# SYNTHESIS AND CHARACTERIZATION OF MERCURY(II) COMPLEXES WITH DIPHENYLPHOSPHINEACETIC ACID*

Jana PODLAHOVÁ and Jiří GRACIAS

*Department of Inorganic Chemistry,
Charles University, 128 40 Prague 2*

Complexes of divalent mercury with diphenylphosphineacetic acid (HA) of the composition $HgX_2(HA)_2$, $HgX_2(HA)$, $HgX(A)(HA)$, $HgA_2$, and $Na_2HgA_4$ (X = Cl, Br, I) were synthesized and characterized by means of spectroscopic and further techniques in the solid state and in solution. The coordination environment of mercury is constituted by halides and/or phosphine ligands in tetrahedral arrangement. HA acts as a monodentate P-donor, the $A^-$ anion either as a monodentate P-donor (in $Na_2HgA_4$) or as a chelating P,O-donor (in the remaining cases).

Divalent mercury forms a number of complexes with tertiary phosphines involving a variety of structure types[1,2]; the coordination number of mercury is usually $2-6$ and the idealized geometrical arrangements of the complexes are linear, trigonal, tetrahedral, trigonal bipyramidal or octahedral, the extent and type of a distortion being controlled primarily by the steric demands of the phosphine involved. In addition to the phosphine, halides, pseudohalides and oxoanions such as acetate or nitrate are usually coordinated to mercury. Ligands of the class of phosphineacetic acids, the simplest of which is diphenylphosphineacetic acid, $(C_6H_5)_2PCH_2COOH$ (HA), are representatives of functionalized phosphines[3,4] which can be bonded to metal ions via their phosphorus and/or oxygen donors[5]. The actual bonding mode is determined by steric and electronic properties of the metal ion ("hard" or "soft" type) and by the degree of dissociation of the carboxyl group(s) of the ligand. The above HA bonding types have been demonstrated for Ni(II) (ref.[6]), Pd(II) (refs[7,8]), Pt(II) (refs[9,10]), Rh(I) (ref.[11]) and Cu(I) (ref.[12]). Occasionally, two different ways of ligand bonding were observed[10,11] in the same compound. Mercury(II) forms very stable complexes with the ligand in aqueous solution[13] with the Hg : A ratio from 1 : 1 to 1 : 4; their carboxyl groups can be protonated independently. It follows that HA can be coordinated to Hg(II) in a variety of ways, particularly if mercury is not coordinatively saturated by the phosphine ligand. The aim of the present work was to establish the conditions for the synthesis of particular types of solid complexes together with their characterization.
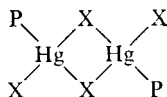
## RESULTS AND DISCUSSION

From a number of factors, the following ones are especially significant for the elaboration of synthetic procedures: *a*) ligand type, *i.e.*, HA or A⁻ (hence, acidity of medium) and X species; *b*) equilibria between the various complexes, which usually establish rapidly and can be influenced by the stoichiometric ratio of the components; *c*) mutual steric and electronic influencing of the ligands; and *d*) other circumstances affecting the above factors indirectly, such as solvent type and temperature.

Since these factors have to be combined in different ways for a particular synthesis, no general procedure can be suggested. On the contrary, the reaction conditions given below for the preparation of the individual complexes should be strictly followed.

The structures proposed are based on analogies with other halide, phosphine, and carboxylate complexes of mercury and with complexes of HA with other metals, particularly with respect to their ultraviolet[15], infrared[16-21] and NMR[2,14,19-25] spectra.

The $HgX_2(HA)_2$ complexes are formed from the components in molar ratios $HA/HgX_2 \geq 2$ by homogeneous or heterogeneous reaction in solvents of medium polarity such as acetic acid or dichloromethane. In the $Cl-Br-I$ series and with increasing solvent polarity, the equilibrium of the reaction $HgX_2(HA)_2 \rightleftarrows HgX_2(HA) +$ $+ HA$ is shifted to the right; this must be taken into account when preparing the bromide and, in particular, the iodide of the series. The properties of the $HgX_2(HA)_2$ complexes indicate a tetrahedral monomeric structure with coordinated halides and HA bonded as a P-donor (the $HgX_2P_2$ coordination polyhedron). Similarly as with other HA-containing complexes, the intermolecular hydrogen bonding of the uncoordinated COOH groups takes place in the solid state, being responsible for a low solubility of the complexes (except of $Na_2HgA_4$) in non-coordinating solvents. The solubility increases in the series $Cl < Br < I$ and $HgA_2 < HgX(A)(HA) <$ $HgX_2(HA)_2 < HgX_2(HA)$.

