The absorption band of medium intensity at 1308 cm.$^{-1}$ in the reagent, which is also probably due to C–O vibrations, is affected to a small extent in the case of Pb(II) and Cd(II) chelates but is shifted to a marked degree in the chelates of the transition metals. This implies that the C–O group vibrations in the metal chelates of 4-hydroxybenzothiazole are influenced to a slight extent by the mass of the metal in the chelate ring. The interaction of the C–O group with the π-bonds in the chelate ring as well as with the d-electrons of the metal atoms play a much more important part in determining the extent of the shifts that are observed in C–O group vibrations as we go from the reagent to the metal chelates. It was found that if the frequency of the band that appears between 1310 and 1335 cm.$^{-1}$ for the transition metal chelates of 4-hydroxybenzothiazole was plotted against the stability constant (log β_2) of the chelate, a linear relationship was obtained. This type of relationship has been found in a number of metal complexes[13,14] and confirms the assignments made for the C–O vibrations in the 4-hydroxybenzothiazole chelates.

Acknowledgment.—The authors are grateful for a grant from the U. S. Atomic Energy Commission in support of this work.

(14) H. F. Holtzclaw, Jr., and J. P. Collman, THIS JOURNAL, **79**, 3318 (1957).

PITTSBURGH 13, PENNSYLVANIA

[CONTRIBUTION NO. 2496 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, PASADENA, CALIFORNIA]

Mercury(II) Complexes of Imidazole and Histidine

BY PHILIP BROOKS AND NORMAN DAVIDSON

RECEIVED AUGUST 31, 1959

The association constants of Hg^{II} with imidazole and L-histidine have been calculated from potential measurements of a Hg, Hg^{II} electrode in solutions containing the complexing agents. For imidazole, the main result is

$$Hg^{++} + 2C_3H_4N_2 \rightleftarrows Hg(C_3H_4N_2)_2{}^{++} \qquad K = 10^{16.7}\ M^{-2}$$

A solid substance, $Hg(C_3H_3N_2)ClO_4 \cdot H_2O$, precipitates from solutions at $pH > 4$. It probably contains an infinite chain: $(C_3H_3N_2Hg-)_n{}^{+n}$. For histidine, the main results are:

$$Hg^{++} + 2L^- \rightleftarrows HgL_2 \qquad Hg^{++} + L^- + HL \rightleftarrows HgL(HL)^+ \qquad Hg^{++} + 2HL \rightleftarrows Hg(HL)_2{}^{++}$$
$$K = 10^{21.2}\ M^{-2} \qquad\qquad K = 10^{18.4}\ M^{-2} \qquad\qquad K = 10^{15.0}\ M^{-2}$$

where $L^- = (C_3H_3N_2)CH_2CH(NH_2)CO_2{}^-$ and $HL = (C_3H_3N_2)CH_2CH(NH_3{}^+)CO_2{}^-$. Because of the tendency of Hg^{++} to form two bonds in a linear configuration, chelate formation contributes only slightly to the ligand binding by Hg^{++}. There is also evidence for the complex HgL^+, with a formation constant of $\approx 10^{15}\ M^{-1}$ (from L^-).

Imidazole and histidine complexes with metal ions are of intrinsic interest as a part of the chemistry of complex ions, as well as being of possible biological significance. Complex ion formation with a number of metal ions has been studied.[1] There is evidence that the imidazole ring is an important binding site for metal ions in serum albumin.[2,3] In general, mercury(II) has the greatest binding power for nitrogen ligands of any of the metal ions; the present investigation is concerned with the mercury(II) complexes of imidazole and histidine.

Experimental

Imidazole, from the Eastman Kodak Co. (m.p. 88-90°, Eastman grade) and the Aldrich Chemical Co., and L-histidine, cfp. grade (99.98% pure by nitrogen analysis) from the California Corporation for Biochemical Research were dissolved in doubly distilled water. Concentrations calculated from pH titrations and from the weight of solute taken agreed within 1%. Imidazolium perchlorate solutions were prepared by adding standard perchloric acid to imidazole solutions. Mercuric perchlorate solutions were prepared by dissolving reagent grade mercuric oxide in a known excess of 9 F perchloric acid and diluting. In all experiments sodium perchlorate was used to keep the ionic strength constant at 0.15 M.

