MERCURY(II) COMPLEXES WITH PHOSPHINEACETIC ACIDS*

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Mercury(II) forms very stable water-soluble complexes with metal-to-ligand ratios of 1 : 1, 1 : 2 and 1 : 3 with phosphineacetic acids of the general formula $Ph_{3-n}P(CH_2COOH)_n$ ($n = 1-3$). At $n = 1$ formation of the further 1 : 4 complex was detected. Stability constants of the complexes were determined polarographically and potentiometrically (mercury electrode) in water and in 50% v/v dioxan at I 0·1 ($NaClO_4$) and 25°C. Protonation of the complexes as followed from pH-titrations and IR spectra demonstrated that the ligands are monodentate through phosphorus. The ability to form higher complexes ($L/Hg > 2$) strongly decreases with increasing charge on the ligand anion.

The high affinity of mercury(II) for soft donors is well known. Complexes containing tervalent phosphorus as the donor atom have been characterized in detail mainly in the solid state and in nonaqueous solutions. In these complexes[1-3], mercury has coordination numbers of 2, 3 and 4 and other donor atoms besides phosphorus are usually bonded to mercury. Information on the aqueous chemistry of phosphine complexes is rather scarce because of the insolubility of phosphine ligands and/or complexes. An exception, the water-soluble *m*-diphenylphosphinebenzenedisulphonate is known to form a series of complexes[4,5] of high stability ($\log \beta_1 = 14{\cdot}46$, $\log \beta_2 = 24{\cdot}72$, $\log \beta_3 = 29{\cdot}76$, $\log \beta_4 = 32{\cdot}4$), characterized by ligand coordination through phosphorus.

This work deals with a study of solutions of mercury(II) complexes with phosphineacetic acids with the general formula $Ph_{3-n}P(CH_2COOH)_n$ [$n = 1$, HA (ref.[6]), $n = 2$, H_2R (ref.[7]); $n = 3$, H_3X (ref.[8])] representing potentially multidentate ligands which are able to coordinate through both phosphorus and carboxyl[6-13].

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EXPERIMENTAL

Chemicals

The synthesis of the ligands has already been described in earlier communications[6–8]. Mercury(II) perchlorate solutions were prepared from mercuric oxide and a slight excess of perchloric acid. A mercury(I) perchlorate solution was obtained from the $Hg(ClO_4)_2$ solution by shaking with mercury for several days followed by filtration; the mercury(I) content in this solution was calculated as the difference between the total mercury and a small amount (1—2%) of unreacted mercury(II). Redistilled mercury ("for polarography", Lachema) was used throughout. The purification of dioxan and sodium perchlorate has already been described[11]. Deuterium oxide (isotopic purity 99·5%) and 6M-DCl in D_2O (isotopic purity 99%) were products of Alfa Inorganics. Other chemicals were *p.a.* products from Lachema and Merck.

Apparatus

Potentials and pH were measured on a Radiometer PHM-64 instrument (readable to 0·1 mV and 0·001 pH, respectively) which was calibrated for potentiometric measurements against a standard Weston cell and for pH measurements with $HClO_4$, NaOH and CH_3COOH solutions in order to yield $-\log [H^+]$ values directly[14]. A J-type mercury electrode with a working surface area of about 60 mm^2 and a Radiometer G 202 C glass electrode were used. A Radiometer K 401 saturated calomel electrode was used as the reference electrode; its exact potential (including the liquid junction potential) was determined at various c_{H^+} values by measuring the electromotive force of the cell

$$\mathrm{Pt}\left|\;\mathrm{H}_2\;\right|\begin{array}{ll} c_{\mathrm{H}^+} & 0{\cdot}1\,\mathrm{M\text{-}ClO}_4^- \\ c_{\mathrm{Na}} = 0{\cdot}1 - c_{\mathrm{H}^+} & (50\%\ \text{dioxan}) \end{array}\;\vdots\;\underbrace{\text{sat. KCl}\;\big|\;\mathrm{Hg_2Cl_2}}_{\text{K 401}}\;\big|\;\mathrm{Hg}$$

Polarographic measurements were carried out at 25°C on a Radiometer PO 4 instrument with a H-type cell equipped with a dropping mercury electrode ($m = 8{\cdot}92$ mg, $t = 4{\cdot}05$ s in 0·1M-$NaClO_4$ at 25°C) and a saturated mercurosulphate electrode. The solutions in water and in 50% dioxan were adjusted to $I = 0{\cdot}1$ using Britton–Robinson buffers and sodium perchlorate. The potential of the reference electrode was simultaneously monitored against a Radiometer K 401 saturated calomel electrode and corrected for the diffusion potential as during potentiometric measurements. The precision of the measured half-wave potential was ±2 mV.

