*Coordination Chemistry Reviews*, 37 (1981) 323—333
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

# 13. MERCURY

M.N. HUGHES

## CONTENTS

## INTRODUCTION

The general presentation of this review is similar to that used for zinc and cadmium. In a few cases, reference should be made to that chapter in order to cover compounds involving both mercury and the other IIB elements. These will be noted in the text.

## 13.1 HALIDE AND PSEUDOHALIDE COMPLEXES

The electronic spectra of [$HgX_2$] (X = Cl, Br or I) have been measured [1] in twenty-three solvents in an endeavour to characterise the solution structures of these compounds. The peak maxima correlate linearly with dielectric constant and Kosower's *Z* value for solvent polarity, in accord with the solvation of linear mercury(II) halides in the equatorial position. The solvent-dependence and intensities of the $^1\Sigma_u^+$ and $^1\Delta_u$ excited states are consistent with linear, or only slightly bent, upper states. The only exceptions reported were for [$HgI_2$] in cyclohexane and 2,2,4-trimethylpentane, where the $^1\Delta_u$

0 010-8545/81/0000—0000/$02.75 © Elsevier Scientific Publishing Company

state was assumed to be strongly bent. X-ray diffraction and Raman studies [2] on these compounds in dmso, and upon $[HgCl_2]$ in methanol, show that for concentrated (2.5 mol dm$^{-3}$) solutions in dmso the angle $X{-}\hat{Hg}{-}X$ is 159° and 165° for $[HgI_2]$ and $[HgBr_2]$, respectively, whilst some slight deviation from linearity due to solvent interference was shown by the presence of a weak $\nu_3$ band in the Raman spectrum for $[HgCl_2]$ in methanol. It should be noted that the results described in ref. 1 were carried out at $10^{-4}$—$10^{-5}$ mol dm$^{-3}$ concentrations, and this may account for the differences observed in these two sets of measurements. The formation of 1 : 1 and 1 : 2 complexes of $[HgI_2]$ with dmso has been shown by spectroscopic techniques, while polynuclear complexes are formed in concentrated solutions [3]. The interaction between $[HgI_2]$ and a range of strong oxygen donor solvents follows the donicity scale of the solvents. Changes in electronic spectra of aqueous $HgX_2$ solutions (X = Cl, Br or I) on adding fluoride have been interpreted [4] in terms of the formation of $[HgX_2F]^-$, and possibly $[HgX_2F_2]^{2-}$. The presence of configurational equilibria has been established for trihalo complexes of Hg(II) in amide solvents by the use of Raman spectroscopy, which indicated the presence of two structural forms of these ions in equilibrium. These are suggested to be the unsolvated $[HgX_3]^-$ ($D_{3h}$ symmetry) and the solvated $[SHgX_3]^-$ ($C_{3v}$ symmetry) anions [5].

The formation of mixed halide and pseudohalide complexes has been studied for the replacement of $Cl^-$ by $[CN]^-$ in $[HgCl_2]$, $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ [6], and for $[HgCl(SCN)]$, $[Hg(CN)(SCN)]$ and $[HgBr(CN)]$ [7]. Log $K$ ($K$ = equilibrium constant) for the redistribution reactions

$$[HgX_2] + [HgY_2] \rightleftharpoons 2[HgXY]$$

are 0.39 ($[CN]^-$, $[SCN]^-$), 0.92 ($Cl^-$, $[SCN]^-$), 0.20 ($Br^-$, $[CN]^-$), 0.59 ($Br^-$, $I^-$) and 0.62 ($Cl^-$, $I^-$) [8].

Log $\beta_n$ values for $[HgI_n]^{(n-2)-}$ ($n$ = 1—4) in aqueous dmf increase with concentration of amide [9], reflecting its weaker solvation. Heats of formation of these compounds have been measured [10].

The structure of mercury(II) fluoride hydroxide, $[Hg(OH)F]$, has been redetermined by X-ray [11] and neutron [12] diffraction. It involves $[Hg(OH)]_n^{n+}$ chains, with three Hg—F interactions at 2.49—2.50 Å, so that the structure approximates to zig-zag columns of $[Hg(O_3F_3)]$ octahedra. The hydrogen atoms are located between the columns and are linked to the fluoride by strong hydrogen bonds. The temperature variation of the lattice parameters of $\alpha$-$[NH_4][HgCl_3]$ have been measured, and the coefficients for thermal expansion determined [13]. The $^{35}Cl$ NQR spectra of the complex of $[HgCl_2]$ with 4-methylpyridine-*N*-oxide, measured over a temperature range, show that resonances due to bridging and terminal chlorides can be distinguished. The lower-frequency resonance, due to bridging chlorine, becomes almost independent of temperature below 125 K, as the bridging chlorine becomes less able to undergo torsional motion [14].

