

Studies on Metal Ion Co-ordination in Solution

I. The Complex Formation of Diphenylphosphinobenzene-*m*-sulphonate with Mercury

BJARNE SALVESEN* and JANNIK BJERRUM

Department of Inorganic Chemistry, University of Copenhagen, Copenhagen, Denmark

Ahrland, Chatt *et al.*¹, have extended studies of metal ion complex formation in aqueous solution to such co-ordinating atoms as arsenic and phosphorus. In this paper we have studied the complex formation of mercury(II) with diphenylphosphinobenzene-*m*-sulphonate (proposed by Chatt *et al.* as a water soluble phosphorus ligand). The complex formation of mercury ions was studied both with mercury and platinum electrodes at low metal and ligand concentrations (due to low solubilities of the complexes as well as of the ligand). It could be shown that mercury(I) ions do not form complexes in the region covered, and for mercury(II) it was found that the formation of a tetra-complex was finished at relatively small concentrations of the ligand. A »stop» in the formation curve for $\bar{n} = 1$ as well as for $\bar{n} = 2$ was remarkable. A complex salt of Hg(II) with diphenylphosphinobenzene-*m*-sulphonate (HgL_2) has been prepared. The following values for the complexity constants were determined in ~ 0.01 M HNO_3 , 1 M KNO_3 at 25°: $K_1 = 10^{14.3}$ l·mole⁻¹, $\beta_2 = 10^{24.6}$ l²·mole⁻², $\beta_3 = 10^{29.7}$ l³·mole⁻³, $\beta_4 = 10^{33.0}$ l⁴·mole⁻⁴. The great stability of the mono-complex is in agreement with Ahrland and Chatt's findings for the silver(I) ion.

In their studies of the complex formation of silver(I) ions with various types of ligand Ahrland and Chatt *et al.*¹ distinguish between three main types of complex formation: (1) those (*e.g.* NH_3 , CN^- , Cl^- , Br^-) which have a stop or inflection at $\bar{n} = 2$; (2) an intermediate type (sulphides, selenides) where the formation of complexes proceeds uniformly to $N = 4$; and (3) those (phosphines, arsines, I^-) with a stop or inflection at $\bar{n} = 1$ and $\bar{n} = 3$.

For mercury(II) ions only complex formation of type (1) with a very pronounced stop at $\bar{n} = 2$ has been examined hitherto. However, it is known that mercury seems to be unable to react with more than one ethylene molecule², and that mercury dialkyl and diaryl compounds are easily converted to

* Present address: Pharmaceutical Institute of the University, Blindern, Norway.

compounds in which mercury is attached to only one carbon atom³. This suggests that mercury in these compounds has the characteristic number one. Ahrland and Chatt suggest for silver(I) a connection between a high stability of the mono-complex and the possibility of the ligand to accept d-electrons from the metal forming a d π -bond. On this background it was interesting to see how mercury(II) behaves towards the sulphonated triphenylphosphine used by Chatt *et al.* as a water soluble phosphorus ligand.

NOTATION AND FUNDAMENTAL EQUATIONS.

We are considering the case where the concentration of a metal ion $[M^v]$ is determined in a constant ionic medium with an electrode of the same metal (Me) or with some other kind of electrode *. Denoting the total concentration of metal salt by (C_M) and the total concentration of complex-forming ligand by (C_L) , a half-cell: Me/ C_M, C_L is defined. In the special case where $C_L = 0$, the concentration of »free» metal ion $[M^v]$ can by definition be set equal to C_M . Now combining a half-cell of this type: Me/ $[M^v]_{C_L = 0}$ with a complex one of the same stoichiometrical metal salt concentration in the same ionic medium, we may write, if C_M and C_L are sufficiently small and polynuclear complexes are not formed:

$$E_M = \frac{RT}{vF} \ln X = \frac{RT}{vF} \ln \sum_0^N \beta_n [L]^n \quad (1)$$

The symbol E_M for the E.M.F. of such a cell as well as the function X were introduced by Fronæus⁴, and it will be seen that X is the reciprocal of Bjerrum's⁵ degree of formation (α_0) of the metal ion:

$$X = \frac{1}{\alpha_0} = \frac{C_M}{[M^v]} \quad (2)$$

β_n ($l^n \cdot \text{mole}^{-n}$) in (1) denotes the gross complexity constants:

$$\beta_n = K_1 \cdot K_2 \cdot \dots \cdot K_n = \frac{[ML_n]}{[M^v][L]^n} \quad (3)$$

N denotes the maximum value for n and $[L]$ the concentration of free ligand.

Now considering only the case of mononuclear complexes, it is easily seen that complex solutions of varying composition but with the same value of E_M are corresponding in the sense of Bjerrum⁶. This is tantamount to their having the same distribution of complexes as well as the same concentration of free ligand. In order to obtain the composition of such corresponding solutions Fronæus⁴ plotted C_L versus the experimentally determined value of E_M for various values of C_M . The concentration of the free ligand is then obtained from a plot of C_L versus corresponding C_M values as the value of C_L for $C_M = 0$, and the formation function \tilde{n} as the slope of the straight lines in this plot.

* *E.g.* a redox electrode with a metal ion in two valence steps, one of which is not complex forming.

The correctness of this treatment follows from the formulae ⁶

$$\bar{n} = \frac{C_L - [L]}{C_M} = \frac{C''_L - C'_L}{C''_M - C'_M} \quad (4)$$

in which the indices to C_L and C_M refer to corresponding solutions. In most cases the upper part of the formation curve can be determined in this way.

