{Mn(CO)_5\}]$, which has been shown by a crystal structural determination to have the structure (18) [85]. A number of mixed ligand complexes [HgL(RE)] (HL = ArN=NNHAr; R = Et or Ph; E = S or Se) have been investigated by ^{199}Hg and ^{77}Se n.m.r. techniques, and evidence has been presented for the establishment of the solution equilibrium [86] :



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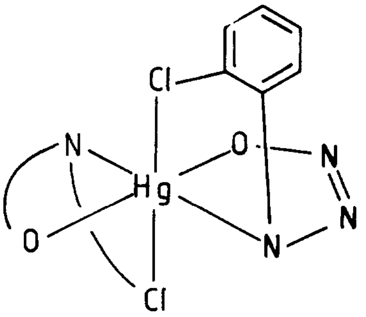

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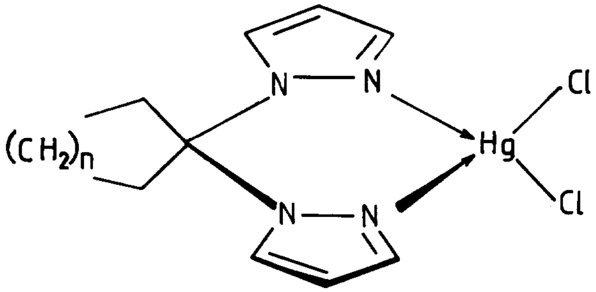
$$2[HgLL'] \rightleftharpoons [HgL_2] + [HgL'_2]$$

The complex $[HgL_2]$ (HL = 3-(2-chlorophenyl)-1-methyltriazene-1-oxide) has also been described, and it is proposed that the complex is pseudooctahedral, with the 2-chloro substituent coordinated to the metal (19) [87]. The related complexes $[HgL_2]$ (HL = 2,2',4,4'-tetrachloro or 2,2',5,5'-tetrachloro diphenyl-1-triazene) have been described [88].

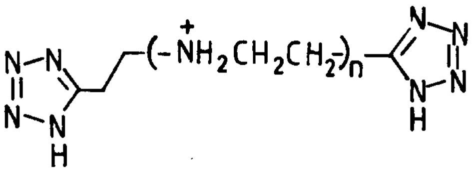
2.1.5 Complexes with nitrogen heterocycles

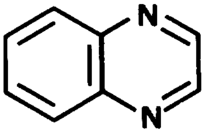
Much of the interest in mercury(II) complexes of nitrogen heterocycles has centred upon naturally occurring ligands (amino acids, peptides, nucleotides etc.), or upon compounds showing specific biological activity, and the majority of complexes which have been reported this year are of this type. The reaction of L-tryptophan with $HgCl_2$ and DL-homocysteine with $HgBr_2$ has been discussed earlier [20] (section 2.1.1). The 1,1'-dipyrazolylcycloalkane complexes [$HgLCl_2$] (20) have been reported [89].



(20)

A number of 1:1 complexes of HgX_2 (X = Cl or NO_3) with bis(5-tetrazolyl)alkanes (21) (from the reaction of azide ion with dicyanamides), and the stability of these species has been related to the number of nitrogen donor atoms [90]. The quinoxaline complexes [{$HgLX_2$}$_n$] and [Hg_2LBr_4] (L = 22; X = Cl, CN or SCN) have been reported [91]. The reaction of chloroquine (23) with mercury(II) salts has been shown to give



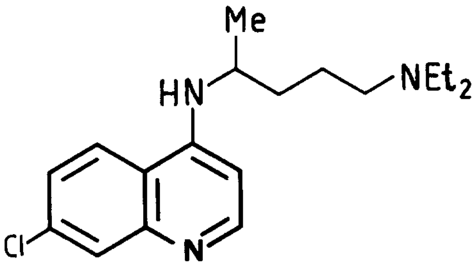


(21)

(22)

1:1 and 1:2 complexes [$HgLCl_2$] and [$L(HgCl_2)_2$] [92]. Vitamin B_1 (thiamine,24) forms complexes with mercury(II), and an n.m.r. investigation (^{1}H, ^{13}C) has indicated that the metal is coordinated to N-3 of the pyrimidine ring [93,94]

Crystal structures of the complexes [HgL_2Cl_2] (L = 8-azaadenine) (25) and [$Hg(H_2O)_4L$] (L = 8-azahypoxanthinato) (26) have been described, and it is seen that the change from the amino to the hydroxy substituent results in very different coordination behaviour [95]. In the crystal, the bases also show a stacking interaction.



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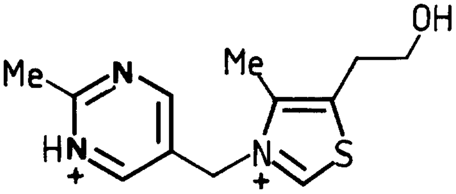

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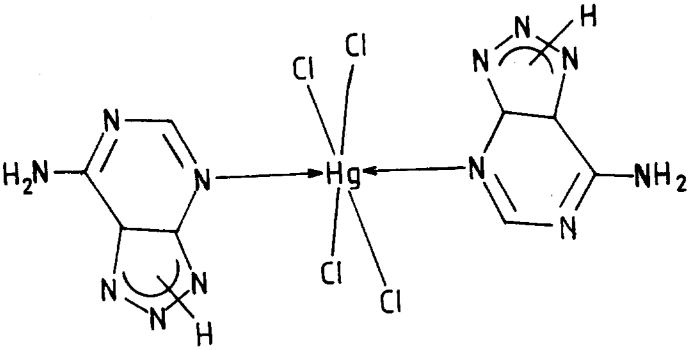