The structures of several bromomercurate species have been reported.

Dicaesium tetrabromomercurate(II) involves a distorted $[HgBr_4]^{2-}$ anion, with Hg—Br distances of 2.552 and 2.597 Å, and Br—$\widehat{Hg}$—Br bond angles 103.87, 117.85, 111.73 and 107.63° [15]. The $[Hg_2Br_5]^-$ group in Cs-$[Hg_2Br_5]$ has been discussed [16] in terms of a complex involving $[HgBr_3]^-$ and $[HgBr_2]$, while the structure of the $[Hg_2Br_6]^{2-}$ anion has been determined [17] as the anion of a complex mixed-valence Cu(II), Cu(III) cation, hexakis-(dibutyldithiocarbamato)triscopper. Electron diffraction data on $HgI_2$ [18] and X-ray diffraction data on a range of compounds with $[HgI_3]^-$ and $[HgI_4]^{2-}$ anions have been published [19]. The presence of the $[Hg_2I_5]^-$ complex anion in $[HgI_2]$ solutions of guanidine hydroiodide in propanone has been established by IR and Raman spectroscopy [3].

A number of bimetallic tetrathiocyanate complexes of the type MM'-$(SCN)_4 \cdot x$ L (M = Zn(II), M' = Cd(II) or Hg(II)) have been discussed under Zinc and Cadmium (Chap. 12) [20]. It should be noted, however, that while for M' = Cd(II) mixed cationic—anionic complexes are formed, in the case of M' = Hg(II), monomeric bridged complexes are formed [21]. Mixed metal complexes involving $[Hg(SeCN)_4]^{2-}$ have been characterised [22]. An interesting species is the compound lead(II) di(isothiocyanato)bis($\mu$-selenocyanato)-di(thiocyanato)cobaltate(II) mercurate(II) [23].

## 13.2 COMPLEXES WITH OXYGEN DONOR LIGANDS

### *13.2.1 Complexes with inorganic oxoanions*

The use of Raman spectroscopy has shown [24] that aqueous solutions of mercury(I) nitrate contain the linear species $[Hg_2(OH_2)(NO_3)]^+$ and $[Hg_2(OH_2)_2]^{2+}$. The hydrolysis of $[Hg_2(NO_3)_2]$ is complex, but it appears now that only three products are obtained, depending upon the conditions. These correspond to the solid phases; Phase C $\{Hg_2(OH)_2 \cdot 3\ Hg_2(NO_3)_2\}$ formed by recrystallising $[Hg_2(NO_3)_2]$ from 0.5 mol $dm^{-3}$ nitric acid, Phase B $\{(2\ Hg_2(OH)_2 \cdot 3\ Hg_2(NO_3)_2 \cdot H_2O)\}$ formed by recrystallising $Hg_2(NO_3)_2$ from water, and Phase A $\{Hg_2(OH)_2 \cdot Hg_2(NO_3)_2\}$, which is yellow, formed by the action of hot water on either of the other phases. Raman spectra of crystalline dimercury(I) nitrate and these three phases have allowed tentative structures to be assigned to components of these phases, namely: Phase A, $[H_2O—Hg—Hg—ONO_2]$; Phase B, $[O_2NO—Hg—Hg—OH_2][NO_3]$; and Phase C, $[Hg_2(NO_3)_2] \cdot [Hg_2(OH)][NO_3]$, where the $Hg_2OH$ cations involve bridging hydroxo groups (—Hg—Hg—OH—Hg—Hg—OH—).

### *13.2.2 Complexes with carboxylic acids and related ligands*

Mercury(II) trichloroethanoate and its complexes with pyridine and 1,10-phenanthroline have been prepared [25]. Determinations of formation constants of complexes have included those for phosphine ethanoates [26], the mixed ligand system [Hg(nta)(phen)](nta = nitrilotriacetate) [27], *trans*-1,2-

diaminocyclohexane-*N,N*′-dimalonic acid, $H_4L\{[HgHL]^-$, $[HgH_2L]$, $[HgL]^{2-}$ and $[Hg(OH)L]^{3-}\}$ [28], bis-(2-aminoethyl ether)-*N,N*-dimalonic acid, $H_4L$-$\{[HgHL]^-$, $[HgL]^{2-}$ and $[Hg(OH)L]^{3-}\}$ [29], mixed complexes with $[Hg(edta)]^{2-}$ and 1,2-diaminoethane [30], and for edta alone [31]. The Hg(II) complexes with ethylenediaminetetraacetamide [32] and *N,N*′-dimethyl-1-ethyl-imidazole-4,5-dicarboxamide [33] have been reported. The antibiotic cycloserine forms the complexes $[HgLX_2]$ (X = Cl or Br), in which the ligand is oxygen-bonded via the carbonyl group [34]. Formation constants are reported for Hg(II) and uracil, which usually coordinates throught the exocyclic oxygen [34a].