The IR spectra of solutions were measured on an UR-20 instrument (Zeiss, Jena) using calcium fluoride cells with 50 μm thick polyethylene spacers.

Analytical Methods

The total mercury content was determined by EDTA titration, if necessary after oxidation with peroxodisulphate with prolonged boiling. The mercury(II) content in mercury(I) solutions was determined by reduction with ascorbic acid[15]. The concentration of the acid in the stock solution was determined by Gran's method[16] after adding excess potassium chloride to suppress the hydrolysis of mercury(II). The purity of the ligands was 99·8 ± 0·3% as verified by analysis (titration with iodine and with NaOH) and by TLC (ref.[13]). All manipulations with ligand solutions were carried out in a pure nitrogen atmosphere and the content of tervalent phosphorus was checked at the end of each experiment.

RESULTS

Standard Potentials of Mercury in 50% Dioxan

Because of the low solubility of HA and H_2R in water, the complexes were also studied in 50% v/v dioxan. For data treatment, knowledge of standard potentials[4] $E^\circ_{0,1}$ (Hg(I)/Hg) and $E^\circ_{1,2}$ (Hg(II)/Hg(I)) is necessary. Their values were measured using the cells

$$\begin{array}{r|l|c|c|l} & c_{\mathrm{Hg^I}}\ c_{\mathrm{Hg^{II}}} & & & \\ \mathrm{Hg\ (or\ Pt)} & c_{\mathrm{HClO_4}} = 0{\cdot}01 & \mathrm{sat\ KCl} & \mathrm{Hg_2Cl_2} & \mathrm{Hg} \\ & c_{\mathrm{ClO_4^-}} = 0{\cdot}1 & & & \\ & (50\%\ \mathrm{dioxan}) & & & \end{array}$$

First, mercury(I) perchlorate solutions (containing 1–2% Hg^{II}) were measured at various $c_{\mathrm{Hg^I}}$ concentrations with the mercury electrode. After potential $E_{0,1}$ became stable (to ±0·2 mV in 30 to 60 min), the mercury electrode was replaced by a bright platinum electrode (Radiometer P 101), a calculated amount of the stock mercury(II) solution containing other constituents to maintain $c_{\mathrm{Hg^I}} \approx c_{\mathrm{Hg^{II}}}$ and to keep the solvent background constant was added and, after proper equilibration, the second equilibrium potential $E_{1,2}$ was recorded. As the hydrolysis of both mercury(I) and (II) can be neglected at $c_{\mathrm{HClO_4}} = 0{\cdot}01\mathrm{M}$, it holds that

$$E_{0,1} = E^\circ_{0,1} + (RT/2F) \ln [\mathrm{Hg_2^{2+}}] = E^\circ_{0,1} + 0{\cdot}02958 \log c_{\mathrm{Hg^I}} ,$$

$$E_{1,2} = E^\circ_{1,2} + (RT/2F) \ln [\mathrm{Hg^{2+}}]^2/[\mathrm{Hg_2^{2+}}] = \\ = E^\circ_{1,2} + 0{\cdot}05916 \log (c_{\mathrm{Hg^{II}}}/0{\cdot}5c_{\mathrm{Hg^I}}) .$$

The mean values of the standard potentials obtained from 12 solutions with various composition are: $E^\circ_{0,1} = 0{\cdot}802 \pm 0{\cdot}002$ V, $E^\circ_{1,2} = 0{\cdot}903 \pm 0{\cdot}002$ V (50% dioxan, 25°C, I 0·1 ($NaClO_4$)). The equilibrium constant of the reaction $\mathrm{Hg^{2+}} + \mathrm{Hg} \rightleftarrows \mathrm{Hg_2^{2+}}$ is $\log K_0 = (E^\circ_{1,2} - E^\circ_{0,1})/0{\cdot}05916 = 1{\cdot}71 \pm 0{\cdot}07$ and the standard potential Hg(II)/ /Hg is $E^\circ_{0,2} = 0{\cdot}852 \pm 0{\cdot}002$ V.