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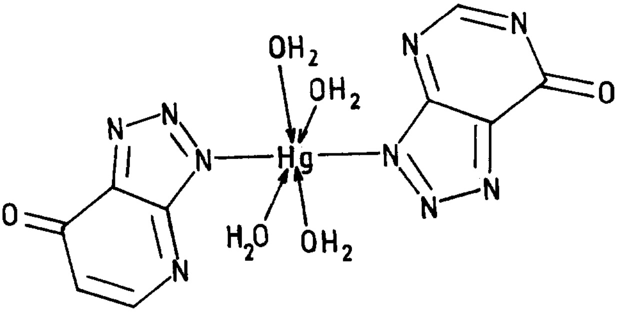

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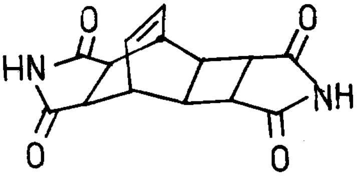
The complexes $HgM(NCS)_4.xL$ (L = morpholine or piperidine; M = Ni or Co) have been described, and a number of different structural types have been characterised, including $[HgL_6][M(NCS)_4]$ and the polymeric species $[L_2M(NCS)Hg(SCN)_2]$ [96].

The extraction of mercury(II) from aqueous iodide media by 4-(5-nonyl)pyridine [97] or other organic bases [98] has also been investigated. Polymeric complexes of Hg(II) with polyimides of type 27 have been reported [99].



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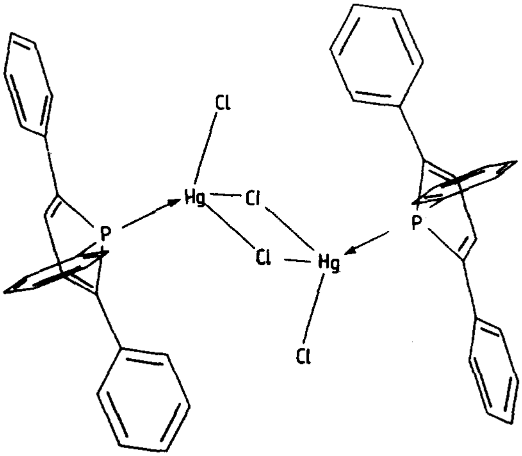
2.1.6 *Complexes with phosphorus and arsenic donor ligands*

There has been some confusion about the simple phosphine complexes of mercury(II) in recent years [1] , but the situation is now being clarified. Bell has reported the crystal structure of the tetrahedral complex $[HgCl_2(PEt_3)_2]$, and has made extensive ^{199}Hg n.m.r. studies of a series of $[HgX_2(PR_3)_2]$ species [100]. Colton has also made intensive multinuclear n.m.r. studies of mercury(II) phosphine complexes, and has demonstrated the power of ^{199}Hg n.m.r. spectroscopy in the interpretation of solution equilibria [71,101,102]. Until recently there has been little unambiguous evidence for the formation of centrosymmetric halogen bridged $L-Hg-X_2-Hg-L$ species, but Bell has now reported crystal structures of three 1:1 adducts of $HgCl_2$ and phosphines adopting this structure [103]. The 1:1 adducts with 1,2,5-triphenylphosphole and triphenylphosphine are dimeric (28 and 29), but the tributylphosphine adduct is a tetramer, 30 . Bell also mentions the formation of 3:2 adducts in the preparation of these compounds.

The heteropolynuclear species $[(py)_4M(NCSe)_2HG(SCN)_2(PPh_3)_2]$ and also $[(bipy)_2M(NCSe)Hg(SCN)_2(PPh_3)_2]$ (M = Co or Ni) have been reported [104].

The reaction of R_3P or R_3As with $Hg(ClO_4)_2$ has been shown to result in the formation of 3-coordinate $[HgL_2(OClO_3)][ClO_4]$ or 4-coordinate $[HgL_3(OClO_3)][ClO_4]$ complexes, in which one perchlorate ion is coordinated to the metal [105]. The compound $[Hg(Ph_3As)_3][ClO_4]_2$ was also prepared [105]. The complexes $[HgX_2(Ph_3PE)_2]$ and $[\{(Ph_3PE)HgX_2\}_2]$ (X = halide; E = Sb or As) have also been reported, and structures analogous to their phosphine analogues proposed on the basis of their vibrational spectra [106].

The reaction of *O*-butyl phenylphosphonite, Ph(n-BuO)P(H)O, with either HgO or mercury(II) acetate results in the formation of $[\{Ph(n\text{-}BuO)PO\}_2Hg]$, and multinuclear n.m.r. studies on this and related complexes have been reported [107]. Tetraphenyl imidodiphosphate reacts with HgO to give the unexpected 2:2 adduct (31), which has



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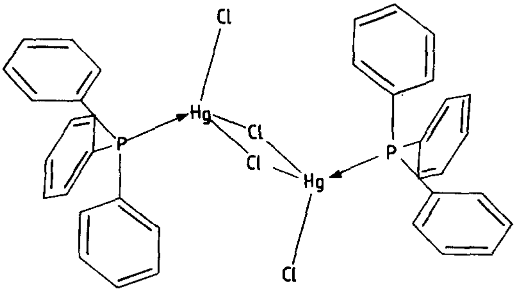

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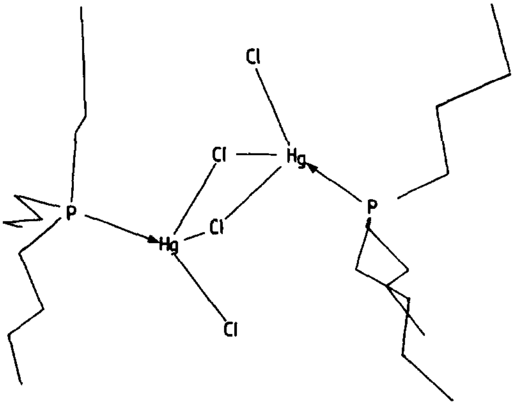