From the various types mentioned, the $HgX_2(HA)$ complexes are prepared most readily, *viz.* by crystallization from solutions with the component ratios $0.7 <$ $< HA/HgX_2 \leq 2.0$ in polar solvents such as acetone or its mixtures with acetic acid. Their properties suggest a dimeric halide-bridged structure:

$$
\begin{array}{ccccc}
P & & X & & X \\
 \diagdown & \diagup & \diagdown & \diagup & \\
 & Hg & & Hg & \\
 \diagup & \diagdown & & \diagup & \diagdown \\
X & & X & & P
\end{array}
$$

Mercury(II) is tetrahedrally coordinated and HA bonds via its phosphorus atom (the $HgX_3P$ coordination polyhedron). This arrangement was confirmed by X-ray structure determination of the bromide[26].

The $HgX_2(HA)_2$ and $HgX_2(HA)$ complexes can be interconverted by modifying the reaction conditions (addition of $HgX_2$ or HA) or by changing the solvent.

Increasing the solvent polarity and adding the ligand as an equimolar mixture of HA and NaA are the conditions necessary for the synthesis of the third type of complexes, $HgX(A)(HA)$. Their properties indicate that the halide, HA as a monodentate P-donor, and $A^-$ as a chelating P, O-donor are coordinated together forming a tetrahedral $HgXOP_2$ coordination polyhedron. Complexes of analogous composition but of a square-planar geometry are known for $Pt(II)$ (ref.[10]) and $Rh(I)$ (ref.[11]). The existence of complexes of such a type for the tetrahedrally coordinated $Hg(II)$ indicates that the chelate bonding, rather than the trans-effect, is the factor mainly influencing their formation.

The $HgA_2$ and $Na_2HgA_4$ complexes are the major species in the $Hg(II)-A^-$ system in aqueous solution[13] and, consequently, they can be readily isolated in the solid state. Their properties again indicate a tetrahedral coordination of $Hg(II)$, realized for $HgA_2$ by two chelating or bridging $A^-$ anions (the $HgO_2P_2$ polyhedron), and for $Na_2HgA_4$ by four $A^-$ anions bonded as P-donors (the $HgP_4$ polyhedron). This concept is supported by the $v_{as}(COO) - v_s(COO)$ wavenumber difference, indicating unambiguously[18] that in $HgA_2$ the carboxyl groups are coordinated to the metal as monodentate O-donors whereas in $Na_2HgA_4$ these groups remain ionic and uncoordinated.

## EXPERIMENTAL

The ligand solutions were handled in an inert atmosphere; this showed unnecessary for the mercury complexes which are air-stable. For isolation, the complexes were washed with acetic acid and diethyl ether and dried at 80°C/0·1 kPa to constant weight unless stated otherwise.

### Apparatus and Methods

X-ray powder patterns: a Mikrometa 2 diffractometer (Chirana), Cu lamp. UV spectra: Unicam SP 800 (tetrahydrofuran solutions, $c = 0·5$ mmol $l^{-1}$) and VSU 2 (Zeiss, Jena; diffuse reflectance). The band positions in the corresponding spectra of solids and solutions are identical. The data given below are maxima wavenumbers in $10^3$ cm$^{-1}$ (molar absorptivities, $l$ mol$^{-1}$ . . cm$^{-1}$). IR spectra (band positions in cm$^{-1}$): a Perkin–Elmer 684, 200—4 000 cm$^{-1}$, Nujol and poly(chlorotrifluoroethylene) mulls. Of the many poorly coordinating solvents tested, acetone was chosen as optimal for further measurements in solution (water for $Na_2HgA_4$). NMR spectra ($\delta$ scale, $J$ in Hz, 25°C): Tesla BS 487 A ($^1$H, internal standard: tetramethylsilane), Varian XL 200 ($^{31}$P, external standard: 85% $H_3PO_4$); the NMR spectra are given only where their obtaining was reasonably time-consuming with respect to a low solubility of the samples. For $HgCl_2(HA)_2$ and $HgBr_2(HA)_2$ the limiting $^1$H NMR spectra were obtained by extrapolation of the individual runs during titration of a HA solution with a $HgX_2$ solution until crystallization commenced. Molecular weight: vapour pressure osmometry on a Knauer instrument, 0·1% solutions. Conductivity: a CDM 3 (Radiometer) with a CDC 314 microcell, solutions $c = 1$ mmol $l^{-1}$. All complexes are non-conducting in solution ($\Lambda_M < 2$) except for $Na_2HgA_4$ ($\Lambda_M = 195$).