Compared with the aqueous solution under the same or similar conditions[4,17,18] ($E^\circ_{0,1} = 0{\cdot}793$ V, $E^\circ_{1,2} = 0{\cdot}9075$ V, $\log K_0 = 1{\cdot}94$), a slight stabilization of mercury(II) in 50% dioxan is apparent. Formation of weak adducts between mercury(II) and dioxan can be suggested as a probable explanation for this difference.

Polarography

Ligand solutions give well-developed anodic waves caused by the formation of mercury(II) complexes. The limiting current is diffusion-controlled, the waves are reversible (with the exception of strongly acid solutions) and correspond to a two-electron process. Their half-wave potentials depend on the ligand concentration and pH of the solution. The composition of the complexes formed was deduced from amperometric titrations of the ligands with mercury(II) perchlorate at various pH values. The stoichiometric ratios at the equivalence points are summarized in Table I and indicate which complexes predominate at the ligand concentration used, 0·001M. The stability of these complexes, expressed as the stability constants, given in Table I, was calculated from the pH-dependence of the half-wave potentials according to the equation[19]

$$0{\cdot}02958 \log \beta_{\mathrm{N}} = E^{\circ}_{0,2} - E_{1/2} + 0{\cdot}02958 \left[\log \left(D_{\mathrm{L}}/D_{\mathrm{C}}\right)^{1/2} + \log \left(2^{\mathrm{N}-1} N^{-1} c_{\mathrm{L}}^{1-\mathrm{N}}\right) + \right.$$
$$\left. + \left(N - 1\right) \log \alpha\right],$$

where N denotes the number of ligands in the complex considered, D_{L} and D_{C} are the ligand and complex diffusion coefficients found from the limiting currents of the cathodic and anodic waves at equal ligand concentrations, c_{L}, and $\alpha = \sum_{\mathrm{j}=0}^{\mathrm{N}} \beta_{\mathrm{j}}^{\mathrm{H}} [\mathrm{H}^+]^{\mathrm{j}}$ denotes the relative percentage of the various acid–base forms of the ligand defined by the protonation constants $\beta_{\mathrm{j}}^{\mathrm{H}}$ (see[6–8]).

The results corresponding to basic, neutral and slightly acidic solutions can be interpreted unambiguously by the formation of one predominating complex, the composition and stability of which is given in Table I. Deviations in weakly acidic media, where the waves are still reversible, are apparently caused by formation of protonated complexes; the limited precision of the polarographic method, however, does not permit quantitative interpretation of these data.

Potentiometry

The Hg(II)–ligand systems were further studied in detail by potentiometry with a mercury electrode using the cell

$$\mathrm{Hg} \left| \begin{array}{l} c_{\mathrm{Hg^{II}}} \quad c_{\mathrm{L}} \\ 0{\cdot}1\mathrm{M}\text{-}\mathrm{ClO}_4^- \\ (50\% \text{ dioxan}) \end{array} \right\vdots \ \text{sat. KCl} \ \Big| \ \mathrm{Hg_2Cl_2} \ \Big| \ \mathrm{Hg}$$

The measurements were carried out at pH 7·0 to 7·5 and in excess ligand ($c_{\mathrm{L}} \geqq c_{\mathrm{Hg^{II}}}$) where the reaction of Hg^{2+} with mercury metal on the electrode can be safely neglected. In the first series of measurements, 50 ml of a titration solution was prepared by mixing a measured amount of a stock solution of mercury(II) perchlorate, a weighted amount of the alkali salt of the ligand, a sodium hydroxide solution for neutralization of excess acid in the Hg(II) stock solution (in that order), a sodium perchlorate

TABLE I

The Composition and Stability Constants of the Complexes from Polarographic Measurements

The L/Hg ratios correspond to the breaks on amperometric titration curves. Values for reversible waves are in parentheses.