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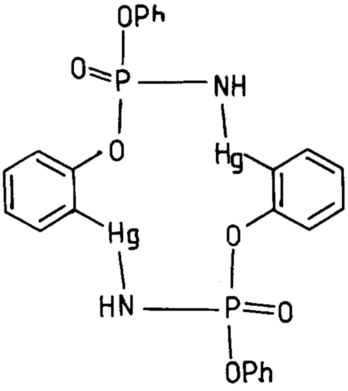

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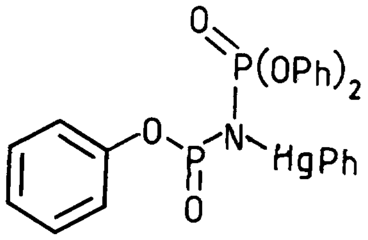


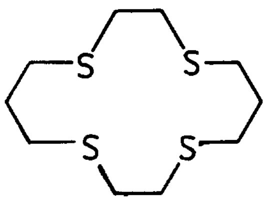
(32)

been characterised crystallographically [108]. The expected product (32) is obtained on reaction with [PhHgOH][108].

A number of trimetaphosphimate complexes $[Hg_3(OH)_2(H_2L)].3H_2O$, $Na[Hg_2(HL)].4H_2O$ and $Na_{1.5}[Hg(H_3L)(OH)_{.5}].2.5\ H_2O$ $(H_3L = H_3P_3O_6N_3H_3)$ have been described [109].

2.1.7 Complexes with macrocyclic ligands

The current trend in macrocyclic chemistry is to investigate ligands containing polyaza or other 'hard' donor sets, and, accordingly, few macrocyclic complexes of mercury(II) have been reported this year. The use of the macrocyclic polythiaethers [14]ane-1,4,8,11-S_4 (33) and [18]ane-1,4,7,10,13,16-S_6 (34) in the extraction of Hg(II) and silver(I) has been investigated [110]. Although 34 acts as an endodentate ligand and forms the macrocyclic complex $[HgL]X_2$ (L = 34; HX = 2,4,6-trinitrophenol) (which acts as a 2:1 electrolyte at all concentrations), the smaller ligand, 33, forms the exodentate complex [HgLX]X (L = 33; HX = 2,4,6-trinitrophenol) which behaves as a 1:1 electrolyte. Another example of a macrocyclic ligand coordinating in an unusual



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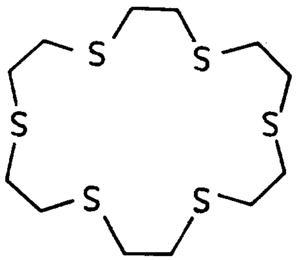
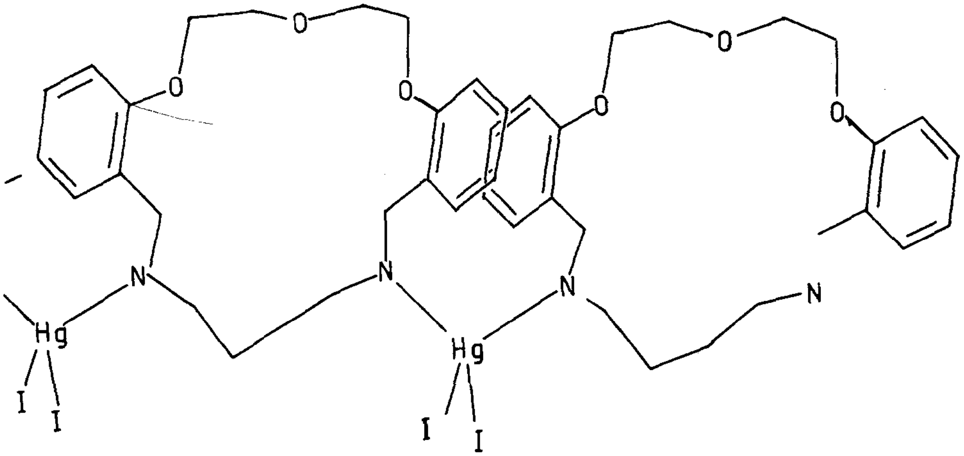


(34)

exodentate manner is found in the complex $[HgLI_2]$ (L = 8,9:18,19-Bzo$_2$-[19]-8,10,16,18-tetraene-11,16-N$_2$-1,4,7-O$_3$), which a crystal structural analysis has shown to consist of HgI_2 units coordinated to one nitrogen atom of each of two ligands. A contributory factor to this unexpected bonding mode may be the stacking interaction observed between the benzo groups of the ligands (35) [111].



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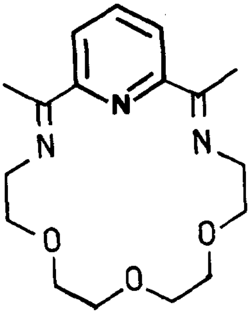
The template condensation of 2,6-diacetyl or 2,6-diformylpyridine with 4,7,10-trioxa-1,13-diazatridecane or 4,7-dioxa-1,10-diazadecane in the presence of $[Hg(SCN)_2]$ leads to macrocyclic complexes with ligands of type 36 or 37 [112]. The preparation



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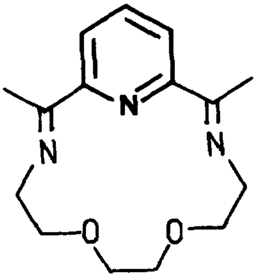
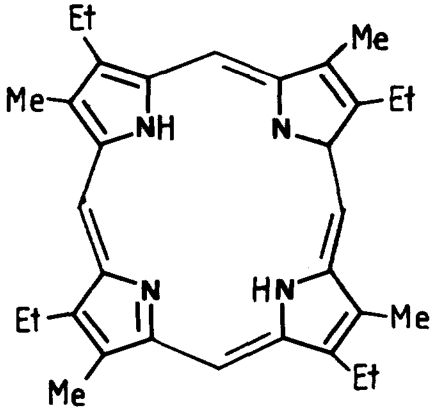


(37)

of the same complexes by transmetallation reactions of the appropriate calcium complexes suggests that the ligand acts as an endodentate donor, although, of course, the oxygen atoms need not be coordinated to the metal.