## 13.3 COMPLEXES WITH SULPHUR OR SELENIUM DONOR LIGANDS

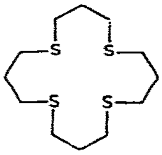
### *13.3.1 Complexes with thiourea and related ligands*

The complex di-μ-bromobis-[bis(tetramethylthiourea)mercury(II)] tetrafluoroborate involves a binuclear cation in which two mercury(II) centres are bridged by two bromide ions and each Hg(II) is *S*-bonded by two tetramethylthiourea (tmtu) ligands. The analogous complexes $[\{Hg(tmtu)_2X\}_2]Y_2$ and $[Hg(tmtu)_4]Y_2$ (where X = Y = $ClO_4$ or $BF_4$; X = Cl or Br; Y = $BF_4$ or $ClO_4$) have also been prepared. The IR spectra of these compounds suggest the presence of Hg—S bonding. The spectra of the 1 : 4 complexes show only one Hg—S stretching frequency, suggestive of a tetrahedral structure [35]. The complexing of Hg(II) by several sulphur ligands, including thiourea, in mixed solvents has been studied [36].

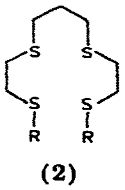
*N,N*-diisopropyldithiocarbamatomercury(II) recrystallises from propanone in two modifications. One of these, the β form, contains both monomeric and dimeric forms of the complex [37]. The complex $[Bu_4N][Hg(S_2CNEt_2)_3]$ has been prepared [38]. Raman and IR spectra have been reported for the complexes of Hg(II) halides with *N,N*′-tetramethylthiuram monosulphide, $[HgLX_2]$ [39].

### *13.3.2 Complexes with thioether ligands*

Unlike other lighter metal cations, Hg(II) does not appear to show the "macrocyclic effect". Thus, Hg(II) exhibits no preference for macrocyclic ligands compared to their open chain analogues. Indeed, formation constants for a series of complexes of Hg(II) with macrocyclic tetrathia-ether ligands, such as (1), are at least an order of magnitude lower than those for



(1)



(2)

complexes with the open chain ligand (2). A possible explanation for this phenomenon, namely that the Hg(II) is not readily encircled by the macrocycle, does not hold for the complex of $Hg(ClO_4)_2$ with (1). In this case, the Hg(II) is situated almost in the centre of the four sulphur atoms, although these atoms are twisted somewhat out of the plane. The coordination is completed by two unequally bonded perchlorate groups in the axial positions. One of these is weakly bidentate, giving seven-coordinate Hg(II). The elimination of this explanation for the non-existence of the macrocyclic effect in Hg(II) raises some interesting questions [40].

A $^{13}C$ NMR spectroscopic study of Hg(II)—thioether compounds has involved the measurement of chemical shifts for *S*-carboxymethyl-L-cysteine and for horse liver dihydrogenase *S*-carboxymethylated at Cys-46, in an endeavour to model and characterise thioether coordination in metalloproteins [41]. $^{35}Cl$ NQR measurements on the compounds $2\ HgCl_2 \cdot Et_2S$ and $3\ HgCl_2 \cdot 2\ Me_2S$ have been reported [42].

### *13.3.3 Complexes with thiocarboxylic acids*

The complexes [HgL] and $[Hg(HL)_2]$ ($H_2L$ = *N*-benzoylcysteine) involve ligands chelated through the protonated mercapto group and carboxyl oxygen [43], whilst the complex [Hg(thiomalate)] is possibly binuclear [44]. Solution studies have been published on complexes of Hg(II) with ethylenedithioacetic acid [45], diethylenetrithiodiacetic acid [46] and thiodipropionic acid [47].

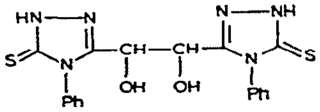
### *13.3.4 Complexes with mercapto ligands*

The compounds [(MeS)HgX] (X = Cl or Br) are isostructural [48], and involve a two dimensional polymeric Hg—S—X sheet, in which parallel chains $(\text{—Hg—SMe—})_n$ are linked into parallel sheets by triply-bridging halide ions coordinated to two mercury atoms in one chain and one mercury atom in an adjacent chain, thus giving a mercury environment of $Hg(\mu\text{-SMe})_2(\mu_3\text{-Cl})_3$, with an additional weak Hg—S contact. The complexing of Hg(II) by 8-mercaptoquinoline in hydrochloric acid solutions has been studied [49].