In order to determine the remaining part of the formation curve, for which $[L]$ is too small to be determined in this way, we have the Bodländer equation:

$$\frac{d \log X}{d \log [L]} = \bar{n} \quad (5)$$

or in its integrated form ^{7,8}

$$\log \frac{[L]^*}{[L]} = \int_{[L]^*}^{[L]} (1/\bar{n}) d \log X \quad (6)$$

This expression can be directly used to determine the free ligand concentration by numerical integration from a knowledge of \bar{n} and X .

In the present study the mercury electrode was used to follow the complex formation with diphenylphosphinobenzene-*m*-sulphonate. There was the complication that a solution of mercuric ions is reduced to mercurous ions by mercury. However, by measurements with a bright platinum electrode in mixed solutions of mercury(I) and mercury(II) we could show that mercurous ions have only a negligible tendency to form complexes with the phosphine ligand. Therefore (1) a redox electrode of this kind could be used to measure directly the concentration of free mercuric ions as well as X in case the solutions are unsaturated with respect to mercury metal, and (2) if using the mercury electrode a knowledge of the equilibrium constant

$$K_o = \frac{[Hg_2^{2+}]}{[Hg^{2+}]} \quad (7)$$

under the conditions (0.01 M HNO₃, 1 M KNO₃ at 25°C) used in this study is sufficient to correct the measured potentials (E'_M) for cells



with the same total osmotic concentration of mercury

$$C_{Hg} = C_{Hg(II)} + [Hg_2^{2+}] \quad (9)$$

in both half cells to true E_M values as defined in eqn. (1).

The nitric acid concentration used by us (~ 0.01 M) is high enough to depress the hydrolysis of the mercuric ions. From the hydrolysis constants determined by Hietanen and Sillén ⁹ it can be estimated that less than 2 % of the mercuric ions is hydrolyzed if $[H^+] \gtrsim 0.01$ M. On the other hand it was considered that protonation of the phosphine ligand could occur at higher acid concentrations. In a single experiment with the glass electrode it was directly shown that addition of the phosphine ligand in a concentration of

Table 1. Infrared spectra of sodium and potassium diphenylphosphinobenzene-*m*-sulphonate in the range from 1000 cm^{-1} to 670 cm^{-1} .

This paper (Na-salt, $2\text{H}_2\text{O}$)	804s	793s	790s	753s	747s	740s	700s	695s	676m
Ahrland, Chatt <i>et al.</i> (s)**	799s	—	788s	753s	746s	738s	700*	691s	673m
This paper (K-salt, $2\text{H}_2\text{O}$)	800s	—	789s	753s	746s	741s	700*	695s	676m

* Shoulders.

** These authors have in their paper interchanged the spectra of $\text{Ph}_2\text{P}\cdot\text{C}_6\text{H}_4\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ and $\text{As}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$.

0.01 M to a 0.01 M hydrochloric acid solution did not diminish the hydrogen ion concentration to a measurable extent. However, extinction measurements in ultraviolet show that phosphonium ions are formed in more concentrated acid solutions.

EXPERIMENTAL

The ligand. Sodium diphenylphosphinobenzene-*m*-sulphonate was prepared according to Ahrland, Chatt *et al.*¹ Recrystallized from water or better from 96 % ethanol, dried at 100°C and kept over silica gel, it gave the dihydrate. (Found: C 54.4; H 4.43; S 7.92. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{SPNa}\cdot 2\text{H}_2\text{O}$ (400.3): C 54.0; H 4.52; S 8.01). We are indebted to Mr. Preben Hansen, who carried out the C, H, and S determinations, and to Mrs. B. Saustrup Kristensen, who examined the salt on a thermo-balance. The dihydrate was found to be stable in the range 100–335°C. The anhydrous salt could not be prepared by further heating. An indefinite transition point found at about 400°C corresponded to a loss of more than 2 moles of water.

The potassium salt was prepared in the same way as the sodium salt using concentrated KOH instead of NaOH. Recrystallized from 96 % alcohol and dried under mild conditions (50 % sulphuric acid), it gave a dihydrate. It began to lose water already at 50°C. A closer examination with the thermobalance showed that the anhydrous salt was formed gradually and was stable in the range 200–300°C. It was less soluble than the sodium salt, and in a 1 M KNO_3 solution the solubility was only about 0.001 M. The sodium salt (the saturated aqueous solution of which is about 0.03 M) dissolved faster in this medium and was used in most of the experiments. Solutions of the salts could be kept unchanged for hours, but after a longer time the ability to complex formation decreased probably due to oxidation of the phosphine group.

We are indebted to Mrs. S. Refn in Professor Stig Veibel's laboratory for an infrared investigation of the two salts (in KBr-tablets). The results are in good agreement with those of Ahrland, Chatt *et al.*¹ (Table 1). None of the salts has bands in the 820 cm^{-1} region where *para*-substituted benzenes have strong bands, and with the above authors we may conclude that all evidence is strongly in favour of *meta*-orientation.

Solutions. The solutions were made up from redistilled water in measuring flasks by pipetting from stock solutions of mercuric nitrate, nitric acid and 2.5 M potassium nitrate. The stock solutions of mercuric nitrate were prepared by dissolving weighed amounts of mercuric oxide in titrated nitric acid. The ligand was either pipetted from stock solutions or directly weighed into the mercuric solution.