Gilsonite bitumen is remarkable in containing high concentrations (∿100 p.p.m.) of nickel petroporphyrins, and Quirke and Maxwell have recently isolated the major C_{32} ætioporphyrin as its mercury(II) complex [113]. By a comparison of the ^{1}H n.m.r. spectrum of this compound with an authentic sample, it was demonstrated to be a complex of ætioporphyrin-III (38), an observation which lends some support to the theory that the Gilsonite porphyrins originate from the defunctionalisation of chlorophyll-a.



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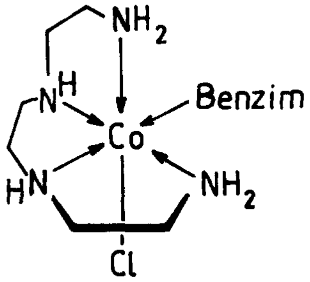


(39)

Finally, the interaction of mercury(II) salts in aqueous solution with the cryptand ligands, Kryptofix 222, 221 and 211 has been investigated [114].

2.1.8 *Aqueous solution chemistry of mercury(II)*

The mercury catalysed aquation of octahedral transition metal chloro complexes continues to be of interest, and evidence continues to accumulate for the involvement of a binuclear chloro-bridged $[\mathrm{M{-}Cl{-}Hg}]^{x+}$ species. Very strong evidence for this mechanism comes from the observation that the treatment of *cis*-$[\mathrm{M(en)_2Cl_2}]^+$ (M = Rh or Co) with mercury(II) chloride results in the rapid and complete formation of a stable long-lived binuclear species of the type $[\mathrm{(en)_2ClRh(\mu{-}Cl)Hg}]^{3+}$ [115]. The mercury(II) catalysed aquation of *cis*-β_2-$[\mathrm{CoCl(benzim)(tren)}]^{2+}$ (39) has been shown to be acid independent, and to proceed with retention of the stereochemistry [116].

In the presence of 2,2'-bipyridine, $HgCl_2$ reacts with $K_4[Fe(CN)_6]$ to produce either $K_2[Fe(CN)_4(bipy)]$ or $[Fe(bipy)_3]^{2+}$, depending whether the $HgCl_2$ or hexacyanoferrate is in excess. On the basis of kinetic and other measurements, it was suggested that these reactions involved 1:1 and 1:2 heteropolynuclear intermediates respectively, and that these were formed *prior* to the cyanide abstraction step [117,118].

2.2 MERCURY(I)

2.2.1 Halide complexes

Mercury(I) compounds have received little attention this year, but several studies of the halides have been made. The solubility of Hg_2Cl_2 in water has been studied, and the solution species shown to include $[Hg_2]^{2+}$, $[Hg_2(OH)]^+$, $Hg(OH)_2$, $HgCl_2$, $[Hg(OH)]^+$ and $[HgCl]^+$ [119]. In contrast, the predominant species formed in aqueous chloride solutions are $[HgCl_3]^-$ and $[HgCl_4]^{2-}$. The thermodynamic parameters for the solution of $[Hg_2Cl_2]$ were reported, and it was noted that some earlier value may be in error. It has been shown that molten mercury(II) bromide is a good stabilising solvent for mercury(I) compounds ($\sim$240° C), although mixed ligand species may be formed in solution [120]. Thus, mixtures of Hg_2A_2, Hg_2BrA, Hg_2Br_2, $HgBr_2$, HgBrA and HgA_2 are formed on the dissolution of Hg_2A_2 in $HgBr_2$. A Raman study of the compound $Hg_2Cl_{1.2}Br_{0.8}$ has revealed the mixed crystal to consist of Hg_2Cl_2, Hg_2Br_2 and Hg_2ClBr [121]. Electrochemical methods have been used in the investigation of the:

$$Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$$

equilibrium for a range of halide and pseudohalide salts [122].

2.2.2 Complexes with oxygen donor ligands

The reaction of $[Hg_2][ClO_4]_2$ with Ph_3PO and Ph_3AsO has been shown to give the complexes $[Hg_2(Ph_3PO)_6][ClO_4]_2$ and $[Hg_2(Ph_3AsO)_3][ClO_4]_2$, and a study of the vibrational spectra of these compounds is now reported [44].

2.2.3 Complexes with nitrogen donor ligands

The reaction of $[PhP{=}C{=}NH_2]Br$ (LHBr) with $Hg_2(NO_3)_2$ in aqueous solution results in the formation of $Hg_2(NO_3)_2(LHBr)_2$ [123].

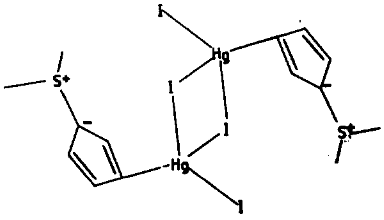
A number of complexes of mercury(I) with substituted pyridines, $[Hg_2L_n][ClO_4]_2$ have been described, and their vibrational spectra investigated (ν Hg-Hg 110-160 cm^{-1} in Raman spectrum) [124]. The reaction of cyanamides $ArSO_2NHCN$ and ArCONHCN with $Hg_2(NO_3)_2$ has been investigated, and a number of mercury(I) complexes isolated [125].