A^-						R^{2-}						X^{3-}					
water			50% dioxan			water			50% dioxan			water			50% dioxan		
pH	A/Hg	log β_3	pH	A/Hg	log β_3	pH	R/Hg	log β_2	pH	R/Hg	log β_2	pH	X/Hg	log β_2	pH	X/Hg	log β_2
3·10		(35·7)	4·45	3·09	(34·0)	3·09		(29·4)	1·42		(31·4)	1·66		(30·8)	5·38	1·95	(32·1)
3·75	3·02	(35·3)	4·64		(34·1)	3·52		(29·3)	2·95	2·12	(29·9)	2·29		(30·1)	6·10		32·8
			4·94		(34·4)	3·81		(29·6)	4·00		(30·7)	2·82	2·04	(29·8)	6·90	2·12	32·2
4·19		35·1	5·40		(34·1)	4·34		30·6	4·73		31·4	3·22		(30·5)			
4·91		35·4	5·81		34·2	5·05	2·04	31·3				3·98		31·8	7·69		33·9
5·58		35·7				5·72		31·6	5·95	2·00	33·5				8·31		33·8
6·09		35·5	6·12		34·8				6·54		33·6	4·78		32·9	9·12	2·01	33·8
6·68	2·93	35·6	6·54	3·03	34·9	6·24		32·1	7·40		33·8	5·57		33·3	10·23		33·7
7·40		35·6	7·01		34·8	6·80	2·11	32·1	8·05		33·8	6·27	1·96	33·2			
8·68		35·5	7·47		34·8	7·50		32·1	9·80	2·07	33·8	7·16		33·5			
9·43		35·6	8·01	2·90	34·9	8·27		32·0	10·35		33·5	8·39		32·9			
9·97	2·98	35·5	10·46		35·0	9·51	2·06	32·0				9·33	1·98	32·6			
10·58		35·6				10·55		31·9				10·33		32·9			
log β_3 = = 35·31 ± 0·03			log β_3 = = 34·87 ± 0·02			log β_2 = = 32·03 ± 0·02			log β_2 = = 33·67 ± 0·05			log β_2 = = 33·1 ± 0·1			log β_2 = = 33·8 ± 0·1		

solution and the solvent. The resulting solution was titrated in an inert atmosphere with a solution of the alkali salt of the ligand in a concentration enabling attainment of a ratio $c_L/c_{Hg} = 8$ after addition of 10 ml of the titrant (20–30 successive additions). In the second series of titrations, a neutral solution containing the ligand and mercury(II) ions in a 6 : 1 ratio was titrated by mercury(II) perchlorate solution with simultaneous neutralization of the excess acid present in the titrant by precise additions of the NaOH solution from a second burette. The equilibrium potentials equilibrated within 5–10 min and were stable to ±0·3 mV over several hours. The reproducibility of the individual titrations was better than 1 mV. Several concantrations of mercury ranging between 0·0001 and 0·002M were used.

All the titrations were characterized by a well-pronounced potential drop (over several hundred mV) at a stoichiometric ratio equal to that found by amperometric titration.

The data were treated by the MINIQUAD program[20] using the polarographically obtained stability constants for the predominant complexes as the initial guesses. The large region of metal-to-ligand ratios used enables identification of additional consecutive complexes. Formation of the 1 : 4 complex was detectable only for diphenylphosphineacetate with a large excess of the free ligand.

Table II summarizes the stability constants and relevant statistical parameters characterizing the goodness-of-fit of the experimental data. The distribution of the complexes can be seen on Fig. 1.