Analytical Methods

Mercury and phosphorus were determined photometrically; the former as $HgI_4^{2-}$ (ref.[27]) after sample mineralization[28] with a mixture of concentrated $H_2SO_4$ and 30% $H_2O_2$, the latter, with vanadate and molybdate[29] after mineralization with a mixture of $HNO_3$ and $HClO_4$. For the determination of halides, the sample was ignited in oxygen following Schöniger, the absorbate was allowed to stand overnight in 5% acetic acid with excess zinc metal for the reduction of mercury, and the halides in the filtrate were titrated with silver nitrate using potentiometric indication. Carboxyl groups were determined by potentiometric titration with NaOH in 50% acetone using a glass electrode. The results of analyses are given in Table I.

Synthesis of the Complexes

$HgCl_2(HA)_2$: to a solution of 1·36 g (5·00 mmol) of $HgCl_2$ in 15 ml of acetone was added a solution of 2·47 g (10·1 mmol) of diphenylphosphineacetic acid (HA) in 20 ml of acetic acid and the mixture was allowed to crystallize. Yield 3·40 g (89%), white crystals, m.p. 153°C. UV spectrum: 39·4 (10 180) ligand + CT(Cl → Hg). IR spectrum: 2 700—3 100 s, b $\nu$(OH), 1 720 vs, 1 250 s COOH, 298 m $\nu$(Hg-Cl). $^1$H NMR spectrum: 3·79 d, $^2J$(P, H) = 9, 4 H, $PCH_2$; 7·3—7·9 m, 10 H, $C_6H_5$.

$HgCl_2(HA)$: to a stirred solution of 1·36 g (5·00 mmol) of $HgCl_2$ in 15 ml of acetone was dropwise added a solution of 1·25 g (5·05 mmol) of HA in 10 ml of acetic acid, and the crystalline precipitate separated was stirred with the mother liquor for several hours. Yield 2·25 g (87%), white crystals, m.p. 167°C. UV spectrum: 39·2 (11 700) ligand + CT(Cl → Hg). IR spectrum: 2 800—3 400 s, vb $\nu$(OH), 1 708 vs, 1 258 s COOH, 295 m $\nu$(Hg-Cl terminal), 240 w $\nu$(Hg-Cl bridging).