2.3 ORGANOMERCURY(II)

2.3.1 Halide and pseudohalide complexes

The preparation of mesitylmercury(II) chloride from bis(mesityl)zinc(II) and $HgCl_2$

has been reported [126]. The crystal structure of $[\{(Me_2SC_5H_4)HgI_2\}_2]$ has been determined, and the compound shown to exist as a diiodo bridged dimer (40) in the solid state [127]. In the solid, the Hg-C σ-bond is localised, as shown, although this structure may not be maintained in solution. A comparison of the above structure with that of $[\{(Ph_3PC_5H_4)HgI_2\}_2]$ reveals significant differences in the conformations adopted by the cyclopentadienyl rings.



(40)

It is now established that the trichlorovinyl group confers considerable stability to organomercury(II) complexes, and the complexes of $[HgL_2]$ and [LHgHal] (L = trichlorovinyl) with a series of α,α'-diimine derivatives have been described [128,129] The vibrational spectra of a series of [LHgX] (L = 2-chlorovinyl) species have been investigated [130]. A crystal structural analysis of $[ClHgCH_2HgCl]$ has been reported (< Hg-C-Hg 111.6°, C-Hg 2.04, 2.12 Å) [131]. A series of $[CH_{4-n}(HgCl)_n]$ compounds have been investigated by ^1H and ^{13}C n.m.r. techniques, and the deshielding of ^1H, ^{13}C and ^{199}Hg nuclei shown to decrease with an increase in the value of n. The constants $^1J_{(C-H)}$ and $^2J_{(Hg-H)}$ were interpreted in terms of the carbon 2s contribution to the C-X bonds, although it is evident that $^1J_{(Hg-C)}$ cannot be interpreted solely in terms of such Fermi interactions [132].

2.3.2 *Complexes with oxygen donor ligands*

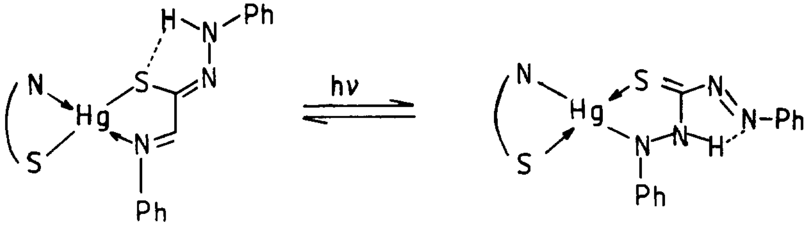
A series of alkylmercury sulphates, $[(RHg)_2(SO_4)]$ have been prepared by the reaction of [RHgHal] with $Ag_2(SO_4)$ [133]. Raman and infra-red spectroscopic studies have demonstrated the phenoxy compounds [RHgOPh] (R = Me or Ph) are monomeric both in solution and in the solid state. These compounds, thus, differ from [PhHgOR] (R = Me or Et) which are dimeric in the solid state [134]. Complexes of $[PhHg]^+$ with a series of hydroxamic acid derivatives have also been described [135].

The formation of $[MeHg]^+$ complexes with a range of naturally occurring carboxylic acids (L-serine, L-cysteine, L-methionine, L- asparaginine, pyruvic acid and levulinic acid) has been investigated, and the mode of binding of the cation to these ligands discussed [136].

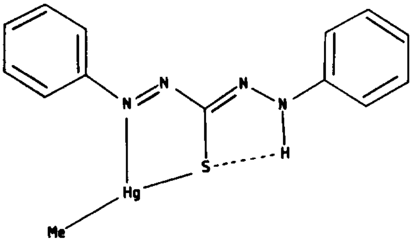
2.3.3 *Complexes with sulphur donor ligands*

The rearrangement of 2-methyl-2-(2'-pyridyl)thiazolidine on treatment with transition metal ions has been discussed earlier, and [HgMeX] species have been shown to initiate a similar rearrangement [50].

The blue-yellow photochromism of [HgL$_2$] (HL = dithizone) in organic solvents has been attributed to the phototautomerism:



and organomercury dithizone derivatives have been shown to exhibit the same behaviour [137]. No such photochromic behaviour is shown in the solid state, and only the yellow form may be obtained as a solid. A crystal structural analysis has demonstrated the yellow form to have the structure (41).

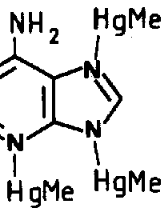


(41)

The phenylmercury(II) complexes of 8-mercaptoquinoline and 2(1*H*)-pyridinethione have been investigated, and there is some evidence from their electronic spectra for the intramolecular coordination of the mercury atom to the heterocyclic nitrogen atom [138]

2.3.4 *Complexes with nitrogen donor ligands*

The interaction of organomercury species with biologically important bases such as nucleotides and amino-acids is of considerable ecological and biochemical interest, and a number of studies of $[MeHg]^+$ complexes of nucleotides have been reported. Crystal structural analyses of both the nitrate and the perchlorate salts of μ-(adeninato-N_3,N_7,N_9)tris(methylmercury(II)) have been described [139,140]. In both compounds the methylmercury groups are bonded to the ring nitrogen atoms, rather than to the amino group (42). In contrast, the tris(methylmercury(II)) complexes of guanosine and inosine have been shown to have the structure shown in (43) [141]. Complexes of this type might be implicated in the mutagenic activity of these alkylmercury derivatives.



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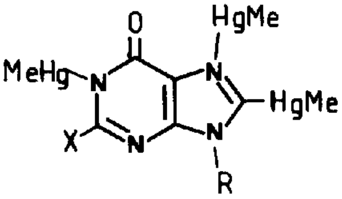
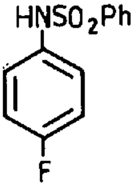


X = NH , H
R = ribosyl

(43)

The complexes [MeHgL][NO_3] (L = Ph_2CH(2-py), PhCH$(2\text{-py})_2$, $(2\text{-py})_2$CHOH or $(2\text{-py})_2$(N-Me-2-Im)CHOH have been described [142]. A ^{19}F n.m.r. study of the complexes [ArHgL] (HL =44) [143] has also been reported.