Electrodes. The E.M.F. measurements were performed in a similar manner as described before^{10,11}. The electrode vessels (with a volume of about 50 ml) have a sealed-in platinum wire in a cavity in the bottom (in order to establish contact with a pool of mercury), and were equipped with a syphon type bridge with stop-cock as well as with inlet and outlet for nitrogen. Thus it was possible to shake the solutions in an inert atmosphere in the electrode vessels in order to reach equilibrium with mercury before the measurement. The cylinder nitrogen used was purified for oxygen by passing through a Meyer-Ronge apparatus. As reference electrode the 1 M KCl-calomel electrode was employed. The electrodes were prepared according to Gjaldbæk¹² in electrode vessels of the model introduced by Lewis, Brighton and Sebastian¹³. The E.M.F. measurements were per-

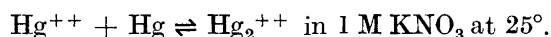
Table 2. The mercury standard potentials $E_{0,1}^\circ$ and $E_{1,2}^\circ$ relative to the M 1 calomel electrode, and the equilibrium constant K_0 in 1 M KNO_3 at 25°C.

o.	C_{HNO_3}	$[\text{Hg}_2^{2+}]$	E	$E_{0,1}^\circ$	$[\text{Hg}^{2+}]$	$[\text{Hg}_2^{2+}]$	E	$E_{1,2}^\circ$	K_0
1	0.0999	0.0988	0.4552	0.4849	0.0503	0.0494	0.5698	0.6079	120
2	0.0999	0.0985	0.4556	0.4853	0.0503	0.0493	0.5694	0.6075	117
3	0.0499	0.0493	0.4458	0.4844	0.0251	0.0246	0.5592	0.6062	115
4	0.0499	0.0492	0.4454	0.4840	0.0251	0.0246	0.5583	0.6053	113
					0.0169	0.0328	0.5442	0.6052	112
5	0.2135	0.01884	0.4340	0.4850	0.00956	0.00942	0.5450	0.6045	105
6	0.0214	1.884×10^{-3}	0.4045	0.4851	0.958×10^{-3}	0.942×10^{-3}	0.5150	0.6041	103
7	0.0550	0.942×10^{-3}	0.3955	0.4850	0.479×10^{-3}	0.471×10^{-3}	0.5053	0.6033	100
8	0.0150	0.942×10^{-3}	0.3955	0.4850	0.479×10^{-3}	0.471×10^{-3}	0.5049	0.6029	98.5
9	0.0241	0.377×10^{-3}	0.3838	0.4851	0.1916×10^{-3}	0.1884×10^{-3}	0.4930	0.6028	98
0	0.0100	0.377×10^{-3}	0.3837	0.4850	0.1916×10^{-3}	0.1884×10^{-3}	0.4927	0.6025	97
1	0.0500	0.1884×10^{-3}	0.3744	0.4845	0.0958×10^{-3}	0.0942×10^{-3}	0.4831	0.6018	96
2	0.0244	0.1884×10^{-3}	0.3748	0.4849	0.0958×10^{-3}	0.0942×10^{-3}	0.4828	0.6015	93.5
3	0.0150	0.1884×10^{-3}	0.3746	0.4847	0.0958×10^{-3}	0.0942×10^{-3}	0.4826	0.6013	93.5
4	0.0050	0.1884×10^{-3}	0.3744	0.4845	0.0958×10^{-3}	0.0942×10^{-3}	0.4825	0.6012	94
5	0.0020	0.1884×10^{-3}	0.3737	0.4838	0.0958×10^{-3}	0.0942×10^{-3}	0.4790	0.5977	(84)

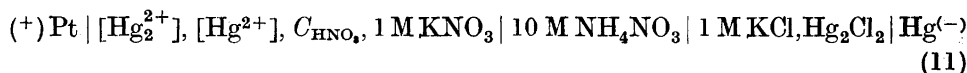
formed with a precision Vernier potentiometer and a Cambridge galvanometer. The electrodes were placed in a water thermostat and the liquid-liquid junctions between them were established through a 10 M ammonium nitrate solution. Merck's *p.a.* chemicals were employed for solutions and electrodes. The mercury was purified in Lothar Meyer's apparatus and distilled in vacuum.

Analytical methods. The mercuric concentration was determined by EDTA titration (addition of excess of complexon III and back titration with zinc sulphate with eriochrom-black as indicator). In a few other cases the total mercury concentration in mercurous containing solutions was determined gravimetrically as calomel after complete reduction with phosphorous acid in the presence of hydrochloric acid¹⁴.

THE MERCURY STANDARD POTENTIALS AND THE EQUILIBRIUM:



In Table 2 are placed together some E.M.F. data at 25° for the cells:



The mercury-mercurous standard potential $E_{0,1}^\circ$ corresponding to (10) is given by

$$E = E_{0,1}^\circ + 0.02958 \log [\text{Hg}_2^{2+}] \quad (12)$$

and the mercurous-mercuric redox potential $E_{1,2}^\circ$ corresponding to (11) by

$$E = E_{1,2}^\circ + 0.02958 \log \frac{[\text{Hg}^{2+}]^2}{[\text{Hg}_2^{2+}]} \quad (13)$$

From the standard potentials $E_{0,1}^\circ$ and $E_{1,2}^\circ$ we get

$$\log K_o = \frac{E_{1,2}^\circ - E_{0,1}^\circ}{0.05916} \quad (14)$$

where K_o is the mercurous-mercuric equilibrium constant (7).

The mercury-mercurous potential was measured in equilibrium solution prepared by shaking mercuric nitrate solutions with liquid mercury in an atmosphere of purified nitrogen. Complete equilibrium was always reached after one night of shaking in thermostat. This was directly checked by determining the total mercury concentration in some of the solutions after the equilibrium establishment. However, we can only confirm the result of Sillén and coworkers¹⁵ that the mercury-mercurous potential is quickly established at the surface of the mercury electrode (if not shaken) long before the solution as a whole has come to an equilibrium. The formal mercurous ion concentration given in the 3rd column of Table 2 is about 1 % less than the mercury concentration in the initial mercuric nitrate solution ($C_{\text{Hg}(\text{NO}_3)_2}^\circ$), and is directly estimated from the relationship:

$$[\text{Hg}_2^{2+}] = \frac{K_o}{1 + K_o} C_{\text{Hg}} \quad (15)$$

where C_{Hg} ($=C_{\text{Hg}(\text{NO}_3)_2}^\circ$) as defined in (9) is unchanged during the mercurous ion formation.