### *13.3.5 Complexes with thione ligands*

Complexes with 1,4,6-trimethylpyrimidine-2-thione(L) and the 1-methylpyrimidine-2-thione (L′) $[HgL_2X_2]$ (X = Cl, Br or I), $[Hg_2L'_3X_4]$ (X = Cl or Br), and $[HgL'X_2]$ [50] involve *N, S* chelating thione ligands for $[HgL_2X_2]$ and $[HgL'I_2]$. The far IR spectrum of the last compound includes a band at 154 $cm^{-1}$ assigned to $\nu(Hg\text{—}I)_{terminal}$, implying it to be tetrahedral in structure: the others involve halogen-bridged octahedral structures. The compounds $Hg_2L'_3X_4$ probably involve structures of the type $[HgL'_3][HgX_4]$. The compound $[HgLCl_2]$ (L = 1,2-bis(4-phenyl-1,2,4-triazoline-5-thione-3-yl)ethane-

1,2-diol; 3) involves a polymeric structure with Hg—thione interactions [51].



(3)

*N*-methylthiopyrrolidin-2-one (nmtp) gives 2 : 1 complexes with $HgX_2$ (X = Cl, Br or I) and also the complex $[Hg(nmtp)_5][ClO_4]_2$: complexes $[HgL_2X_2]$ involve four-coordinate structures while $[Hg(nmtp)_5][ClO_4]_2$ is a 2 : 1 electrolyte, implying a five-coordinate species. Complexes with $[Hg_2]^{2+}$ could not be prepared, disproportionation taking place [52]. The [Hg(2-thiouracil)$_2$Cl$_2$] complex is probably octahedral with bridging halide and *S*-bonded thiouracil [53].

### *13.3.6 Complexes with selenium ligands*

The red modification of the tetrakis(diphenylseleno)dimercury(I) cation involves 3-coordinate mercury, $[L_2Hg—HgL_2]^{2+}$ [54]. $Hg_2P_2S_6$ and $Hg_2P_2Se_6$ involve $P_2E_6$ groups linked by Hg, which is tetrahedrally coordinated by E [55].

## 13.4 COMPLEXES WITH NITROGEN DONOR LIGANDS

### *13.4.1 Complexes with ammines and various aliphatic nitrogen ligands*

Studies on $[Hg(NH_3)_2X_2]$ (X = Cl or Br) indicate that both compounds retain entropy at the absolute zero, and are therefore still disordered. This is attributed largely to dimer disorder [56]. Thermochemical measurements have also been reported on these mercury(II) halides with propylamine, isopropylamine, butylamine and isobutylamine [57]. Formation constants have been reported for complexes of mercury(II) with *N,N'*-dimethyl-1,2-diaminoethane and other diamines [58], while the formation of complexes with diamines and polyamines in dmso has been investigated through the anodic dissolution of mercury electrodes in the presence of the ligand. Some short-lived species have been detected by cyclic voltammetry [59].

Complexes studied include $[Hg(HL)Cl_2] \cdot H_2O$ {where HL is the hydrazone derived from Girard T and chromone (i.e. 6-formyl-7-hydroxo-5-methoxy-2-methylchromone-Girard T hydrazine)} [60] and those of triphenylphosphoimine $Ph_3P = NH$ (L), $[HgLX_2]_2 \cdot CHCl_3$ (X = Cl or Br) and $[Hg_2L_3I_4]$. These phosphoimine complexes are prepared readily by the in situ alcoholysis of $Ph_3P{=}NSiMe_3$ in the presence of the anhydrous mercury(II) halide. Complexes $[Hg_2L_3I_4]$ are suggested to involve a 1 : 1 molecular lattice of $[HgL_2I_2]$ and $[HgLI_2]$, which units are bridged by iodide, and in which the mercury atoms in the chain are alternatively tetra- and penta-coordinate [61]. The platinum(II) complex *trans*-[$PtCl(PEt_3)_2(CH{=}NC_6H_4$-4-$CH_3$)] acts as a monodentate ligand to [$HgCl_2$], giving a 1 : 1 complex [62].