TABLE II

The Stability Constants of the Complexes from Potentiometric Measurements. $\beta_n = [HgL_n]/([Hg][L]^n)$ (charges are omitted), $R = (\sum \Delta c_i^2 / \sum c_i^2)^{1/2}$.

log β_n (3σ)	A^-		R^{2-}		X^{3-}	
	water	50% dioxan	water	50% dioxan	water	50% dioxan
β_1	18·7 (5)	19·4 (2)	19·7 (3)	22·2 (1)	19·93 (6)	22·8 (2)
β_2	28·9 (1)	30·3 (1)	31·92 (3)	33·27 (2)	32·27 (2)	33·76 (5)
β_3	35·38 (4)	35·39 (8)	34·21 (5)	35·14 (7)	34·16 (8)	34·93 (9)
β_4	37·2 (1)	36·5 (2)				
Number of titrations (experimental points)	8 (283)	9 (265)	6 (207)	8 (218)	8 (251)	7 (220)
R	0·043	0·042	0·061	0·059	0·045	0·070

pH *Measurement*

The formation of the protonated complexes was studied by pH-titrations. Solutions containing mercury(II) and the ligand in a ratio corresponding to the predominating complex at $I = 0{\cdot}1$ and 25°C were first titrated with a standard sodium hydroxide solution to pH > 12 and subsequently by a standard perchloric acid solution to pH < 2. Owing to the high stability of the predominant complexes, their dissociation to the ligand and mercury(II) ions could be neglected and the titration curves were treated assuming simple acid–base equilibria. Formation of hydroxo complexes was not observed in any of the systems; the composition and dissociation constants of protonated complexes calculated by the MINIQUAD program are given in Table III.

IR *Spectra*

To elucidate the mechanism of proton uptake, the changes of the IR spectra of the predominant complexes in solutions in dependence on the acidity were studied.

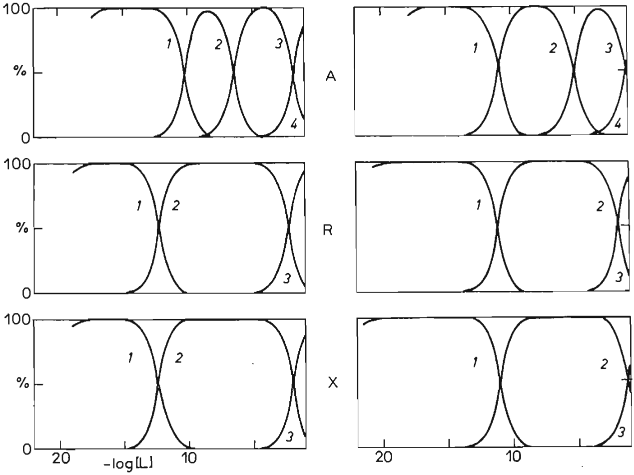

FIG. 1

The Distribution Diagrams for the Complexes

Left water, right 50% dioxan. The numbers denote the number of ligands in the complex.

Measurements were carried out in deuterium oxide to eliminate interference from $\delta(H_2O)$ with the bands measured: $\nu_{as}(COOH)$, $\nu_{as}(COO—Hg)$ and $\nu_{as}(COO^-)$ at ca. 1 710, 1 650 and 1 590 cm^{-1}, respectively[21,22].

Solutions for measurement were prepared by dissolving the appropriate stoichiometric amounts of mercuric chloride (competition of chloride complexes is negligible) and an anhydrous alkali salt of the ligand in D_2O or in a 1 : 1 D_2O–dioxan mixture so that $c_{COOH} = 0{\cdot}4$M, and then adjusted to the proper pD with a solution of DCl in D_2O. All the spectra displayed only the bands of a dissociated uncoordinated carboxyl at 1 588 ± 6 cm^{-1} and an undissociated, uncoordinated carboxyl at 1 711 ± 3 cm^{-1}, whose relative intensities agreed approximately with the contribution calculated from the dissociation constants of the protonated complex. For comparison, a solution of the PdA_2 complex containing coordinated carboxyl[12] was found to exhibit a maximum at 1 650 cm^{-1}, regardless of the acidity, under the same conditions.

DISCUSSION

The results obtained clearly demonstrate the prevailing importance of the phosphorus donor atom in complexes of phosphineacetic acid and divalent mercury. The dissociated ligand anions give series of consecutive complexes 1 : 1, 1 : 2 and 1 : 3 of similar stability for all the ligands. No general trends were observed in the series A-R-X and also when water was replaced by 50% dioxan as a solvent.

In the consecutive series, the 1 : 1 complexes are the least precisely defined because the mercury electrode can be used only at $c_L \geqq c_{Hg}$; attempts to determine the stability constants more accurately by measuring the redox potential $E_{1,2}$ on addition of the

TABLE III

The Dissociation Constants of the Protonated Complexes

$pK_n = -\log [H] [H_{n-1}B] [H_nB^{-1}]$, where B is the complex anion.

