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13. MERCURY

E.C. CONSTABLE

CONTENTS

Introduction 367
13.1 Mercury(I) 367
    13.1.1 Halide complexes 367
    13.1.2 Other complexes 368
13.2 Mercury(II) 368
    13.2.1 Halide oomplexes 368
    13.2.2 Pseudohalide complexes 369
    13.2.3 Complexes with oxygen donor ligands 370
    13.2.4 Complexes with sulphur or selenium donor ligands 371
    13.2.5 Complexes with nitrogen donor ligands 373
    13.2.6 Complexes with phosphine or arsine ligands 375
    13.2.7 Complexes with macrocyclic ligands 376
    13.2.8 Miscellaneous complexes 377
    13.2.9 Alkylmercury(II) complexes 377
    13.2.10 Aqueous chemistry of mercury(II) 379
    13.2.11 Mercury compounds in organic synthesis 380
    13.2.12 ^{199}Hg NMR spectroscopic studies 382
References 383

INTRODUCTION

The format adopted for this review is described in the introduction to the reviews for zinc and cadmium in this volume.

13.1 MERCURY(I)

13.1.1 Halide complexes

An *ab initio* study of the molecules [Hg_2F_2] and [Hg_2Cl_2] has demonstrated that, although the polar Hg-X bond favours a head-to-tail orientation in the dimer, the moderately strong Hg-Hg bond dictates a linear structure; [Hg_2Cl_2] was calculated to be *ca.* 0.6 eV more stable than equimolar amounts of Hg and $HgCl_2$ [1]. The electrochemical reduction of [Hg_2X_2] (X = Cl or Br) has been investigated, and the enhanced rates observed in the presence of V(III) interpreted in terms of the reaction scheme (1) [2].

Neutron and Raman [3] and ^{35}Cl NQR [4] spectroscopic studies of [Hg_2Cl_2] have been reported, and the chemistry of [Hg_2F_2] has been reviewed [5].

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$$\begin{aligned} V(III) + e^- &\longrightarrow V(II) \\ V(II) + Hg(I) &\longrightarrow V(III) + Hg(0) \end{aligned} \tag{1}$$

13.1.2 Other complexes

The mercury(I) salt, $[Hg_2][ClO_4]_2$, has been described for the first time, and its thermal decomposition shown to give the air-stable basic compound $[Hg_2][ClO_4]_2.HgO$ [6]. The complex $[Hg_2(amq)_2][ClO_4]_2$ has been prepared and is thought to have a polymeric structure in the solid state [7].

It is claimed that pulse-radiolysis of aqueous solutions of $[HgL]^{2+}$ (L = [14]ane-1,4,8,11-N_4) produces the mononuclear mercury(I) complex, $[HgL]^+$, which reacts rapidly with solvent or starting materials [8].

13.2 MERCURY(II)

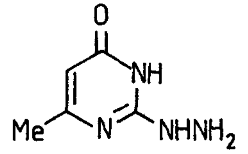
13.2.1 Halide complexes

The energy levels in $HgCl_2$ and $HgBr_2$ have been calculated, and the results discussed in relation to the development of HgX_2 lasers [9]. The ^{35}Cl NQR spectrum of $HgCl_2$ has been reported and a Cl-Hg-Cl bond angle of 177.2° calculated (*cf.* 177.8° from the crystal structure) [10,11]. The thermodynamics of the formation of $[HgX_n]^{(2-n)+}$ (X = Cl or Br; n = 1 or 2) species has been discussed [12]. A number of compounds of formula $M[Hg_5X_{11}]$ (M = Tl, K, Rb, Cs or NH_4; X = Cl or Br) have been prepared and a crystal structure of $TlHg_5C_{11}$ has been reported; the compounds are double salts of the type $MX.5HgX_2$ [13]. An intensive study of the electronic spectra of the mixed halides HgClI, HgBrI, and HgBrCl has been made [14] and the spectra of equimolar mixtures of HgX_2 and HgY_2 or HgX_2 and Y^- compared with those calculated for the above species [15]. The mixed fluorohalides HgFX (X = Cl, Br or I) have been reported for the first time and their structures established by vibrational spectroscopy [16].

The coordination chemistry of mercury(II) halides [17] and of HgF_2 [5] has been reviewed. The halogen in neutral and anionic Hg(II) halide complexes is readily displaced by nucleophiles and the stepwise reactions of $[CN]^-$ with $HgBr_2$ [18], or $[HgBr_4]^{2-}$ [19], have been investigated. Similarly, the exchange of Cl^- or Br^- for I^- in a number of iodomercury(II) complexes has been studied [20].

Raman spectra have been reported for $[NH_4][HgCl_3]$ [21] and a number of $[HgX_3]^-$ (X = Cl or Br) salts [22]. It was shown that the latter compounds gave different configurational isomers, with varying numbers of coordinated solvent molecules (dma, dea, hmpa or dmf), in coordinating solvents. The mixed haloacids $H[HgCl_3].2Et_2O$, $H[HgBr_2Cl].2Et_2O$, and $H[HgI_2Cl].2Et_2O$ react with $PhNH_2$ to produce complexes which have been formulated as $[PhNH_3][(PhNH_2)HgCl_3]$, $[PhNH_3][(PhNH_2)HgBr_2Cl]$ and $[PhNH_2...H...H_2NPh][HgI_2Cl]$, respectively [23].