### *13.4.2 Complexes with nitrogen heterocyclic ligands*

The complexes with *N*-(2-pyridyl)acetamide (L) [$HgL_2Cl_2$] and [$HgLCl_2$] involve a monodentate heterocyclic-*N*-bonded ligand and a bidentate ligand, respectively [63]. The ligand 2,5-diphenyloxazole (ppo) is *N*-bonded in the complexes [$Hg(ppo)_2X_2$] (X = Cl, Br, I, $NO_3$ or NCS) [64]. The complexes with 2,5-dimethyl-1,3,4-thiadiazole (dtz), [$Hg(dtz)X_2$] (X = Cl, Br or I) and [$Hg(dtz)_2(NO_3)_2$] involve tetrahedral $N_2X_2$ coordination, with *N,N*-bridging ligand, and tetrahedral $N_2O_2$ coordination with monodentate ligand and nitrato groups, respectively [65]. The structure of bis[2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl] mercury(II), $Hg[N(CSCF_3)_4]_2$, involves two-coordinate mercury with monodentate nitrogen-bound ligands, Hg—N = 2.017 Å. It is claimed that this bond length represents an essentially unperturbed measure of an Hg(*sp*)—N($sp^2$) bond [66].

The structures of the complexes of cadmium(II) iodide and mercury(II) iodide with the diaza crown ether 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane involve an approximately hexagonal bipyramid of two nitrogen and four oxygen atoms in a plane with two axial iodide groups. However, there are interesting differences between the two structures. On changing from $Cd^{2+}$ to $Hg^{2+}$, ring expansion is reflected in increased O—O distances and a substantially increased N—N distance (~0.50 Å). This is probably unrelated to the different radii of these ions and reflects rather the very strong I—Hg—I coordination, which weakens the Hg—N interaction [67]. Formation-constant measurements on this system should produce some interesting results.

The structure of dichloro(9-methylhypoxanthine)mercury(II) involves three-coordinate mercury (N, Cl, Cl), with two long-range interactions between Hg and chlorides of neighbouring molecules [68].

## 13.5 COMPLEXES WITH PHOSPHORUS DONOR LIGANDS

A considerable number of papers have been concerned with mercury(II) complexes of phosphines, and have concentrated particularly on structural determinations and $^{31}P$ NMR spectroscopic measurements. The complexes [$HgL(O_2CMe)_2$] (L = tricyclohexylphosphine or tri-2-tolylphosphine) are dimeric in the solid state, but monomeric in solution. These dimers involve a new bridging mode for the ethanoato ligand, in which one oxygen atom only from each of the two ethanoate groups links both mercury atoms in the dimer. Both structures involve three nearly coplanar strong bonds, with a fourth weaker bond (Hg—O = 2.523 Å) forming the bridge. Six-coordination about mercury is achieved by weaker intramolecular interactions with ethanoato oxygens. Cone angle calculations indicate $\theta = 179°$ ($Pcych_3$) or $\theta = 191°$ ($P(2\text{-tol})_3$). In the latter case, the gaps between the 2-tolyl groups are large enough to allow the ethanoato oxygen to approach and form the bridge [69]. The structure of the dimer $[\{Hg(P(2\text{-tol})_3)Cl(ClO_4)\}_2]$ has also been determined [70]. This involves four-coordinate mercury, with monodentate perchlorate and bridging chloride. The structure corresponds to a trigonal bipyramidal stereochemistry, with the phosphorus atom and the chloride group in axial positions and one equatorial position empty.

The dinitrato(trimesitylphosphine)mercury(II) dimer has a 208° cone angle for trimesitylphosphine, the largest cone angle measured so far. This structure involves two different dimers, which differ from each other in the configuration of the nitrate and the trimesitylphosphine groups at each mercury, particularly in the orientation of the non-bridging nitrato groups [71].

Dithiocyanato(triphenylphosphine)mercury(II) exists in two forms. The compound prepared in ethanol as a solvent (the $\alpha$-form) involves a trigonal bipyramidal coordination, with two *S*-bonded thiocyanato groups and the phosphine giving the trigonal planar group, while two Hg—N weak axial interactions are also present. This involves the SCN groups in adjacent molecules, so the thiocyanate bridges mercury centres [72]. The $\beta$ form, which is prepared when propanone is used as the solvent, involves two types of infinite chains, with thiocyanate-bridged mercury atoms. In Chain 1, mercury has the coordination described above for the $\alpha$-form, but Chain 2 involves four-coordinate mercury, in which the mercury is bound to the phosphine, a unidentate *S*-bonded thiocyanato group, and to two bridging thiocyanato groups, one of which will be *S*-bonded and the other *N*-bonded. The chains are held together by Van der Waals' contacts [73].