The mercurous-mercuric redox potentials were measured in direct connection with the measurements of the mercury-mercurous potentials. Equal volumes of the mercurous equilibrium solution and the initial mercuric nitrate solution were mixed in an atmosphere of nitrogen and the redox potential measured at a platinum electrode. This redox potential establishes itself more slowly than the mercury-mercurous potential as discussed by several authors¹⁵⁻¹⁷, and in the solutions low in mercury concentrations it could take more than half an hour to reach the equilibrium potential within a tenth of a millivolt. The formal concentrations of $[\text{Hg}^{2+}]$ and $[\text{Hg}_2^{2+}]$ in the mixed solutions are given in the 6th and 7th columns, respectively. These concentrations fulfill the conditions that the mercurous concentration is half of that in the mercurous equilibrium solution, and that their sum is equal to $C_{\text{Hg}(\text{NO}_3)_2}^\circ$.

The standard potentials $E_{0,1}^\circ$ and $E_{1,2}^\circ$ relative to the 1 M calomel electrode are given in the 5th and 9th columns and the values for K_o obtained by means of (14) in the last column of Table 2. It will be seen that $E_{0,1}^\circ$ is very constant and independent of variations in the mercurous ion and nitric acid concentrations. On the other hand $E_{1,2}^\circ$ as well as K_o increases slightly with increasing concentrations of the added nitrates in the 1 M potassium nitrate medium. The measurements Nos. 1-4 were performed already in 1944 by one of the authors (J.B.), nevertheless they are seen to compare well with the new measurements.

Schwarzenbach and Anderegg¹⁶ have determined K_o in sodium nitrate solutions, and Sillén *et al.*^{15,17} in sodium perchlorate and sodium nitrate solutions. In perchlorate solutions K_o increases much more strongly with the salt concentration than in the nitrate solutions. Hietanen and Sillén¹⁷

Table 3. Measurements with platinum electrode in mixed solutions of mercury(I) ions and mercury(II)-phosphine complexes in 1 M KNO₃ at 25°C.

(⁺)Pt | sol.Nos. 1-7 | 10 M NH₄NO₃ | 1 M KCl, Hg₂Cl₂ | Hg⁽⁻⁾

[Hg₃²⁺] = 0.942 × 10⁻³, C_{Hg(II)} = 0.958 × 10⁻³, C_{HNO₃} = 0.02

No.	C _L × 10 ³	C _L /C _{Hg(II)} = \bar{n}	E	E _M × 10 ³	[Hg ²⁺] × 10 ³	$\frac{1}{\bar{n}}$	log $\frac{[L]^*}{[L]}$	[L]
1	0	0	0.5155	0	0.958	—	—	0
2	0.347	0.362	0.5022	13.3	0.571	2.765	2.283	0.268 × 10 ⁻¹⁴
3	0.463	0.483	0.4970	18.5	0.466	2.07	2.078	0.429 × 10 ⁻¹⁴
4	0.531	0.554	0.4885	23.4	0.385	1.805	1.917	0.623 × 10 ⁻¹⁴
5	0.694	0.725	0.4800	35.5	0.241	1.38	1.590	0.132 × 10 ⁻¹³
6	0.825	0.86	0.4530	62.5	0.0841	1.162	1.020	0.491 × 10 ⁻¹³
7	1.015	1.06	0.3949	120.6	0.00877	0.944	0	0.515 × 10 ⁻¹²

[Hg₃²⁺] = 0.471 × 10⁻³, C_{Hg(II)} = 0.958 × 10⁻³, C_{HNO₃} = 0.02

1a	0	—	0.5239	0	0.958
4a	0.531	0.554	0.4966	23.7	0.381

explain this in terms of complexity constants estimated under certain assumptions. However, we consider it safer to speak only about different values of the formal equilibrium constant K_o in the different ionic media. However, it is noteworthy to see that our value in 1 M KNO₃ at 25°C, $K_o \approx 100$, is in very close agreement with the findings of both Schwarzenbach and Anderegg, and Hietanen and Sillén in 1 M NaNO₃.

We have carried out some measurements of $E_{0,1}^\circ$ and $E_{1,2}^\circ$ at extremely low mercury concentrations ($\geq 10^{-5}$ M) in order to detect a possible dissociation of the dimeric mercurous ion: $\text{Hg}_2^{2+} \rightleftharpoons 2 \text{Hg}^+$. The measurements were performed in potassium nitrate and sodium perchlorate, but the results were somewhat contradictory, and we can only agree with the statement of Linhart¹⁸ that there is no safe experimental evidence for the existence of monomeric mercurous ions in aqueous solutions.