TABLE I

Analytical data of the compounds prepared

| Substance | Molecular weight | | % Hg | | % P | | % X | | % COOH | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calc., | Found | Calc., | Found | Calc., | Found | Calc., | Found | Calc., | Found |
| $HgCl_2(HA)_2$ | 760·1 | 680 | 26·39 | 26·5 | 8·15 | 8·08 | 9·33 | 9·51 | 11·84 | 11·90 |
| $HgCl_2(HA)$ | 515·8 | 1 080 | 38·90 | 38·5 | 6·00 | 5·80 | 13·75 | 13·60 | 8·72 | 8·81 |
| HgClA(HA) | 723·7 | 770 | 27·72 | 27·3 | 8·56 | 8·48 | 4·90 | 4·71 | 6·22 | 5·99 |
| $HgBr_2(HA)_2$ | 849·0 | 840 | 23·63 | 23·7 | 7·30 | 6·92 | 18·82 | 18·90 | 10·60 | 10·40 |
| $HgBr_2(HA)$ | 604·7 | 1 250 | 33·17 | 33·1 | 5·12 | 4·96 | 13·21 | 13·50 | 7·44 | 7·20 |
| HgBrA(HA) | 768·1 | 725 | 26·11 | 25·9 | 8·06 | 8·14 | 10·40 | 10·20 | 5·86 | 5·97 |
| $HgI_2(HA)_2$ | 943·0 | 990 | 21·27 | 21·2 | 6·57 | 6·51 | 26·91 | 27·00 | 9·54 | 9·38 |
| $HgI_2(HA)$ | 698·7 | 1 390 | 28·71 | 28·8 | 4·43 | 4·37 | 18·16 | 18·30 | 6·44 | 6·05 |
| HgIA(HA) | 815·1 | 840 | 24·61 | 24·8 | 7·60 | 7·53 | 15·57 | 15·80 | 5·52 | 5·51 |
| $HgA_2$ | 687·2 | 650 | 29·19 | 28·8 | 9·02 | 8·91 | — | — | — | — |
| $Na_2HgA_4$ | 1 219·8 | 930$^a$ | 16·45 | 16·3 | 10·17 | 10·20 | — | — | — | — |

$^a$ Partial dissociation in aqueous solution to $HgA_3^-$, ref.[13]

HgCl(A)(HA): to a stirred solution of 1·36 g (5·00 mmol) of $HgCl_2$ in 25 ml of acetone was dropwise added a solution of 1·22 g (5·00 mmol) of HA in 25 ml of acetone and then a solution of 1·33 g (5·00 mmol) of NaA in 10 ml of water. To the boiling solution was dropwise added water until turbidity persisted; the mixture was allowed to cool and the separated product was recrystallized from aqueous acetic acid. Yield 2·99 g (76%), white crystals, m.p. 152°C. UV spectrum: 39·7 (7 170) ligand + CT(Cl → Hg), 36·9 (2 070) CT(O → Hg). IR spectrum: 3 100 to 3 400 m, b $\nu(OH)$, 1 705 s, 1 258 m COOH, 1 605 s, 1 405 w $COO^-$, 287 w $\nu(Hg-Cl)$, 233 w $\nu(Hg-O)$.

$HgBr_2(HA)_2$: to a solution of 1·80 g (5·00 mmol) of $HgBr_2$ in 20 ml of acetone was added a solution of 3·13 g of HA (12·8 mmol) in 35 ml of acetic acid and the mixture was allowed to crystallize. Yield 2·83 g (66%), white crystals, m.p. 177°C. UV spectrum: 39·5 (4 600) ligand, 37·0 (9 900) CT(Br → Hg). IR spectrum: 2 850—3 250 s, b $\nu(OH)$, 1 722 vs, 1 250 s COOH. $^1H$ NMR spectrum: 3·83 d, $^2J(P, H) = 9$, 4 H, $PCH_2$; 7·3—8·0 m, 10 H, $C_6H_5$.

$HgBr_2(HA)$: prepared as $HgCl_2(HA)$ from 5·00 mmol of $HgBr_2$. Yield 2·75 g (95%), white crystals, m.p. 192°C. UV spectrum: 39·0 (4 200) ligand, 37·0 (8 500) CT(Br → Hg). IR spectrum: 2 900—3 300 s, b $\nu(OH)$, 1 708 vs, 1 257 m COOH. $^1H$ NMR spectrum: 4·04 d, $^2J(P, H) = 11$, 2 H, $PCH_2$; 7·2—8·0 m, 10 H, $C_6H_5$.

HgBr(A)(HA): prepared as HgCl(A)(HA) from 5·00 mmol of $HgBr_2$. Yield 3·06 g (80%), white crystals, m.p. 140°C. UV spectrum: 40·2 (4 400) ligand, 37·0 (10 200) CT(Br → Hg) + + CT(O → Hg). IR spectrum: 3 100—3 350 m, b $\nu(OH)$, 1 699 s, 1 259 s COOH, 1 598 m, 1 402 w $COO^-$, 241 w $\nu(Hg-O)$.