A range of complexes of triphenylphosphine with mercury(II) ethanoates and fluoroethanoates have been prepared: these include $[Hg(PPh_3)_n(O_2CR)_2]$ ($n = 1$, 2 or 3 and $R = CH_3$, $CH_2F$, $CHF_2$ or $CF_3$). The 1 : 1 and 2 : 1 complexes have been isolated and the formation of the 3 : 1 complex in solution has been inferred from $^{31}P$ NMR spectral data. The 1 : 1 and 2 : 1 complexes are monomeric species, in which the carboxylate groups are bidentate. The $^{199}Hg$—$^{31}P$ coupling constants and the $^{31}P$ chemical shifts for these complexes increase in the order $O_2CCH_3 < O_2CCH_2F < O_2CCHF_2 < O_2CCF_3$. Possible correlations with the p$K_a$ values of the carboxylic acid are discussed [74]. $^{31}P$—$^{199}Hg$ coupling constants for a range of complexes $[HgL_2(ClO_4)_2]$ (L = tertiary phosphine) increase with decreasing basicity of the phosphine [75]. These coupling constants are also discussed with reference to the bulkiness and basicity of the phosphine ligands in $[(R_3P)_nHg(O_2CMe)_2]$ $\{n = 1$ or 2, $R_3P = (4\text{-tolyl})_3P$, $(4\text{-F-}C_6H_4)_3P$, $Ph_2MeP$, $Ph_2EtP$, or $PhEt_2P$; $n = 1$, $R_3P = (2\text{-tolyl})_3P\}$ [76]. Variable temperature $^{31}P$ NMR spectral data have been used to investigate ligand exchange rates in a wide range of aryl—phosphine complexes [76,77].

$Hg(CN)_2$ forms 1 : 2 complexes with triphenylphosphine and tri-4-tolylphosphine, 1 : 1 and 1 : 2 complexes with tricyclohexylphosphine, and 1 : 1 complexes with tri-*tert*-butylphosphine. The 1 : 2 complexes have a pseudotetrahedral structure, whilst the 1 : 1 complexes may be dimeric with terminal and bridging cyanide ligands [78]. Other studies involve the preparation of complexes $[(XCN)_2(L_2)M(NCX)_2Hg(PPh_3)_2]$ (where {M = Co(II), Ni(II), Cu(II) or Zn(II); L = pyridine or nicotinamide; X = S or Se) [79], and the thermal decomposition of $[Hg(\text{tri-4-xylylphosphine})X_2]$ (X = Cl, Br or I) [80].

## 13.6 MISCELLANEOUS

The reaction of mercury with $AsF_5$ in liquid $SO_2$ gives the chain compound $Hg_{2.82}(AsF_6)_{0.94}$, an anisotropic superconductor [81]. The reaction of $Na[Mn(CO)_5]$ in thf solution with $(C_2H_5)_2AlCl \cdot thf$, in the presence of an excess of sodium amalgam, gives $[(CO)_5Mn]_2Hg \cdot thf$. $Hg[Mn(CO)_5]_2$ could also be isolated, but did not give $[(CO)_5Mn]_2Hg \cdot thf$ on addition of thf [82].