MEASUREMENTS OF THE MERCURY(II)-PHOSPHINE COMPLEX FORMATION WITH A MERCURY(I)-REDOX ELECTRODE

As already mentioned it is possible to show by redox measurement with a bright platinum electrode that mercurous ions have only a negligible tendency to complex formation with the phosphine ligand. The measurements in Table 3 give an example of this. Solutions Nos. 4 and 4a contain same total concentrations of mercuric nitrate and phosphine ligand, but the concentration of mercurous nitrate in No. 4a is only half of that in No. 4. One should therefore theoretically expect an increase of $0.02958 \log 2 = 0.0089$ V in the measured potential E , if mercurous ions do not form complexes with the ligand. Experimentally one finds 0.0081 V. However, a corresponding comparison of the ligand-free solutions 1 and 1a shows that also here the experimentally found increase $E_{(\text{No.1a})} - E_{(\text{No.1})} = 0.0084$ V is somewhat smaller than the

theoretical increase 0.0089 V. It seems therefore safe to neglect complex formation between mercurous ions and the phosphine ligand. This assumption is supported by the recent studies of Yamane and Davidson¹⁹ who state that mercurous complexes of ligands such as ammonia and cyanide are unstable toward disproportionation to give mercuric complexes but »ionic» chelating ligands such as pyrophosphate and oxalate can form stable mercurous complexes.

From the E.M.F. data in Table 3, one can compute the concentration of free mercuric ions (in column 6) and the variation in the concentration of free ligand (column 9). The differences in the measured potential E between Nos. 1 and 1a (the ligand free solutions) and the rest of the solutions determine E_M for which we have according to the expressions (1) and (2):

$$E_M = 0.05916 \log \frac{0.958 \times 10^{-3}}{[\text{Hg}^{2+}]} = 0.05916 \log X \quad (16)$$

Aqueous solutions of mercurous ions and mercury(II)-complexes are thermodynamically stable with regard to formation of metallic mercury, if $[\text{Hg}_2^{2+}] < K_0 [\text{Hg}^{2+}] \sim 100 [\text{Hg}^{2+}]$. It will be seen that this condition is fulfilled for the solutions Nos. 1–6 and nearly fulfilled for No. 7. Solution No. 7 was completely stable during the measurements, but solutions with higher concentrations of ligand gave shortly after their preparation dark precipitations of mercury.

$\log [L]^*/[L]$ in the 8th column of Table 3 determines the concentration of free ligand in the solutions 1–6 relative to that in No. 7. This integral was computed by means of expression (6) from a graph in which $\frac{1}{\bar{n}} (= \frac{C_{\text{Hg(II)}}}{C_L})$ was plotted *versus* $\log X$ as abscissa. The integral was estimated from point to point using Simpson's formula. The concentration of free ligand in solution 7 ($[L]^* = 0.515 \times 10^{-12} \text{M}$) and the $[L]$ -concentrations derived from there in the last column of Table 3 were estimated from the measurements with a mercury electrode mentioned in the next section.

MEASUREMENTS OF THE PHOSPHINE COMPLEX FORMATION WITH A MERCURY ELECTRODE

Table 4 gives the experimental data for three series with the initial concentrations of mercuric nitrate 0.00019, 0.00038 and 0.00095 M, respectively, and varying concentrations of ligand. It was not necessary to take special precautions to establish the equilibrium with mercury before measurements of the cells. Mercury(II) solutions with more than 1 mole of ligand per Hg-atom are very close to equilibrium, but also for solutions with a smaller content of ligand the potential E of the cells gave directly the equilibrium potential as discussed in the section on the mercury standard potential. In the series with $C_{\text{Hg}} = 0.38 \times 10^{-3} \text{M}$ some of the solutions (marked with an asterisk) were prepared as mixed solutions of equal parts of mercuric and mercurous nitrate, but nevertheless gave (as seen from Table 4) the same potential within a few tenths of a millivolt as the initially mercurous-free solutions.

Table 4. Mercury(II)-phosphine complex formation in 1 M KNO₃ at 25°C. Measurements of cells with mercury electrode.

Hg C _{Hg} , C _L , 0.01 M HNO ₃ , 1 M KNO ₃ 10 M NH ₄ NO ₃ 1 M KCl, Hg ₂ Cl ₂ Hg								
C _{Hg} = 0.19 × 10 ⁻³			C _{Hg} = 0.38 × 10 ⁻³			C _{Hg} = 0.95 × 10 ⁻³		
C _L × 10 ³	E	E' _M × 10 ³	C _L × 10 ³	E	E' _M × 10 ³	C _L × 10 ³	E	E' _M × 10 ³
0	0.3748	0	0	0.3837	0	0	0.3955	0
0.1093	0.3668	8.0	0.1126	0.3786	5.1	0.547	0.3845	11.0
0.1125	0.3628	12.0	0.1126*	0.3784	5.3	1.093	0.3507	44.8
0.1408	0.3577	17.1	0.1402	0.3775	6.2	1.366	0.3357	59.8
0.1690	0.3439	30.9	0.1402*	0.3780	5.7	1.640	0.3130	82.5
0.2186	0.3398	35.0	0.1689	0.3762	7.5	1.913	0.2731	122.4
0.2733	0.3014	73.4	0.1689*	0.3760	7.7	2.050	0.0704	325.1
0.328	0.2691	105.7	0.2252	0.3716	12.1	2.186	0.0469	348.6
0.547	-0.0496	424.4	0.2252*	0.3723	11.4	2.186	0.0435	352.0
0.601	-0.0746	449.4	0.2733	0.3678	15.9	2.460	0.0178	377.7
0.656	-0.0982	473.0	0.2815	0.3666	17.1	2.73	-0.0245	420.0
0.683	-0.1080	482.8	0.2815*	0.3669	16.8	3.01	-0.0595	455.0
0.820	-0.1335	508.3	0.3505	0.3535	30.2	3.28	-0.1006	496.1
0.850	-0.1417	516.5	0.547	0.3107	73.0	3.83	-0.1506	546.1
0.929	-0.1472	522.0	0.683	0.2497	144.0	4.37	-0.1685	563.9
1.023	-0.1548	529.6	0.820	0.0459	337.8	4.92	-0.1777	573.2
1.093	-0.1598	534.6	0.957	-0.0030	386.7	5.25	-0.1825	578.0
1.115	-0.1608	535.6	1.093	-0.0472	430.9	5.47	-0.1851	580.6
1.160	-0.1703	545.1	1.366	-0.1190	502.7			
1.64	-0.1893	564.1	1.640	-0.1457	529.4			
1.69	-0.1938	568.6	1.913	-0.1660	549.7			
1.705	-0.1943	569.1	2.186	-0.1788	562.5			
1.79	-0.1956	570.4	2.459	-0.1847	568.4			
			2.733	-0.1931	576.8			

* Solutions prepared as mixed solutions of equal parts of mercuric and mercurous nitrate.