Raman studies of PCl_5–$HgCl_2$ melts indicate the presence of the salts $[PCl_4][HgCl_3]$ and $[PCl_4]_2[HgCl_4]$ [24]. The complex ions $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ may be extracted (the former the more readily) from aqueous HCl by solutions of Aliquat 336 (tricaprylmethylammonium chloride) in $CHCl_3$ [25,38]. The ion $[HgX_4]^{2-}$ is present in $[H_2L][HgCl_4].2H_2O$ {L = (1)} [26] and in $Ag_2[HgI_4]$; the latter is formed in a solid-state reaction at the surface of crystals of AgI and HgI_2 which are in contact [27]. ^{35}Cl Zeeman NQR studies of the complexes $Co[HgCl_4].4H_2O$ and $Co[HgCl_4].4D_2O$ have been made [28]. A number of alkylammonium tetrachloromercurate(II) salts, $[C_nH_{2n+1}NH_3]_2[HgCl_4]$ (n = 8–16) have been described, the compounds being of interest for the phase transitions they show in the solid state (which are due to the organic part of the crystal 'melting', whilst the inorganic portion remains virtually unchanged) [29].


(1)

The crystal structures of $Tl_4[HgI_6]$ [30] and $[Tl_{10}Hg_3Cl_6]$ [31] have been reported; the former compound contains compressed octahedral $\{HgI_6\}$ units. The ions $[(PhC{\equiv}C)_2HgI]^-$ and $[(PhC{\equiv}C)_2HgI_2]^{2-}$ have been proposed as intermediates in the protodemercuration of $[(PhC{\equiv}C)_2Hg]$ in aqueous dmf by $[NBu_4]I$; it was claimed that they were formed in a pre-kinetic step. These results obviously deserve reexamination since they are at variance with the accepted mechanism for this, and similar, reactions [32].

13.2.2 Pseudohalide complexes

The thermal decomposition of the salt $[Ph_2I]_2[Hg(CN)_4]$, which contains the tetrahedral tetracyanomercurate(II) anion, has been investigated and the products shown to include PhI, PhCN, and $(CN)_2$ [33]. Of the various tricyanometallate(II) ions which may be present in aqueous solution, only $[Hg(CN)_3]^-$ has been isolated in the solid state (as its Cs salt). A study of the IR and Raman spectra of $Cs[Hg(CN)_3]$ has been made and the $[Hg(CN)_3]^-$ unit shown to occupy a site of C_1 symmetry in the solid [34]. The effect of high pressures upon the Raman spectrum of $[Hg(CN)_2]$ has been determined and the results interpreted in terms of structural distortion within the crystal [35].

A number of salts of the empirical formula $[MHg(CN)_2X].nH_2O$ (M = Na, K, Rb or Cs; X = [NCO], [NCS] or $[N_3]$) have been formed by the reaction of MX with $Hg(CN)_2$. The compounds were formulated as double salts, and crystal structures were reported for $NaHg(CN)_2(NCO).2H_2O$, $KHg(CN)_2(NCO)$ and $CsHg(CN)_2(NCO)$ [36].

13.2.3 Complexes with oxygen donor ligands

13.2.3.1 Complexes with inorganic oxoanions

A neutron and X-ray structural study of $[Hg(SO_4)(H_2O)]$ has shown the crystal to consist of discrete formula units, connected by hydrogen bonds. The mercury is in an irregular octahedral environment, interacting with the oxygen atoms of four distant $[SO_4]$ tetrahedra [37]. The thermal decomposition of $Hg[ClO_4]_2.3H_2O$ leads to a basic salt, which has been characterised crystallographically [6].

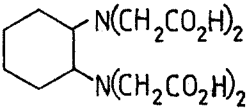
Mercury(II) dialkylphosphites $[\{(RO)_2PO\}_2Hg]$ react with the metal(0) compounds $[M(PPh_3)_3]$ (M = Pd or Pt) to give $[\{(RO)_2PO\}_2M(PPh_3)_2]$. If the reaction with $[Pt(PPh_3)_3]$ is conducted at $-22\ ^\circ C$, the intermediate complex $[\{(RO)_2PO\}HgPt(PPh_3)_2\{OP(OR)_2\}]$ may be isolated [39].

13.2.3.2 Complexes with carboxylates and related ligands

This section includes complexes with amino acids, even though, in many cases, it is probable that the ligands act as nitrogen rather than oxygen donors.

A number of carboxylic acid complexes, $[Hg(O_2CR)_2]$ ($R = C_nH_{2n+1}$; n = 2-9), have been characterised and their vibrational spectra studied [40]. The phenoxyethanoate complexes $[HgL_2]$ ($HL = ArOCH_2CO_2H$) have been prepared and shown to involve octahedral co-ordination at the metal, with bridging carboxylate groups [41].

Interest in 2-aminoethanoate based ligands continues and mercury(II) complexes of $(HO_2CCH_2)_2NCH_2CHOHCH_2OH$ [42], $(HO_2CCH_2)_2NCH_2CO_2H$ [43], $(HO_2CCH_2)_2NCH_2CH_2OH$ [44] and DL-$(HO_2CCH_2)_2NCH_2CH(CO_2H)N(CH_2CO_2H)_2$ [45] have been described. A ^1H NMR study of the mercury(II)/$\{(HO_2CCH_2)_2NCH_2CH_2NHCH_2\}_2$ system has indicated that a tetrahedral complex is formed, in which the ligand acts as an N_4 donor; the changes in configuration which occur upon protonation of the 1:1 complex were discussed [46]. The natural abundance ^{15}N NMR spectrum of $[HgLCl]^{3-}$ {L = (2)} has been reported [47].

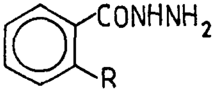


(2)

13.2.3.3 *Complexes with amides and related ligands*

These ligands may act as either nitrogen, oxygen or bidentate donors and, in many cases, it is not clear which mode of coordination is adopted.