## REFERENCES

1 T.R. Griffiths and R.A. Anderson, J. Chem. Soc., Faraday Trans. 1, (1979) 957.
2 M. Sandstrom, Acta Chem. Scand., Ser. A, 32 (1978) 627.
3 J.P. Joly and I.F. Nicolau, Spectrochim. Acta, Part A, 35 (1979) 281.
4 T.R. Griffiths and R.A. Anderson, Inorg. Nucl. Chem. Lett., 15 (1979) 41.
5 D.N. Waters, Z. Kantarci and N. Nazmun, J. Raman Spectrosc., 7 (1978) 288.
6 V.I. Belevantsev, T.I. Koroleva, B.I. Peshchevitskii and K.A. Udachin, Zh. Neorg. Khim., 24 (1979) 2378; Koord. Khim., 5 (1979) 27.
7 V.I. Belevantsev, B.I. Peshchevitskii and A.V. Shuvaev, Chem. Abstr., 91 (1979) 129731.
8 A.V. Shuvaev, Zh. Neorg. Khim., 24 (1979) 2091.
9 F.M. Tulyupa, E.Ya. Baibarova and V.N. Movchan, Zh. Neorg. Khim., 24 (1979) 2385.
10 U. Biader Ceipidor, G. D'Ascenzo and M. Tomassetti, Thermochim. Acta, 33 (1979) 231.
11 C. Stalhandske, Acta Crystallogr., Sect. B, 35 (1979) 949.
12 Yu.Z. Nozik, L.E. Fykin, V.I. Bukin and N.M. Laptash, Koord. Khim., 5 (1979) 276.
13 J. Sadanandam and S.V. Suryanarayana, Acta Crystallogr., Sect. A, 35 (1979) 923.
14 L. Ramakrishnan, S. Soundararajan, V.S.S. Sastry and J. Ramakrishna, Aust. J. Chem., 32 (1979) 931.
15 V.I. Pakhomov, P.M. Fedorova and I.N. Ivanova-Korfina, Koord. Khim., 4 (1978) 1765.
16 V.I. Pakhomov, P.M. Fedorova and I.N. Ivanova-Korfina, Koord. Khim., 5 (1979) 1245.
17 A.L. Spek, Cryst. Struct. Commun., 8 (1979) 577.
18 V.P. Spiridonov, A.G. Gershikov and B.S. Butaev, J. Mol. Struct., 52 (1979) 53.
19 G. Szasz, M. Medgyaszay and L. Csordas, Magy. Kem. Foly., 85 (1979) 289.
20 M.N. Hughes, Coord. Chem. Rev., 37 (1981) 297.
21 P.P. Singh, S.A. Khan, M. Dubey and O.P. Agrawal, Inorg. Chim. Acta, 33 (1979) 15.
22 P.P. Singh, A.K. Srivastava and L.P. Pathak, J. Coord. Chem., 9 (1979) 65; M. Nagao, H. Inoue and S. Yanagisawa, J. Inorg. Nucl. Chem., 40 (1978) 1686.
23 P.P. Singh and N. Singh, J. Mol. Struct., 54 (1979) 207.
24 K.-H. Tan and M.J. Taylor, Aust. J. Chem., 31 (1978) 2601.
25 Yu.A. Ol'dekop, N.A. Maier, A.A. Erdman and Z.P. Zubreichuk, Zh. Obshch. Khim., 49 (1979) 411.
26 J. Podlahova and J. Podlaha, Collect. Czech. Chem. Commun., 44 (1979) 1343.
27 K. Kapoor, V. Kumari and R.C. Sharma, Chem. Era, 14 (1978) 33.
28 T.I. Smirnova and I.P. Gorelov, Zh. Neorg. Khim., 23 (1978) 2719.