The differences between the potential E of the ligandfree solutions and the rest of the solutions determined the E.M.F. for a cell of type (8):

$$E'_M = 0.02958 \log \frac{K_o \cdot C_{Hg}}{(1 + K_o)[Hg_2^{2+}]} = 0.02958 \log \frac{C_{Hg}}{(1 + K_o)[Hg_2^{2+}]} \quad (17)$$

Complex solutions of different mercury concentrations, but with the same values of E'_M have according to (17) also the same value of $[Hg_2^{2+}]_{C_L=0}/[Hg^{2+}]$ and are *eo ipso* corresponding solutions. They can therefore be treated according to Fronæus⁴ as we know that mercurous ions do not form complexes. In Fig. 1 (in the graph on the left) C_L for each of the three series is plotted *versus* E'_M . Interpolated sets of C_L at rounded-off values of E'_M obtained from this graph are plotted in Fig. 1 (in the graph on the right) *versus* the corresponding values of $C_{Hg(II)}$. In this graph the intercept at the ordinate axis determines directly the free ligand concentration, and the slopes of the straight lines the formation function according to eqns (4). For values of $E'_M \gtrsim 100$ mV $C_{Hg(II)} = C_{Hg}$, but for lower values of E'_M $[Hg_2^{2+}]$ is calculated from the first of the eqns. (17) and $C_{Hg(II)}$ as the difference $C_{Hg} - [Hg_2^{2+}]$ according to (9).

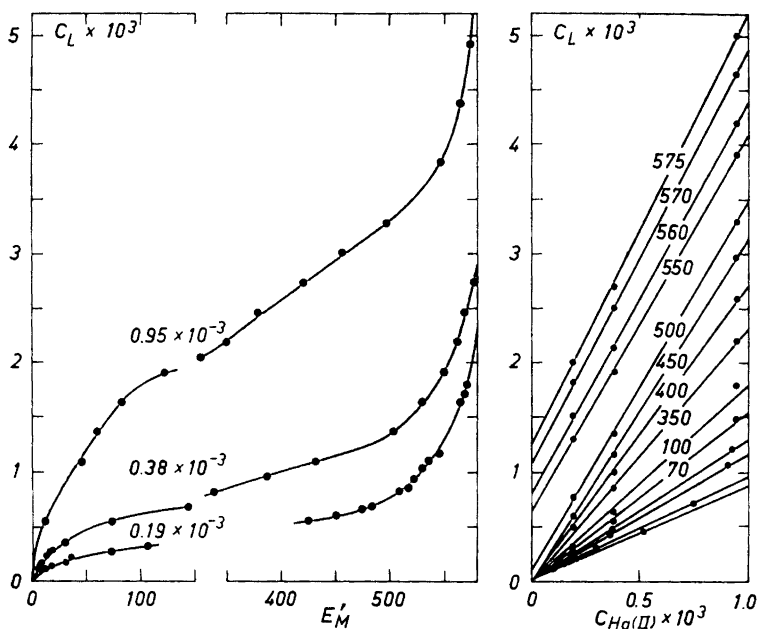


Fig. 1. The E.M.F. measurements are plotted on the left: C_L , versus E'_M for the three mercury concentrations in Table 4. The straight lines plotted on the right give C_L versus $C_{Hg(II)}$ for values of E'_M corresponding to the data in Table 5.

In Table 5 are given (in column 1) the used rounded-off values of E'_M and (in column 2) the interpolated values of C_L for one of the measured series ($C_{Hg} = 0.95 \times 10^{-3}$). Column 3 gives the values of $C_{Hg(II)}$, and columns 4 and 5 the graphically derived values of \bar{n} and $[L]$ from Fig. 1. Column 6 gives the ratio $C_L/C_{Hg(II)}$ which is seen to deviate only a little from \bar{n} as long as the graphically determined $[L]$ (1) is negligible. Column 7 gives the corrected values for E'_M according to the relationships:

$$E_M = E'_M + 0.02958 \log \frac{C_{Hg(II)}}{[Hg^{2+}]_{C_L=0}} = 0.02958 \log X \quad (18)$$

Finally the last column gives $[L]$ (2), the integrated values of the free ligand concentration computed from a graph in which $1/\bar{n}$ was plotted versus $\log X$ (eqn. (6)). In this calculation the highest $[L]$ (1) value was taken as reference ($[L]^* = 1.26 \times 10^{-3}$ M).