The acid hydrazide complexes $[HgL_2Cl_2]$ {L = **(3)** or **(4)**} have been prepared



(3; R = H)
(4; R = OH)

by the reaction of $HgCl_2$ with the appropriate ligand. Both ligands appear to act as neutral monodentate donors, coordinating through the terminal amino group [48].

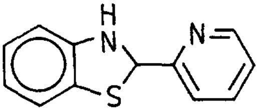
Other complexes which have been investigated include $[HgLCl_2].H_2O$ (L = $PhCH{=}CHCONHNH_2$) [49], $[Hg(tmu)X_2]$ (X = Cl or Br) [50] and $[Hg(dma)Cl_2]$ [51].

13.2.3.4 *Complexes with ethers*

The reaction of $[Hg(tfa)_2]$ with 1,4-dioxan produces [HgL(tfa)][tfa] [52]. A number of mercury(II) halide-polyether complexes have been investigated by ^{35}Cl, ^{81}Br or ^{127}I NQR spectroscopy and shown to give $[Hg_2X_2]$ dimers in solution, with non-equivalent Hg-X bonds [53].

13.2.4 *Complexes with sulphur or selenium donor ligands*

A spectroscopic study (IR, Raman and ^1H NMR) has been made of the complexes $[HgL_2]$ and [HgLX] (HL = 8-mercaptoquinoline; X = Cl, Br, I or Me) [54]. The reaction of $Hg(O_2CMe)_2$ with **(5)** resulted, not in the expected coordination



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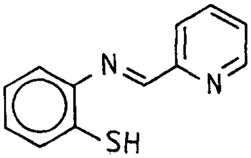
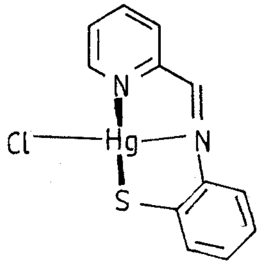


(6)

compounds, but in the formation of complexes of the ring-opened compound **(6)**: after treatment with HCl, [HgLCl] {HL = **(6)**} was isolated [55]. The complex was thought to be tetrahedral, with the structure shown as **(7)**. A crystal structure of an Hg(II) complex of the thiosteroid, **(8)**, has been reported [56].

A number of cysteine complexes of Hg(II), including [Hg(cys)Cl], $[Hg_2(cys)_3]$, $[Hg(cys)_2]$ and $[Hg_2(cys)_2Cl]$, have been characterised by IR and ESCA measurements. The 1:2 complex is thought to have an *S,S,O,O* coordination sphere and the 2:2



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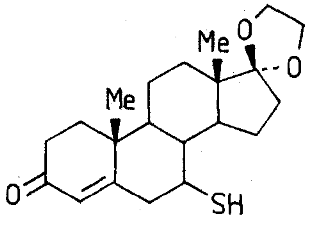

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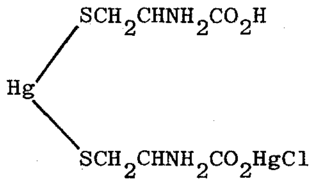

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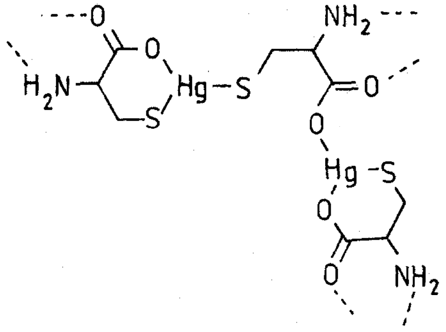
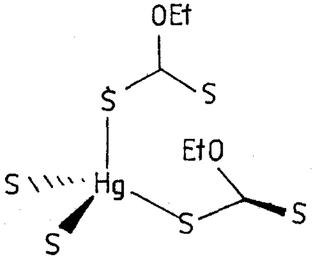


(10)

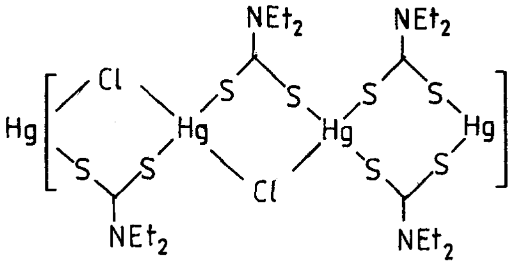
and 3:2 complexes to have structures (9) and (10) respectively [57].

The structure of [Hg(EtOCS$_2$)$_2$] has been reported and the solid shown to consist of Mica-like two-dimensional sheets, with mutual bridging of Hg(II) and xanthate (11) [58].



(11)

A number of alkanedithiobis(2-aminopropane) complexes of Hg(II) have been described, the ligands giving 1:1 chelates of comparable stability to the edta complexes [59]. The reaction of HgCl$_2$ with sodium *N*,*N*-diethyldithiocarbamate, Na[S$_2$CNEt$_2$], produces [Hg(S$_2$CNEt$_2$)$_2$]$_2$ and [Hg$_3$(S$_2$CNEt$_2$)$_4$Cl$_2$]. The trimetallic compound has been shown to consist of polymeric chains, with three different types of distorted tetrahedral mercury sites, as shown in (12) [60].



(12)

Stability constants have been reported for the mercury(II) complexes of a number of sulphur-containing ligands, (including DL-penicillamine, *N*-acetyl-DL-penicillamine, 2,3-dimercaptopropanesulphonic acid and 2,3-dimercaptopropan-1-ol) [61]. The formation of Hg(II) complexes with a range of mesoionic 2-mercapto-1,3,4-thiadiazoles and 5-mercaptotetrazoles [62], 9-methyl-6-mercaptopurine [63], MeNHCSCSNHMe [64], 2-amino-5-methyl-1,3,4-thiadiazole [65], and ethylenethiourea [66] has been investigated.