29 Yu.M. Kozlov and V.A. Babich, Zh. Neorg. Khim., 24 (1979) 2690.
30 G. Lesgards and A. Raymond, C.R. Acad. Sci., Ser. C, 288 (1979) 417.
31 T.J. Janjic, L.B. Pfenat and V. Popov, J. Inorg. Nucl. Chem., 41 (1979) 6365.
32 R.W. Hay, K.B. Nolan and M.H. Shuiab, Transition Met. Chem., 4 (1979) 142.
33 G.V. Tsintsadze, A.Yu. Tsivadze and T.V. Kuchuloriya, Chem. Abstr., 90 (1979) 214472.
34 C. Preti, G. Tosi and P. Zannini, Z. Anorg. Allg. Chem., 453 (1979) 173.
34a R.C. Srivastava and M.N. Srivastava, J. Inorg. Nucl. Chem., 40 (1978) 1439.
35 L.P. Battaglia, A.B. Corradi, G. Marcotrigiano and G.C. Pellacani, J. Chem. Soc., Dalton Trans., (1979) 1039.
36 V.V. Movchan, F.M. Tulyupa and E.Ya. Baibarova, Zh. Neorg. Khim., 24 (1979) 2557.
37 H. Iwasaki, M. Ito and K. Kobayashi, Chem. Lett., 12 (1978) 1399.
38 A. Nieuwport, A.H. Dix, P.A.T.W. Porskamp and J.G.M. van der Linden, Inorg Chim. Acta, 35 (1979) 221.
39 C.F. Barrientos and J.G. Contreras, An. Quim., 75 (1979) 245.
40 T.E. Jones, L.S.W.L. Sokol, D.B. Rorabacher and M.D. Glick, J. Chem. Soc., Chem. Commun., (1979) 140.
41 R.G. Khalifah, Inorg. Chim. Acta, 32 (1979) L53.
42 K.R. Buck, Inorg. Nucl. Chem. Lett., 15 (1979) 117.
43 G.D. Segzhda, S.I. Neikovskii, F.M. Tulyupa and A.P. Gulya, Koord. Khim., 5 (1979) 632.
44 P.R. Patel and V. Krishnan, J. Inorg. Nucl. Chem., 40 (1978) 1255.
45 A. Napoli, Ann. Chim. (Rome), 68 (1978) 363.
46 A. Napoli and M. Paolillo, Ann. Chim. (Rome), 69 (1979) 145.
47 K.M. Koul, M.K. Puri and K.P. Dubey, Chem. Era, 14 (1978) 151.
48 A.J. Canty, C.L. Raston and A.H. White, Aust. J. Chem., 32 (1979) 311; 1165.
49 V.I. Suprunovich and S.T. Vashchenko, Zh. Neorg. Khim., 24 (1979) 2371.
50 D.M.L. Goodgame and G.A. Leach, Inorg. Chim. Acta, 32 (1979) 69.
51 V.J. Ram, L. Mishra and H.N. Hirdya, Transition Met. Chem., 4 (1979) 237.
52 P. Rechberger and G. Gritzner, Inorg. Chim. Acta, 31 (1978) 125.
53 D.M.L. Goodgame and G.A. Leach, Inorg. Chim. Acta, 37 (1979) L505.
54 L. Brodersen, G. Liehr and M. Rosenthal, Z. Naturforsch., Teil B, 33 (1978) 1227.
55 M.Z. Jandali, G. Eulenberger and H. Hahn, Z. Anorg. Allg. Chem., 447 (1978) 105.
56 M.D. Cooke, R.G. Linford, L.A.K. Stavely and R.D. Worsnick, J. Chem. Soc., Faraday Trans. 1, (1978) 2363.
57 M.A. Bernard, F. Busnot and J.F. Le Querler, Thermochim. Acta, 33 (1979) 249.
58 A.K.S. Ahmed, M.A. Salam, M.A. Taher and B.K. Das, J. Bangladesh. Acad. Sci., 2 (1978) 65; A.K.S. Ahmed, M.A. Salam, M.Y. Meach and M.M. Rahman, Nucl. Sci. Appl. Ser. B, 10 (1977) 96, Chem. Abstr., 90 (1979) 110803.
59 R. Seeber, P. Zanello, A. Cinquantini and G.A. Mazzocchin, J. Chem. Soc., Dalton Trans., (1979) 1274.
60 A.M. Shallaby, M.M. Mostafa and M.M. Bekheit, J. Inorg. Nucl. Chem., 41 (1979) 267.
61 E.W. Abel and S.A. Mucklejohn, Inorg. Chim. Acta, 37 (1979) 107.
62 F. Bonati and H.C. Clark, Can. J. Chem., 57 (1979) 483.
63 C. Airoldi and A.S. Goncalves, J. Inorg. Nucl. Chem., 40 (1978) 1817.
64 M. Biddau, M. Massacesi, R. Pinna and G. Ponicelli, Rec. Trav. Chim., 98 (1979) 405.
65 A.C. Fabretti, G. Peyronel and G.C. Franchini, Spectrochim. Acta, Part A, 35 (1979) 229.
66 D.J. Brauer, Acta Crystallogr., Sect. B, 35 (1979) 1770.
67 L-A. Malmsten, Acta Crystallogr., Sect. B, 35 (1979) 1702.
68 N. Barba-Behrens, B.A. Cartwright, D.M.L. Goodgame and A.C. Skapski, Inorg. Chim. Acta, 31 (1978) L471.

69 E.C. Alyea, S.A. Dias, G. Ferguson, M.A. Khan and P.J. Roberts, Inorg. Chem., 18 (1979) 2433.
70 E.C. Alyea, S. Dias, G. Ferguson and M. Khan, Can. J. Chem., 57 (1979) 2217.
71 E.C. Alyea, S.A. Dias, G. Ferguson and M. Parvez, Inorg. Chim. Acta, 37 (1979) 45.
72 C. Gagnon and A.L. Beauchamp, Acta Crystallogr., Sect. B, 35 (1979) 166.
73 R.C. Makhija, R. Rivest and A.L. Beauchamp, Can. J. Chem., 57 (1979) 2555.
74 T. Allman, R.G. Goel and P. Pilon, Can. J. Chem., 57 (1979) 91.
75 T. Allman and R.G. Goel, Inorg. Nucl. Chem. Lett., 15 (1979) 199.
76 E.C. Alyea and S.A. Dias, Can. J. Chem., 57 (1979) 83.
77 S.O. Grim, D.P. Shah, C.K. Haas, J.M. Ressner and P.H. Smith, Inorg. Chim. Acta, 36 (1979) 139.
78 R.G. Goel, W.P. Henry and W.O. Ogini, Can. J. Chem., 57 (1979) 762.
79 P.P. Singh and S.P. Yadav, Can. J. Chem., 57 (1979) 394.
80 D. Negoiu and M. Negoiu, Rev. Roum. Chim., 23 (1978) 1043.
81 N.D. Miro, A.G. Macdiarmid, A.J. Heeger, A.F. Garito, C.K. Chiang, A.J. Schultz and J.M. Williams, J. Inorg. Nucl. Chem., 40 (1978) 1351.
82 G.P. Kinstle and E.P. Schram, Inorg. Chim. Acta, 32 (1979) L61.