The data in Table 5 show that using the mercury electrode the complex formation curve for \bar{n} -values lower than about one can only be reached with high experimental uncertainty due to mercurous ion formation. It is fortunate that these measurements just overlap the measurements with the platinum electrode in Table 3. By comparison of eqns. (16) and (18) it will be seen that a value of E'_M corresponding to a certain value of $\log X$ is twice as high as

Table 5. Derived data from Fig. 1. Interpolated values of C_L for one of the measured series ($C_{\text{Hg}} = 0.95 \times 10^{-3}$), graphically derived values of \bar{n} and $[L]$ (1) using all three series, and integrated values of $[L]$ (2) using the relation for $\log ([L]^*/[L])$.

$$[\text{Hg}^{2+}]_{C_L=0} = 0.96 \times 10^{-5}, [\text{Hg}_2^{2+}]_{C_L=0} = 0.94 \times 10^{-3}$$

$E_M' \times 10^3$	$C_L \times 10^3$	$C_{\text{Hg(II)}} \times 10^3$	\bar{n}	$[L](1)$	$C_L/C_{\text{Hg(II)}}$	$E_M \times 10^3$	$\frac{1}{\bar{n}}$	$[L](2)$
10	0.45	0.518	0.86	0	0.87	61.2	1.162	0.515×10^{-12}
20	0.71	0.752	0.95	0	0.945	76.0	1.052	0.184×10^{-11}
40	1.07	0.908	1.16	0	1.18	98.5	0.862	0.987×10^{-11}
50	1.22	0.931	1.28	0	1.31	108.8	0.782	0.191×10^{-10}
70	1.48	0.946	1.54	0	1.56	129	0.650	0.585×10^{-10}
00	1.79	0.950	1.78	0	1.88	159	0.547†	0.233×10^{-9}
.50	2.20	0.950	2.30	0	2.31	409	0.435	0.354×10^{-5}
.00	2.59	0.950	2.70	0	2.73	459	0.371	0.170×10^{-4}
.50	2.97	0.950	3.10	0	3.13	509	0.323	0.70×10^{-4}
.00	3.30	0.950	3.37	0.10×10^{-3}	3.48	559	0.297	0.235×10^{-3}
.50	3.92	0.950	3.44	0.64×10^{-3}	4.13	609	0.291	0.74×10^{-3}
.60	4.20	0.950	3.57	0.81×10^{-3}	4.42	619	0.280	0.925×10^{-3}
.70	4.65	0.950	3.74	1.09×10^{-3}	4.90	629	0.2673	1.14×10^{-3}
.75	5.00	0.950	3.92	1.26×10^{-3}	5.26	634	0.255	$1.26 \times 10^{-3*}$

† Calc. with the average 1.83 of the values found for $C_L/C_{\text{Hg(II)}}$ and \bar{n} .

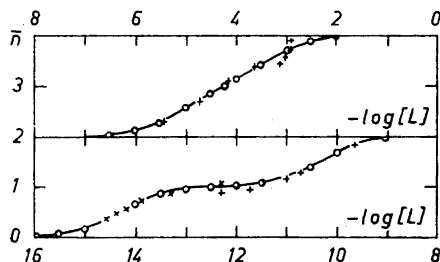
in case of the measurements with the mercury electrode. This means that the lowest of the values in Table 5 ($E_M = 61.2$ mV) corresponds very nearly to the value for solution 7 in Table 3 ($E_M = 120.6$ mV). Due to this coincidence $[L]^*$ for this solution is taken to be equal to the corresponding ligand concentration $[L](2) = 0.515 \times 10^{-12}$ M in Table 5.

Fig. 2 shows graphically the complete formation curve as far as $N = 4$. It will be seen that there is a pronounced »stop» in the formation curve for both $\bar{n} = 1$ and $\bar{n} = 2$, but also the separation of the third and fourth steps is much higher than usually found for mercuric complexes. Due to the separation of the steps the consecutive constants are equal to the reciprocal concentrations of free ligand for all half values of \bar{n} . From the formation curve is interpolated:

\bar{n}	0.5	1.5	2.5	3.0
$-\log [L]$	14.30	10.30	5.10	4.22

Fig. 2. The complex formation curve of mercury(II) ions and diphenylphosphino-benzene-*m*-sulphonate in 1 M KNO_3 at 25°C. The lower part of the figure gives the curve from $\bar{n} = 0$ to $\bar{n} = 2$, and the upper part from $\bar{n} = 2$ to $N = 4$.

- × Exptl. points (Pt-electr.). + Exptl. points (Hg-electr.).
- Calc. points (from $K_1, \beta_2, \beta_3, \beta_4$).



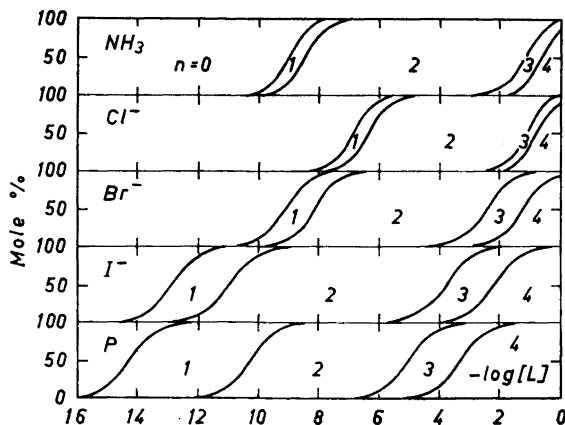


Fig. 3. Comparison of the distribution of mercury(II) between the various complexes as a function of $-\log [L]$ for the ammonia⁵, the halide²¹, and the phosphine systems.

This gives directly the following values for the complexity constants:

$$\begin{aligned} \log K_1 &= 14.3 \\ \log \beta_2 &= 14.3 + 10.3 = 24.6 \\ \log \beta_3 &= 24.6 + 5.1 = 29.7 \\ \log \beta_4 &= 24.6 + 2 \times 4.22 = 33.0 \end{aligned}$$

There seems to be a higher uncertainty in the experimental points for \bar{n} -values between 3 and 4, and this is the reason why the value of $-\log[L]$ for $\bar{n} = 3$ instead of for $\bar{n} = 3.5$ is used in the calculation of β_4 .