Complexes of other sulphur-containing ligands, which may or may not be *S*-bonded to the metal, described this year include: $[HgLX_2]$ (L = MeEtC=NNHCSNH$_2$; X = Cl, I or SCN) [67], $[Hg_2L].2H_2O$ (H_4L = $HO_2CCH_2CH(CO_2H)SCH(CO_2H)CH_2CO_2H$) [68], $[HgLX_2]$ (L = PhNHNHCSNHNHPh; X = Cl, Br, I, $[NO_3]$ or [SCN]) [69], $[Hg(HL)_2X_2]$ and $[HgL_2]$ (HL = 4,6-dimethylpyrimidine-2(1*H*)-thione; X = Cl, Br or I) [70,71], $[HgL_2Cl_2]$ (L = 2-thiouracil) [72], $[Hg(HL)_3]X_2$ (HL = 4,6-dimethylpyrimidine-2(1*H*)-thione; X = $[ClO_4]$, $[BF_4]$ or [tfa]) [71], [HgL(tfa)][tfa] (L = Me_2S or dmso) [73], $[HgL_2X_2]$ (L = 2-amino-6-methyl- or 2-amino-6-chlorobenzothiazole; X = $[O_2CMe]$, [SCN] or Br) [74] and [HgL] (HL = $H_2NCSNHCS_2H$) [75].

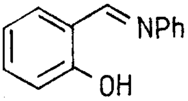
The complexes $[Fe(NCE)_2Hg(ECN)_2]$ (E = S or Se), in which the mercury is, presumably, in an E_4 coordination sphere, react with various σ-donor ligands to give $[L_2Fe(NCE)_2Hg(ECN)_2]$ (L = dmso, py, py-3-CONH$_2$ or PPh$_3$) [76]. Anionic analogues of these compounds are formed in the reaction of $Pb(SCN)_2$, $M(SCN)_2$ (M = Ni or Co) and $Hg(SCN)_2$, to give $Pb[(SCN)_2M(NCS)_2Hg(SCN)_2]$; these compounds react with Lewis bases at either Pb or M [77].

13.2.5 Complexes with nitrogen donor ligands

13.2.5.1 Complexes with amines and aliphatic ligands

The nature of the species present in Millon's base continues to be of interest and two studies of the vibrational spectra of the complex amino species, formed from the reaction of NH_3 with HgO, have been reported [78,79]. The reaction of $[Hg(tfa)_2]$ with Et_3N produces $[Hg(tfa)(Et_3N)][tfa]$ [80].

The species $[(LH)Hg_2X_5]$ (HL = *N*-benzylpiperazine; X = Cl or Br) and $[(LH)Hg_2Br_3]$ have been isolated from the reaction of $[LH_2]^+$ with HgX_2. A crystal structure of $[(LH)Hg_2Cl_5]$ has been reported and the crystal shown to consist of distorted $\{HgCl_3N\}$ tetrahedra, forming chains with chlorine bridges. The vibrational spectra of the compounds are in accord with this formulation [81]. Complexes of Hg(II) with (13) have been described, in which the ligand acts as



(13)

a bidentate *N*,*O* donor [82]. .

The alcoholysis of $Ph_3P{=}NSiMe_3$, in the presence of mercury(II) halides, results in the formation of the complexes $[\{HgLX_2\}_2]$ (X = Cl or Br) or $[Hg_2I_4L_3]$ (L = $Ph_3P{=}NH$). Structures were proposed for these novel complexes [83]. The unusual platinum-containing ligands, $[(dppe)Pt(MeOC{=}NR)_2]$ (R = Me or cych), act as bidentate *N*,*N* donors and form the complexes $[HgLCl_2]$ (R = Me or cych) and $[(HgCl_2)L]$ (R = Me) [84].

13.2.5.2 Complexes with nitrogen heterocyclic ligands

Pyridine complexes of Hg(II) continue to be of interest, and a number of three-coordinate complexes $[HgLX_2]$ (L = 2-benzylpyridine; X = [CN]: L = 4-benzylpyridine; X = [SCN]), which are thought to possess trigonal planar symmetry in the solid state, have been described [85]. Benzoylpyridines also favour the formation of three-coordinate complexes and species such as $[HgLX_2]$ (L = 2,3 or 4-benzoylpyridine; X = Cl, Br, [CN] or [SCN]) have been prepared [86]. The tetrahedral complexes $[HgL_2X_2]$ (L = 4-benzylpyridine; X = [CN]: L = 3-benzylpyridine; X = [CN]: L = 4-benzoylpyridine; X = Cl) are also known [85,86]. Potentiometric titrations of solutions containing Hg(II) and LH_2 (LH_2 = 2,6-pyridinedimethanol) indicate the formation of $[Hg(LH_2)_2]^{2+}$, $[Hg(LH)]^+$, and [HgL], and the complex $[HgL].3H_2O$ has been isolated [87]. The complex $[HgLBr_2]$ (L = 2,4-dimethylpyridine) contains five-coordinate mercury atoms, with bromine bridges forming infinite chains; $[HgLCl_2]$ is thought to have a similar structure [88]. A ^{14}N NQR study of the complex $[Hg(py)Cl_2]$ has been reported [89]. A number of pyridinecarboxylic acid complexes $[HgBr_2L_3]$ or $[HgBr_2L_2]$ have been prepared, in which the ligand appears to act as an *N* donor [90].