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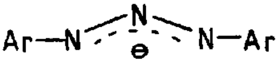

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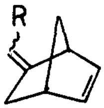
The triazenato ligand (45) may act as a monodentate, bidentate or bridging ligand, and a range of phenylmercury(II) complexes, [PhHgL] (L = Ar_2N_3) have been investigated by multinuclear n.m.r. techniques [83]. It was suggested that the nature of the aryl groups affected the mode of coordination of the ligands, and a large range of substituted triazines were investigated.

2.4 MERCURY IN ORGANIC SYNTHESIS

A review of the uses of mercury(II) acetate in organic synthesis has appeared this year, and this should prove to be an invaluable source book for any workers with an interest in this field [144].

The best known reaction of mercury(II) acetate is with alkenes to give 2-acetoxy-1-mercurio species, and the mechanism of this reaction continues to be of interest. The addition of $Hg(OAc)_2$ to (46) occurs at the endocyclic double bond in weakly polar solvents (MeOH, thf-H_2O) the exocyclic double bond is the more reactive [145]. The reaction rate was shown to be solvent dependent, and this was thought to indicate a change in the reaction mechanism. The reaction of (47) with mercury(II) acetate in acetic acid containing KBr gives a mixture of the *cis-endo* (48) and *cis-exo* (49) adducts [146]. In contrast, the addition of $Hg(OAc)_2$ to 50 proceeds in a *trans* manner, contrary to earlier suggestions, and a crystal structure of the adduct (51) has been reported [147].



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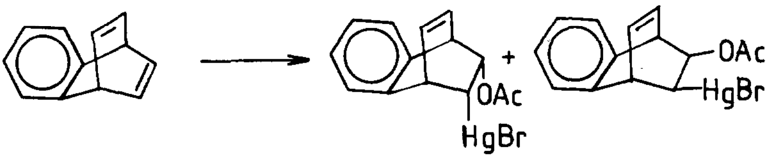
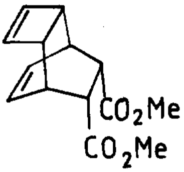
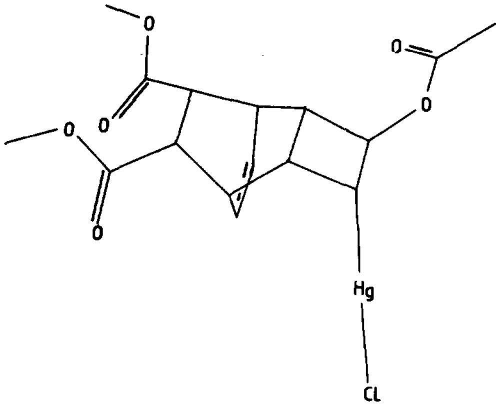


(47) (48) (49)

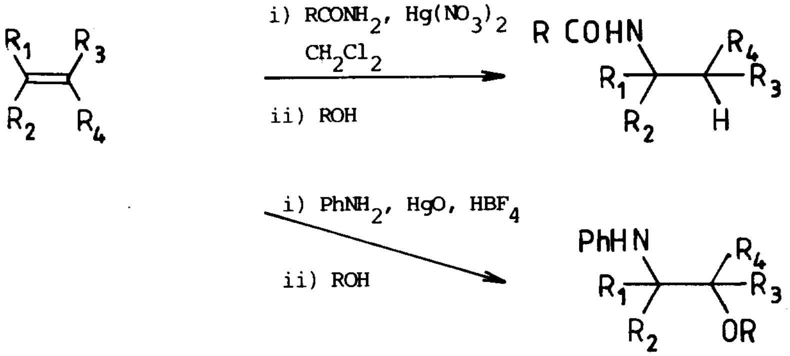


(50)

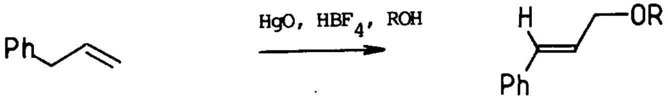


(51)

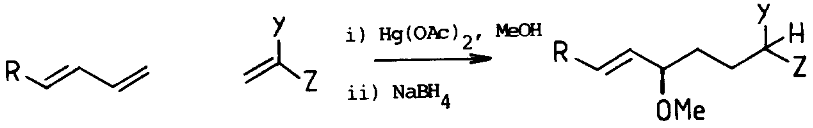
In the presence of other nucleophiles the products are not necessarily 2-acetoxy derivatives, and the reaction of $[Hg(dmso)_6][F_3CSO_3]_2$ with ethene in methanol results in the formation of $[Hg(CH_2CH_2OMe)(F_3CSO_3)]$ [36]. Barluenga and his co-workers have investigated the reaction of olefins with Hg(OAc) in the presence of a wide range of nitrogen containing nucleophiles, and has demonstrated aminomercurationdemercuration to be a useful one-pot method for the amination of double bonds [148-151] :

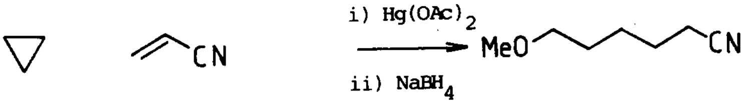


The reaction has been extended to acetylenes in the presence of catalytic amounts of mercury(II) acetate, and the products shown to include imines, enamines, *N*,*N*'-disubstituted acetamidines and acetamides, and 1,2,3,4-tetrahydroquinoxalines [148]. Barluenga has also demonstrated the formation of cinnamoyl ethers in the reaction sequence[152] :