Ligand	Medium	H_nB $n =$	1	2	3	4	5	6
A^-	water	$HHgA_3$	3·25	—	—	—	—	—
	50% dioxan	$H_3HgA_3^{3+}$	1·99	3·06	4·76	—	—	—
R^{2-}	water	$H_4HgR_2^{2+}$	1·3	1·76	2·51	3·34	—	—
	50% dioxan	$H_4HgR_2^{2+}$	2·00	3·03	3·66	4·40	—	—
X^{3-}	water	H_4HgX_2	1·8	2·64	3·57	4·54	—	—
	50% dioxan	$H_6HgX_2^{2+}$	2·2	2·96	3·52	4·04	4·70	6·17

ligand[4] were unsuccessful. A possible reason is a certain complexation interaction between the ligand and univalent Hg, caused by the presence of "hard" carboxyl atoms in the ligand. Anomalies in the data increased in the series $A < R < X$, *i.e.* with increasing number of carboxyl groups.

The complexes predominating in the region of the ligand concentrations used are best characterized. The stability constants of these complexes, found by the orientative polarographic method, are in good agreement with the more precise potentiometric values.

The tendency to form higher complexes falls considerably with increasing ligand charge in the series $A^- \gg R^{2-} > X^{3-}$: in contrast to R and X, ligand A predominantly forms the 1 : 3 complex and, at large excess of the ligand, the HgA_4^{2-} complex is also detectable; the step on the formation curve at $\bar{n} = 2$ which is typical for mercury(II) complexes[17] where linear coordination number 2 is preferred for electronic reasons, is well pronounced only for ligands R and X. Numerically, this behaviour is expressed by opposite trends of the stability constants for 1 : 2 $(A < R < X)$ and 1 : 3 $(A > R > X)$ complexes. The increase in the electrostatic repulsion connected with the addition of a ligand anion with greater charge to the negatively charged complex is the obvious explanation of these phenomena.

Substitution of water for 50% dioxan as a solvent increases the stability of lower-charged species as a consequence of a decrease in the dielectric constant.

In order to elucidate the structure of the complexes, a decision as to possible coordination of the carboxyl groups is important; apparently, the coordination of phosphorus follows from the high values of the stability constats which are much higher than those of the corresponding nitrogen analogues[17] ($C_6H_5N(CH_2COOH)_2$ $\log \beta_2 = 12{\cdot}9$, $N(CH_2COOH)_3$ $\log \beta_2 = 14{\cdot}6$). All the results obtained indicate that the mercury(II) phosphinoacetate complexes contain only uncoordinated carboxyl groups. *E.g.* the existence of 1 : 3 R- and X-complexes and 1 : 3 or 1 : 4 A-complexes with the coordinated carboxyls should require an uncommon coordination number of 6 or even higher for mercury(II). The complexes are readily protonated to the same degree as the free ligands; certain acidification of the ligands on coordination following from the proton dissociation constants can be satisfactorily explained by the inductive effect of the very stable $P \rightarrow Hg$ coordination bond: the degree of protonation clearly decreases with an increasing number of carboxyl groups in the complex (*e.g.*, a total degree of protonation for six COO^- groups in HgX_2^{4-} is comparable with that for the three COO^- groups in HgA_3^-). In contrast, the PdA_2 complex containing coordinated carboxyl groups exhibits no basicity at all.

The most convincing argument that the carboxyl groups are uncoordinated in Hg(II) complexes follows from the IR spectra of the complexes in dependence on the acidity. All the spectra contained only the bands of uncoordinated carboxyl groups (dissociated or protonated according to the acidity of the solution).

In summary, the ligands studied form very stable water-soluble complexes with mercury(II) containing the ligands coordinated as monodentate through the phosphorus atom. The structure of the complexes is probably linear for L/Hg $\leqq 2$ and tetrahedral for L/Hg > 2 with possible completion of the coordination sphere with solvent molecules. For practical applications, the high selectivity of the ligand towards mercury(II), which is greater than that of many other complexing reagents, is important.

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