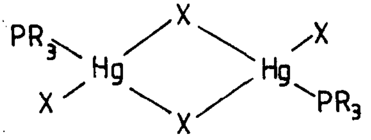
A number of other, apparently three-coordinate, complexes $[HgLX_2]$ (L = benzo(f)quinoline; X = [CN] or [SCN]) have been described [91], and the thiocyanate ligands in $[HgL(SCN)_2]$ have been shown to be *S* bonded, in contrast to those in $[ZnL_2(NCS)_2]$ [92]. The tetrahedral complex $[Hg(amq)Cl_2]$ has been described [93]. The complexes $[HgLX_2]$ (L = bis(2-pyridyl)ketone; X = Cl, Br or I) have been prepared and $[HgLCl_2]$ shown to be dimeric in solution; $[HgLCl_2]$ is, thus, of interest as providing the first example of a bridging bis(2-pyridyl)ketone ligand [94]. A crystal structure has been reported for $[HgLCl_2]$ (L = nicotine) and the nicotine ligand shown to coordinate to two adjacent mercury atoms, to give polymeric chains. The mercury is in a highly distorted tetrahedral $\{N_2Cl_2\}$ coordination sphere [95].

Crystal structures have been reported for $[Hg(phen)_3][CF_3SO_3]_2$, in which the cation is distorted from octahedral symmetry towards a trigonal prism [96], and $[Hg(bipy)_2][NO_3]_2.2H_2O$, in which the diimine nitrogen atoms form a flattened tetrahedron about the mercury atom [97]. A number of complexes of Hg(II) with 4,4'-bipy and its 1,1'-dioxide have been reported [98]. A number of nucleoside complexes of Hg(II) have been isolated, and investigated by ^{13}C NMR and Raman spectroscopy [99].

13.2.6 Complexes with phosphine or arsine ligands

The complex $[Hg(PR_3)(NO_3)_2]$ (R = 2,4,6-trimethylphenyl) has been prepared by the reaction of $[Hg(NO_3)_2]$ with PR_3. The crystal structure reveals that the bulky ligand forces the mercury to adopt a three-coordinate structure, with nearly coplanar bonds from the metal to the phosphorus and two oxygen atoms. Weaker bonds to three more distant nitrate groups complete the coordination sphere. The compound is of interest as it exhibits the largest $^{199}Hg-^{31}P$ coupling constant yet observed $\{\delta(^{31}P)$ -1.81 p.p.m. (w.r.t. H_3PO_4); $J_{(^{199}Hg-^{31}P)}$ 10 278 Hz$\}$ [100]. In contrast, the reaction of $[Hg(tfa)_2]$ with PPh_3 produces the complex $[Hg(PPh_3)(tfa)][tfa]$ [101].

The dimeric complexes $[Hg_2X_4(PBu_3)_2]$ (X = Br, I or Cl) have been investigated by ^{199}Hg and ^{31}P NMR techniques. In the complexes with X = I or Br, it was shown that two species were present in solution (chlorinated solvent) and the structures (14) and (15) were proposed for these species [102]. Structure (15)



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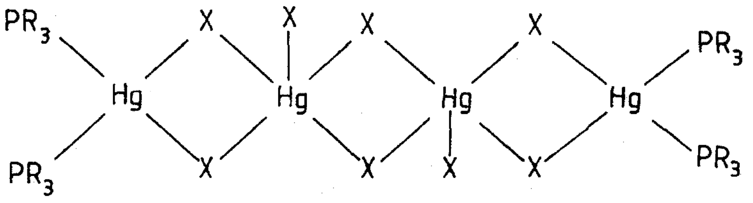
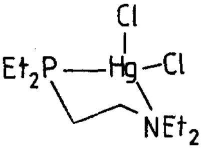


(15)

with a pentacoordinate mercury atom, is not entirely satisfactory, and it may be relevant to these observations that a compound which was thought to be $[Hg(PMe_2Et)_2Cl_2]$ has been shown to be a mixture of this and $[HgCl(PMe_2Et)_3][HgCl_3(PMe_2Et)]$. A crystal structure of the latter compound has been reported [103]. The complexes $[HgLX_2]$ and $[HgL_2X_2]$ (L = PPh_3 or $P(cych)_3$; X = Cl, Br or I) have been investigated; their vibrational spectra are compatible with the former compound being a centro-symmetric dimer and the latter possessing pseudo-tetrahedral symmetry [104].

The bidentate ligand (*N*,*N*-dimethylaminoethyl)diphenylphosphine forms the complex $[Hg(LL')Cl_2]$, in which the mercury atom is in a slightly distorted tetrahedral $\{HgPNCl_2\}$ coordination sphere (16) [105].



(16)

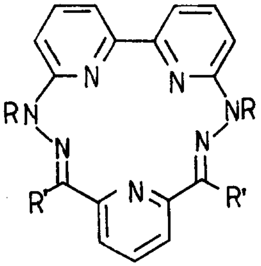
The reaction of Hg with Me_2PCl gives the diphosphine complex $\{(LL)HgCl_2\}_n$ (LL = Me_2PPMe_2), which is polymeric with a high chemical stability. The crystal structure of the compound reveals the structure to consist of infinite chains with bridging diphosphine units (*i.e.* -Hg-*P*-*P*-Hg-*P*-*P*-Hg- *etc.*). On heating, the complex gives very pure Me_2PCl, whilst the reaction with $[OH]^-$ gives Me_2PH [106].

A number of 1:1 complexes of $HgCl_2$ with 1-naphthylarsines have been described [107].