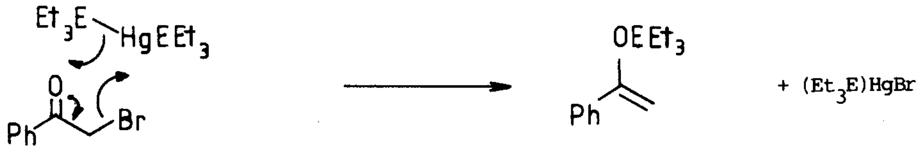


Brown has also noted rearrangements in the oxymercuration-demercuration of olefins [153]. Giese has demonstrated that useful modifications of olefin reactivity may occur in the presence of mercury(II) acetate, and has reported reactions with 1,3-dienes and cyclopropanes [154,155] :

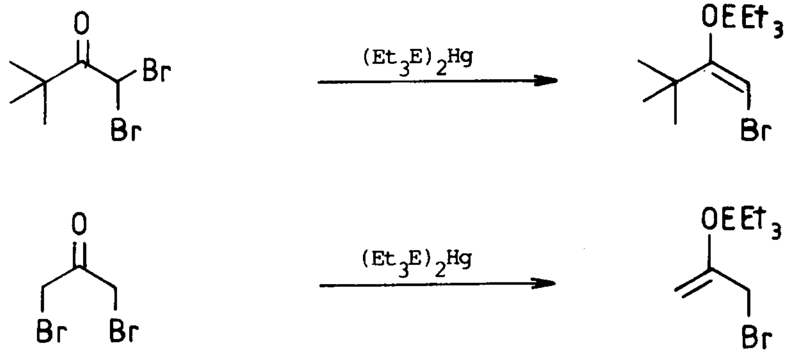




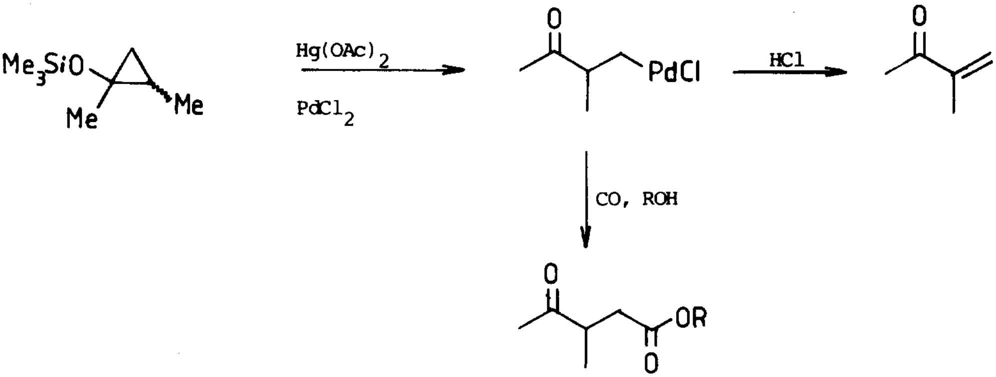
The reaction of $(Et_3E)_2Hg$ (E = Si or Ge) with α-bromoketones leads to the formation of vinyl ethers, possibly *via* an electrocyclic mechanism [156]:



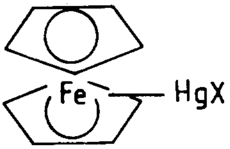
Similar reactions are observed with α,α-dibromoketones [157] and α,α'-dibromoketones [157]:



In contrast, trimethylsilyloxycyclopropanes react with $Hg(OAc)_2$-$PdCl_2$ to give α,β-unsaturated ketones in a one-pot synthesis [158]. If the reaction is conducted in the presence of carbon monoxide and an alcohol, γ-ketoesters are obtained [158]:

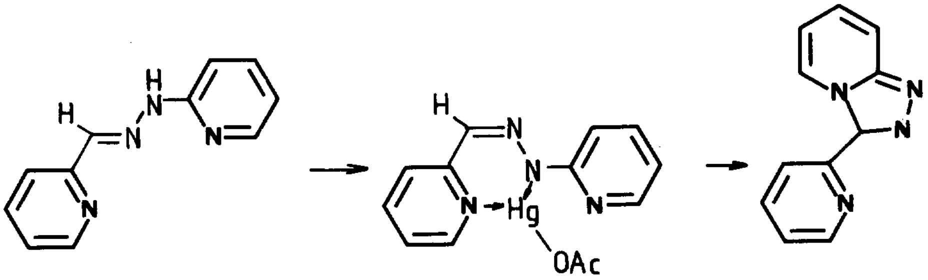


The mercuriation of aromatic compounds continues to be of interest, and $Hg(F_3CSO_3)_2$ has been shown to be a superior reagent for such reactions [159]. There is renewed evidence for the intermediacy of a 1:1 iron-bound mercury intermediate (52) in the mercuriation of ferrocene [160].



(52)

The reaction of aldehyde phenylhydrazones with mercury(II) acetate was known to result in mercuriation of the ring, and it has now been shown that ketone phenylhydrazones undergo rearrangement to give α-acetoxy phenylhydrazones and 1,2-bis(-phenylhydrazones) [161]. In contrast, (53) reacts with mercury(II) acetate to give fused 1,2,4-triazoles (55) *via* an intermediate (54), which has been characterised for the first time [162].