A MERCURY(II)-PHOSPHINE COMPLEX SALT

Mercuric ions and diphenylphosphinobenzene-*m*-sulphonate can in case of sufficient small concentrations be mixed in all ratios. If the mercuric concentration is essentially higher than 0.001 M, and the concentration of ligand approximately twice that of the metal ion concentration, a complex salt with two moles of ligand per mercuric ion separates out of the solutions on standing overnight. We tried to prepare a complex salt corresponding to the mono complex from a solution of the composition: $C_{\text{Hg}} = 0.003$, $C_{\text{L}} = 0.003$, but the infrared spectra of the precipitates (in KBr-tablets) showed that the same complex salt separated in both cases.

The analysis of the white crystalline precipitates dried over silica gel agreed approximately with the formula $\text{Hg}[(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$, corresponding to a formula weight of 919. (Found: C 45.9; H 3.3; S 7.4; Hg 21.9. Calc. for $\text{C}_{36}\text{H}_{32}\text{O}_8\text{P}_2\text{Hg}$; C 47.0; H 3.5; S 7.0; Hg 21.8). The mercury was

precipitated and weighed as $[\text{Cuen}_2][\text{HgI}_4]^{20}$ after complete decomposition of the complex salt with a 1:1 mixture of conc. H_2SO_4 and HNO_3^* .

DISCUSSION

In Fig. 3 our results with diphenylphosphinobenzene-*m*-sulphonate and mercury(II) are compared with earlier results for the ammonia system⁵ and with Sillén²¹ and coworkers' results for the mercury halide systems. The figure shows the distribution of the various complexes HgL_1 to HgL_4 as a function of the ligand exponent $-\log [\text{L}]$. The di-complex has in all cases a very large range of existence, but it will be seen that the range of existence of the mono-complex as well as that of the tri-complex increases much from chloride to iodide and again from the iodide to the phosphine system. For this system it is especially the mono-complex which has a great range of existence, and the first coordination number is clearly one. It will be seen that the complex affinity increases in the series: $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{phosphine}$.

For silver(I) Leden *et al.* have found that the coordination number two decreases in importance for ligands such as chloride and bromide²², and for both iodide²³ and phosphine¹ the coordination numbers one and three, instead of two, are virtually found. But also here it is remarkable that the complex affinity increases in the series: $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{phosphine}$.

The first subgroup metal ions Cu^+ , Ag^+ , Au^+ , and Hg^{2+} have all a strong tendency to form linear complexes with ligands which cannot participate in π -bonding as, *e.g.*, ammonia or as cyanide only have p-orbitals available for such bonding. However, after a large range of existence of the linear di-complex a tetrahedral complex is formed in most cases. Our data for the mercury(II)-phosphine system now seem to support the idea of Ahrland and Chatt that ligands furnished with d-orbitals capable of accepting d-electrons from the metal, such as, *e.g.*, phosphines, arsines and the halide ions to an increasing extent from chloride to iodide, interfere with this condition and strongly favour the coordination numbers one and three.

REFERENCES

1. Ahrland, S., Chatt, J., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* **1958** 264, 276.
2. Brandt, P. and Plum, O. *Acta Chem. Scand.* **7** (1953) 97.
3. Jensen, F. R. *J. Am. Chem. Soc.* **82** (1960) 2469.
4. Fronæus, S. *Komplexsystem hos koppar*. Thesis. Lund 1948, pp. 13, 18 ff.
5. Bjerrum, J. *Metal ammine formation in aqueous solution*. Thesis. P. Haase and Son, Copenhagen 1941, pp. 22, 28. Reprinted 1957.
6. Bjerrum, J. *Kgl Danske Videnskab. Selskab, Mat.-fys. Medd.* **21** (1944) No. 4, p. 5.
7. Leden, I. *Potentiometrisk undersökning av några kadmiumsalters komplexitet*. Thesis. Lund 1943, p. 19.
8. Bjerrum, J. *Kemisk Månedsblad* **24** (1943) 22.
9. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
10. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **12** (1934) No. 15.

* We are indebted to Mr. Gunnar Borch, who carried out the Hg determination, and to Mr. Preben Hansen, who carried out the C, H, and S determinations in Professor K. A. Jensen's laboratory.

11. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* **2** (1948) 297.
12. Gjaldbæk, J. K. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd* **5** (1924) No. 9.
13. Lewis, G. N., Brighton, T. B. and Sebastian, R. L. *J. Am. Chem. Soc.* **39** (1917) 2245.
14. Treadwell, F. P. *Lehrbuch der analytischen Chemie*, 5. Aufl. (1911) p. 14.
15. Jonsson, A., Qvarfort, I. and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 461.
16. Schwarzenbach, G. and Anderegg, G. *Helv. Chem. Acta* **37** (1954) 1289.
17. Hietanen, S. and Sillén, L. G. *Arkiv Kemi* **10** (1956) 103.
18. Linhart, G. A. *J. Am. Chem. Soc.* **38** (1916) 2356.
19. Yamane, T. and Davidson, N. *J. Am. Chem. Soc.* **82** (1960) 2123.
20. Spacu, G. and Suciú, G. *Z. anal. Chem.* **77** (1929) 334.
21. Sillén, L. G. *Acta Chem. Scand.* **3** (1949) 539.
22. Berne, E. and Leden, I. *Svensk Kem. Tidskr.* **65** (1953) 88; *Z. Naturforsch.* **8a** (1953) 719.
23. Leden I. *Acta Chem. Scand.* **10** (1956) 812.

Received October 7, 1961.