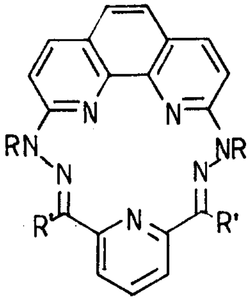
13.2.7 Complexes with macrocyclic ligands

The natural abundance ^{15}N NMR spectrum of $[HgL][ClO_4]_2$ (L = [14]ane-1,4,8,11-N_4) has been reported [108]. The template reactions of 6,6'-bishydrazino-2,2'-

bipyridines or 2,9-bishydrazino-1,10-phenanthrolines with 2,6-diacetyl- or diformyl pyridine in the presence of Hg(II) results in the formation of macrocycles of type **(17)** and **(18)**. These macrocycles were isolated as mercury complexes of the form $[HgL]_2[HgCl_4]$ [109,110,111].



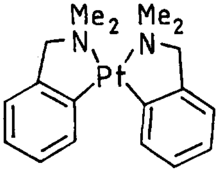
(17; R,R' = H or Me)



(18; R,R' = H or Me;

13.2.8 *Miscellaneous complexes*

The reaction of a number of organoplatinum(II) species with Hg(II) salts has been investigated, and the product of the reaction of **(19)** with $Hg(O_2CMe)_2$ shown to be the novel bimetallic complex, **(20)**. A crystal structure of the product has confirmed this formulation [112]. Another example of a species containing an Hg-Pt bond is given in Section 13.2.3.1.



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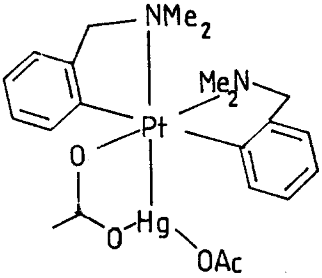


(20)

The reaction of HgTe with excess Hg(II) in H_2SO_4 gives a complex cation $[Hg_4Te]^{6+}$, which may be converted to $[Hg_5TeCl_8]$ on treatment with HCl [113].

13.2.9 *Alkylmercury(II) complexes*

13.2.9.1 *Halide and pseudohalide complexes*

The reaction of $HgCl_2$ with LiR (R = 2,4,6-tri-*tert*-butylphenyl) produces

[RHgCl], which is converted to [R_2Hg] by the action of Cu in pyridine [114]. An extensive study of the vibrational spectra of [$XHg(CY_3)$] (X = Cl, Br or I; Y = H, F or Cl) systems has been reported and it has been shown that the group Y exerts an inductive effect upon the mercury atom, through the σ-framework of the molecule [115]. The compounds [XHgR] (R = C_2H_5 or C_2D_5; X = Cl, Br or I) have been similarly investigated and the results compared with those for [MeHgX] [116]. The vibrational spectra of [RHg(CN)] (R = CH_3 or CD_3) in the solid state and in solution have been investigated. In benzene, a new Raman active band appears, which has been interpreted in terms of the formation of a charge-transfer complex [117]. An inconclusive ^{13}C and ^{1}H NMR study of partially oriented [MeHgX] (X = Cl, Br or I) molecules on Merck Phase IV has been reported [118].

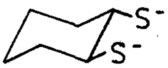
The reaction of LiD with [RHgCl] (R = Ph or Bz) has been investigated, and numerous products isolated [119].

13.2.9.2 *Complexes with oxygen donor ligands*

The reaction of [ArHg(OMe)] with H_2O_2 produces the peroxides [$ArHg(O_2)HgAr$], although with excess H_2O_2 some [ArHg(OOH)] is formed; the chemistry of these novel peroxy compounds has been discussed [120]. A ^{13}C and ^{1}H NMR spectral study of [MeHg][NO_3] in the nematic and lyotropic phases has been made and, although the structure appears similar in each, differences in J(^{199}Hg-H) were detected [121].

13.2.9.3 *Complexes with sulphur donor ligands*

$[RHg]^+$ has a high affinity for thiolate ligands and several complexes of this type have been reported. The formation of a number of complexes of $[MeHg]^+$ and the dithiolate ligands **(21)**, **(22)** and **(23)** has been investigated



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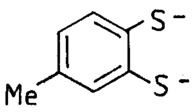

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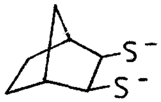


(23)

and the structure of [Hg_2Me_2L] {L = **(21)**} reported. The ligand bridges the [MeHg] units and one of the S-Hg-C bonds is greatly distorted from the linear geometry commonly observed in [MeHg] complexes [122].

The complex [ArHgL] (Ar = 2-hydroxy-5-nitrophenyl; HL = 2-mercaptopyridine) has been formed from the reaction of [ArHgCl] with 2-mercaptopyridine [123].

13.2.9.4 Complexes with nitrogen donor ligands

The complex $[MeHgL][NO_3]$ (L = 2-benzylpyridine) has been reported and shown to involve a linear N-Hg-C bond. There is a weak interaction the methylmercury group and the phenyl ring, similar to those observed in [MeHg] complexes of tyrosine and 3,3'-Me_2bipy [124]. The crystal structure of the complex $[MeHgL][NO_3]$ (L = 6-amino-9-methyl-9*H*-purine) has also been reported [125]. The complexes $[MeHgL][NO_3]$ (L = 4,4',4''-Et_3terpy or bis(2-pyridyl)methane) have been described. In the solid state, the terpy is tridentate and the bis(2-pyridyl)methane bidentate, but NMR studies have shown that both ligands are bidentate in solution [126].

A range of complexes of the type [PhHgL], containing nitrogen donor ligands, have been shown to react with SO_2, in an insertion reaction, to give the corresponding phenylsulphinate complex, $[PhSO_2HgL]$ [127].