$HgI_2(HA)_2$: to a stirred suspension of 2·27 g (5·00 mmol) of $HgI_2$ in 25 ml of dichloromethane was dropwise added a solution of 2·47 g of HA (10·1 mmol) in 25 ml of dichloromethane. After dissolution of $HgI_2$ the solution was filtered and allowed to crystallize. For removing traces of $HgI_2(HA)$, the product was recrystallized from a hot 1% solution of HA in acetic acid. Yield 3·64 g (77%), white crystals, m.p. 157°C. UV spectrum: 38·3 (12 500) ligand, 32·8 (5 120) CT (I → Hg). IR spectrum: 2 800—3 250 s, b $\nu(OH)$, 1 725 vs, 1 233 s COOH. $^1H$ NMR spectrum: 3·83 d, $^2J(P, H) = 10$, 4 H, $PCH_2$; 7·2—7·9 m, 20 H, $C_6H_5$. $^{31}P\{^1H\}$ NMR spectrum: —0·17 bs, $\Delta = 90$.

$HgI_2(HA)$: prepared as $HgCl_2(HA)$ from a suspension of 5·00 mmol of $HgI_2$. Yield 2·73 g (78%), light-yellow crystals, m.p. 161°C. UV spectrum: 38·7 (6 200) ligand, 32·4 (4 990) CT (I → Hg). IR spectrum: 2 850—3 250 s, b $\nu(OH)$, 1 699 vs, 1 277 m COOH. $^1H$ NMR spectrum: 4·06 d, $^2J(P, H) = 11$, 2 H, $PCH_2$; 7·3—8·0 m, 10 H, $C_6H_5$. $^{31}P\{^1H\}$ NMR spectrum: 11·33 bs, $\Delta = 350$.

HgI(A)(HA): prepared as HgCl(A)(HA) from a suspension of 5·00 mmol of $HgI_2$. Yield 2·84 g (70%), white crystals, m.p. 128°C. UV spectrum: 39·2 (15 500) ligand, 37·0 sh CT(O → Hg), 33·0 (2 410) CT(I → Hg). IR spectrum: 3 100—3 400 m, b $\nu(OH)$, 1 704 s, 1 265 m COOH, 1 597 m, 1 392 w $COO^-$, 245 w $\nu(Hg-O)$. $^1H$ NMR spectrum: 3·72 d, $^2J(P, H) = 11$, 2 H, $PCH_2$ in HA; 4·91 bs, 2 H, $PCH_2$ in $A^-$; 7·1—7·7 m, 20 H, $C_6H_5$. $^{31}P\{^1H\}$ NMR spectrum: —0·22 bs, $\Delta = 100$, HA; 9·90 bs, $\Delta = 350$, $A^-$.

$HgA_2$: to a solution of 1·67 g (5·00 mmol) of $Hg(NO_3)_2 . 0·5 H_2O$ in 50 ml of 0·01M-$HNO_3$ at 50°C was dropwise added a solution of 2·66 g (10·0 mmol) of NaA in 50 ml of ethanol. After hot filtration over kieselguhr the solution was allowed to cool very slowly and the crystalline product was washed with 50% ethanol and ether. Yield 2·44 g (71%), white crystals, m.p. 154°C. UV spectrum: 40·0 (6 300) ligand, 37·0 sh CT(O → Hg). IR spectrum: 1 608 vs, 1 363 vs $COO^-$, 238 m $\nu(Hg-O)$.

$Na_2HgA_4$: 0·76 g (2·00 mmol) of $HgA_2$ was stirred with a solution of 1·06 g (4·00 mmol) of NaA in 5 ml of water until dissolution of the solids. The solution was filtered over kieselguhr and evaporated to dryness at 50°C/2 kPa, the residue was dried over $H_2SO_4$ and crystallized

from hot 2-propanol in the absence of moisture. The crystals were washed with dry diethyl ether. Yield 1·53 g (63%), white hygroscopic crystals, m.p. 210—215°C (decomp.). UV spectrum: 39·2 (35 700) ligand. IR spectrum: 1 577 vs, 1 412 vs $COO^-$. $^1H$ NMR spectrum: 3·66 s, 8 H, $PCH_2$; 7·1—7·7 m, 40 H, $C_6H_5$. $^{31}P\{^1H\}$ NMR spectrum: 29·09 bs, $\Delta = 320$; 36·35 s,P=O (approximately 5% air oxidation).

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