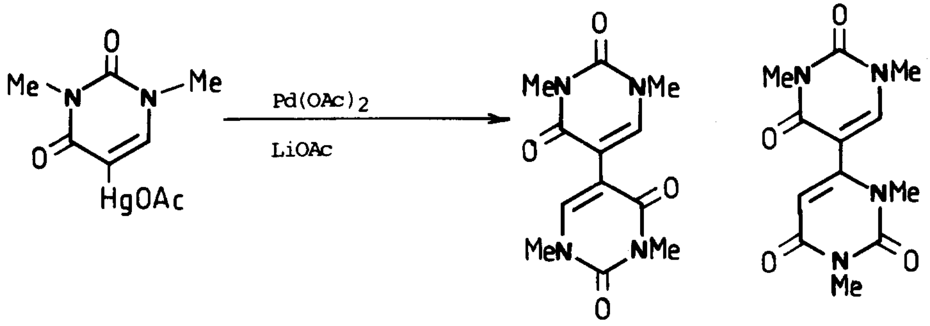
(53) (54) (55)

The intermediacy of radical species in organomercury mediated synthesis is well established, and a Hunsdiecker type mechanism is now proposed for the formation of iodomethane in the reaction of acetic acid with iodine and mercury(II) acetate [163]. The iodo-demercuration of heterocyclic $Fe(cp)(CO)_2$ complexes has been investigated [164]. Radical mechanisms are also proposed for the reactions:

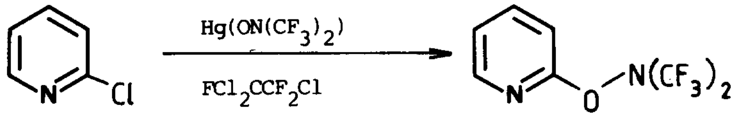
$$\{(Me_3Si)_2N\}_2Hg \xrightarrow[\text{thf, } 130^\circ]{PhCHRCN} NCCPhRCPhRCN \qquad [165]$$

$$\{(Me_3Si)_2N\}_2Hg \xrightarrow[\text{thf}]{Ph_2CHCO_2Me} MeO_2CCPh_2CPh_2CO_2Me \qquad [165]$$

$$2Hg^{2+} + CrCH_2OH^{2+} \longrightarrow Cr^{3+} + Hg_2^{2+} + HCHO + H^+$$ [166]



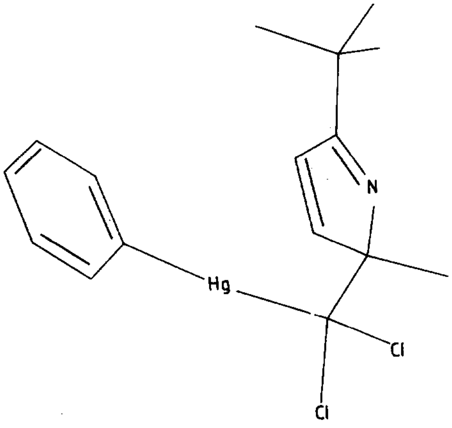
[167]



[168]

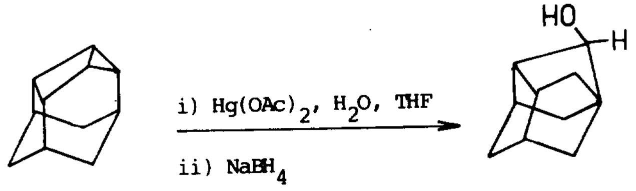
The role of mercury(II) acetate in the oxidation of alcohols by NBS has been investigated, and it has been shown that the mercury i) complexes with the bromide ii) lowers the acid concentration and iii) assists the decomposition of the transient ester [169].

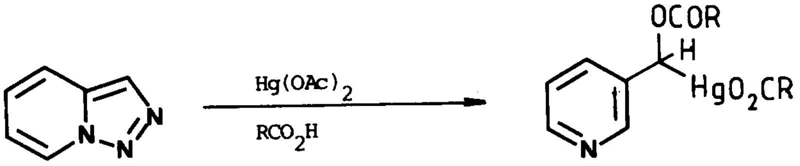
The complex $PhHgCCl_3$ is a commonly utilised dichlorocarbene precursor, but an intermediate in the reaction with 2-tert-butyl-5-methylpyrrole has been shown by a crystal structural analysis to be the species (56) [170].

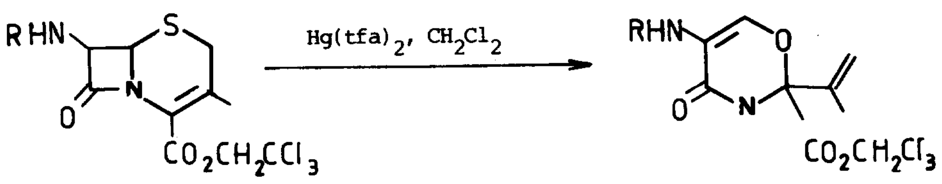


(56)

A number of mercury(II) catalysed rearrangements have been investigated, including the following [171-173]:







2.5 ^{199}Hg N.M.R. SPECTROSCOPY

The application of ^{199}Hg n.m.r. techniques to the investigation of mercury(II) coordination compounds continues, and a number of reports of such studies have appeared this year.

Colton has investigated the Hg(II)-halide system, and reports the ^{199}Hg n.m.r. parameters for a large number of tetrahalomercurate(II) species, including the mixed halide ions [29]. Peringer has reported ^{199}Hg n.m.r. data for a number of complexes, including $[\mathrm{Hg_2(F_3CSO_3)}]$, $[\mathrm{PhHg(dmso)_2}][\mathrm{F_3CSO_3}]$, $[\mathrm{Hg(dmso)_6}][\mathrm{F_3CSO_3}]$ and $[(\mathrm{MeOCH_2CH_2})\mathrm{Hg(F_3CSO_3)}]$[36]. A range of triazenato complexes have also been studied by Peringer [83,84,86].

Phosphine [70,71,100-102] and phosphine sulphide and selenide [70,71] complexes have been widely studied, and one report of phosphonite complexes has been made [107].

The dialkylmercury(II) species $[\mathrm{Hg(CH_2COEt)_2}]$ and $[\mathrm{Hg(CH_2CO\ CH_2CO_2Me)_2}]$ have been investigated by multinuclear n.m.r. techniques, and it is proposed that Hg-O interactions are important in solution [174]. Studies of $[HgMe_2]$[175]and also RCOCHR'HgBr [163,176] have been reported.

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