The phosphorescence spectra of benzimidazole and tryptophan complexes of [MeHg] have been reported and a detailed analysis described [128]. Novel complexes have been isolated from the reaction of amines or pyridines with [(ArE)HgPh] (Ar = 4-nitrophenyl; E = S or O) [129]. The reaction of $Li[MeNBMe_2]$ with [MeHgCl] results in the formation of $[HgMe(MeNBMe_2)]$, whilst $HgCl_2$ reacts to give $[Hg(MeNBMe_2)_2]$. Both these compounds are thermally stable and show no tendency to polymerise [130].

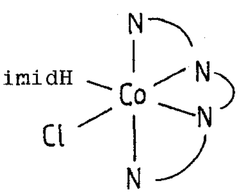
13.2.9.5 Miscellaneous

Although complexes of $[R_2Hg]$ are uncommon, several examples have been reported this year. The reaction of $[R_2Hg]$ (R = 2-thienyl or 2-furyl) with a number of bidentate donors was investigated and, although no complexes were isolated with bipy, dppe, Ph_3P or $MeSCH_2CH_2SMe$, the 2-furyl compound gave complexes with 2,9-Me_2phen and 2,4,7,9-Me_4phen whereas the 2-thienyl compound only gave complexes with the former reagent [131]. A crystal structure of $[R_2HgL]$ (R = 1,1,2-trichlorovinyl; L = 3,4,7,8-Me_4phen) has been reported. The C-Hg-C bond is non-linear, with an angle of 165° [132]. The tetrahedral complex $[R_2HgL]$ (R = 3-chloropropynyl; L = phen) has been reported and a crystal structure described [133].

The rate of exchange of mercury between Hg^{2+} and $[MeHg]^+$ in aqueous solution has been studied, using ^{203}Hg as a tracer [134].

13.2.10 Aqueous chemistry of mercury(II)

It has long been known that the aquation of transition metal complexes $[ML_5X]^{2+}$ (M = Co, Rh, Cr or Ru; X = halogen or pseudohalogen; L = amine) is accelerated by Hg(II) ions and a species such as $[L_5M\text{-}X\text{-}Hg]^{4+}$ has been proposed as the intermediate. Further examples of this phenomenon have been provided by the aquation of *unsym-fac-cis*[Co(dien)L_2Cl]$^{2+}$ (L = amine) [135], [Co(NH_3)$_5$Cl]$^{2+}$, *trans*-[Co(en)$_2$$Cl_2$]$^+$ and [$ReCl_6$]$^{2-}$, in the presence of aqueous Hg(II) ions [136]. It was demonstrated that a significant difference existed between [$ReCl_6$]$^{2-}$ and the other complexes [136]. The effect of [MeSO_3]$^-$ and [PhSO_3]$^-$ upon the Hg(II)-catalysed aquation of a number of Co(II) complexes has been reported [137]. The aquation of the two isomeric complexes **(24)** and **(25)** has been studied and the



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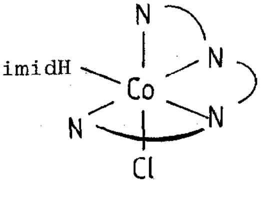


(25)

rate shown to be compatible with an I_d mechanism [138].

Evidence for the existence of the postulated L_5M-X-Hg intermediates comes from the isolation of the complex [{Co(NH_3)$_5$(NCS)}$_2$Hg][ClO_4]$_6$ from the reaction of [Co(NH_3)$_5$(NCS)][ClO_4]$_2$ with Hg[ClO_4]$_2$ in $HClO_4$ [139]. The Hg(II)-catalysed aquation of [Cr(CN)$_2$(H_2O)$_3$(NO)] has been studied electrochemically and [(NO)(H_2O)$_3$Cr(NCHgCN)$_2$Cr(H_2O)$_3$(NO)]$^{4+}$ proposed as an intermediate [140].

The nature of the ionic species present in aqueous solutions containing Hg^{2+} continues to be of interest, and the ion [Hg(OH)]$^+$ has been shown to be involved in the hydrolysis of Hg(II) compounds in aqueous perchlorate media [141]. This ion is also present, together with aquated Hg^{2+}, [Hg(OH)$_2$], [Hg(HCO_3)]$^+$, [Hg(CO_3)(OH)]$^-$ and [Hg(CO_3)$_2$]$^{2-}$ in aqueous solutions containing Hg^{2+} and [CO_3]$^{2-}$ [142].

13.2.11 Mercury compounds in inorganic synthesis

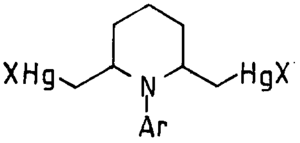
Mercury(II) compounds are widely used in organic synthesis and many examples of such applications have been reported this year. The majority of these are routine, and will not be described in detail unless they provide examples of novel applications, routes to hitherto inaccessible compounds, or insight into the mechanism of the reaction.

The reaction of alkenes with a solution of HgO in H[BF_4] in the presence of amines leads directly to the formation of 1,2-diamines, without the need to isolate and demetallate the organomercury intermediate. The reaction appears to offer considerable promise as a new synthetic route to these compounds [143]. A number of other examples of the acetoxymercuriation of alkenes with Hg(O_2CMe)$_2$ have been reported [144].

The mercuriation of arenes continues to be of interest and the reaction has been extended to ferrocinium and ethylferrocinium trichloroethanoates, which react with $Hg(O_2CMe)_2$ in a reaction which is first order in ferrocinium salt and in $Hg(O_2CMe)_2$ [145]. The mercuriation of aromatics with $Hg(tfa)_2$ or $[Hg(tfa)(O_2CMe)]$ appears to proceed *via* a rapidly formed complex and the mechanism of this reaction has been investigated in considerable detail [146]. The formation of Hg(II)-arene compounds in liquid SO_2 has been examined [147].

The mercuriation of PhCH=NNHPh with $Hg(O_2CMe)_2$ in $MeCO_2H$ occurs exclusively at the *ortho* position of the *N*-bonded phenyl group, *via* an interaction with the imino group [148]. Synthetic applications of the mercuriation reactions include the use of [RHgX] (X = halide) as a carbonium ion precursor in Friedel-Crafts reactions. Thus, anisole reacts with $ROCHMeCH_2HgBr$ in the presence of a Lewis acid catalyst to give a mixture of *ortho* and *para* $ROCHMeCH_2$-derivatives [149].

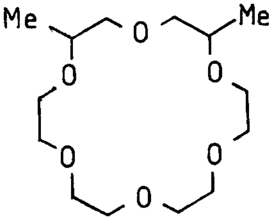
A new route to the preparation of arylpiperidines has been developed, based on the $Na[BH_4]$ reduction of the organomercury(II) compounds, **(26)**, formed by



(26)

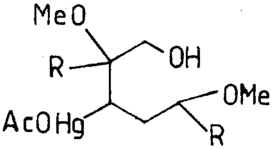
the reaction of 1,6-heptadienes with anilines in the presence of $Hg(O_2CMe)_2$ [150]. In a related reaction, 1,4-diaryl-*trans*-2,5-bis(bromomercuriomethyl)piperazines are formed by treatment of allylarylamines with mercury(II) halides [151].

The use of an oxymercuriation-demercuriation sequence enabled 2,6-dimethyl-18-crown-6 **(27)** to be prepared from diallyl ether and tetraethylene glycol, by



(27)

reaction with $Hg(O_2CMe)_2$ followed by $Na[BH_4]$ [152]. Cyclopropyl epoxides are ring-opened by $Hg(O_2CMe)_2$ to produce alkylmercury(II) ethanoates **(28)**, and a mechanism has been proposed for this reaction [153]. In contrast, the reaction



(28)

of cyclopropanes with methanolic $Hg(O_2CMe)_2$ results in the formation of 3-methoxypropylmercury(II) compounds, which may be demercuriated with $Na[BH_4]$ or $Na[BH(OMe)_3]$. The reductive-demetallation is thought to involve alkyl radicals and support comes for this from the isolation of 5-methoxypentane derivatives on treatment with complex hydrides in the presence of an alkene [154]. Similarly, in AcOH the product is a 3-acetoxymercury(II) compound, which may be demetallated in high yield by $Na[BH_4]$ [155]. The reaction of bis(trifluoromethyl)ketenes or bis(trifluoromethyl)ketimines with $Hg(O_2CR)_2$ gives adducts which may be decomposed to give mixed trifluoroethanoyl anhydrides [156].

The conversion of diazoalkenes to acetals may be achieved by the use of [RHgX] (X = halide). Thus, $R'R''CN_2$ reacts to produce RHgCClR'R'', which may be thermolytically demetallated to give $R'R''C(OR''')_2$ [157]. Although Me_2NNH_2 reacts with HgO to give 1,1,4,4-tetramethyltetrazene, $Me_2NN{=}NNMe_2$, $MeNHNH_2$ gives no MeNHN=NHNMe under the same conditions [158]. The authors of this paper stress that this reaction, and presumably some similar ones, is potentially very hazardous, since 5-10% of Me_2Hg is formed. Organometallic tribromomethyl compounds act as dibromocarbene precursors, and $PhHgCBr_3$ is no exception, reacting with carbonyl compounds to produce spirooxiranes and PhHgBr [159].

The alkylchromium complex, $[RCr([15]ane\text{-}1,4,8\text{-}12\text{-}N_4)(H_2O)]^{2+}$, is dealkylated by aqueous solutions of Hg^{2+} or $[MeHg]^+$ [160].

13.2.12 ^{199}Hg NMR spectroscopic studies

The increasing availability of multinuclear NMR machines, the relatively high natural abundance of ^{199}Hg with a nuclear spin $I = \frac{1}{2}$ (16.84%) and a receptivity similar to that of natural abundance ^{13}C, all favour the use of ^{199}Hg NMR in the investigation of mercury compounds. ^{199}Hg is observable at 17.9 MHz on a 100 MHz machine, and is therefore within the range of most modern multinuclear machines. The quadrupolar nucleus, ^{201}Hg ($I = 3/2$) is less readily observed (13.22% abundance, receptivity similar to ^{13}C, 6.60 MHz) and offers no advantage over the more simply studied ^{199}Hg nucleus.

The compounds $[HgX_2]$ (X = Cl, Br, I or CN) and [XHgCN] have been investigated and the position of the ^{199}Hg resonance found to be very sensitive to the temperature, the concentration, and the solvent; it was shown that more polar solvents caused decreased shielding of the mercury nucleus [161]. The mixed cyanocomplexes [XHgCN] (X = Cl, Br, I, OAc, SCN, SPh, SEt, Ph or CF_3SO_3) have been shown to behave in a similar manner [162]. The chemical shift $\delta(^{199}Hg)$, of $Hg(CN)_2$ in a wide range of solvents has been investigated [162].

The ^{199}Hg NMR spectra of a number of $[MeHgL][NO_3]$ (L = substituted pyridine) complexes have been reported, and the authors point out that, although $\delta(^{199}Hg)$ is of little help in structure analysis, the coupling constant, $J(^{199}Hg\text{-}H)$, may be of more use [163].

The use of ^{199}Hg NMR, in determining the structure of a number of phosphine complexes in solution [102,164] has been discussed earlier.

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