The principal experimental data were the potentials of a mercury, mercury(II) electrode as a function of ligand concentration and pH. The cell, in a water bath at 27.0 ± 0.1°, contained a J-type mercury electrode in which the mercury surface could be renewed by overflow, a 1.5 F $NaNO_3$ salt bridge connecting to a saturated calomel electrode and provision for titrating in reagents and for maintaining a nitrogen atmosphere. Potential differences were measured with a Leeds and Northrup K-2 potentiometer and a 0.01 μ amp./mm. galvanometer; pH measurements were made with a Beckman model GS pH meter. In every case ample time was allowed for the system to attain equilibrium before final measurements were made.

Results

Imidazole Complexes.—As anticipated, the binding of mercury by imidazole is so great that, under practical conditions, the equilibrium

$$Hg^{++} + nImH^+ \rightleftarrows Hg(Im)_n{}^{++} + nH^+ \qquad (1)$$

lies far to the right except for rather acid solutions with $pH \leq 2$. Under these circumstances, the pH titration method for the study of complex ion formation is difficult. We have therefore used a potentiometric method.

Insoluble mercury-imidazole compounds precipitate at pH's > 4, so measurements were made in the pH 2–4 range. The predominant imidazole species is the imidazolium ion, ImH^+. Equation 1 then represents the over-all chemical reaction. The Nernst law can be written

$$E = E_0' - \frac{RT}{2\mathfrak{F}} \ln [Hg^{++}] \qquad (2)$$

---

(1) For a general review, see J. Bjerrum, G. Schwarzenbach, L. Sillén, "Stability Constants, Part I," Special Publication No. 6, The Chemical Society, London, 1957, Tables 26 and 207; see also the specific references in Table III.

(2) F. R. N. Gurd and D. S. Goodman, THIS JOURNAL, **74**, 670 (1952).

(3) C. Tanford, *ibid.*, **74**, 211 (1952).

For E_0', the potential of the hypothetical Hg, 1.00 M Hg^{++} electrode at $\mu = 0.15\ M$ *vs.* the s.c.e. (saturated calomal electrode), we take − 0.607 v. It is inconvenient to measure this quantity because of the Hg, Hg^{++}, Hg_2^{++} equilibrium. Our choice is based on the values E_0 (Hg^{++} *vs.* H_2) = −0.841 in 1 F $HClO_4$,[4] E_0 (Hg^{++} *vs.* H_2) = − 0.854 v. ($\mu = 0$).[5] It is to be noted that the quantities E that we quote are oxidation–reduction potentials using the American convention; a Hg, Hg^{++} electrode is electrically positive with respect to s.c.e. For the equilibria

$$Hg^{++} + ImH^+ \rightleftharpoons HgIm^{++} + H^+$$

$$K_1' = \frac{[H^+][HgIm^{++}]}{[Hg^{++}][ImH^+]} \quad (3)$$

$$Hg^{++} + 2ImH^+ \rightleftharpoons HgIm_2^{++} + 2H^+$$

$$\beta_2' = \frac{[H^+]^2[HgIm_2^{++}]}{[Hg^{++}][ImH^+]^2} \quad (4)$$

we have

$$\frac{[\Sigma\ Hg^{II}]}{[Hg^{++}]} = 1 + K_1' \frac{[ImH^+]}{[H^+]} + \beta_2' \frac{[ImH^+]^2}{[H^+]^2} \quad (5)$$

Equation 2 can then be written as

$$E = E_0' - \frac{RT}{2\mathfrak{F}} \ln [\Sigma Hg^{II}] + \frac{RT}{2\mathfrak{F}} \ln \left\{1 + K_1' \frac{[ImH^+]}{[H^+]} + \beta_2' \frac{[ImH^+]^2}{[H^+]^2}\right\} \quad (6)$$

Plots of the quantity $(2\mathfrak{F}/RT)E + \ln (\Sigma\ Hg^{II})$ *vs.* $\ln [ImH^+]/[H^+]$ were linear with a slope of 1.95–2.00. This shows that the dominant term in the power series $1 + K_1'[ImH^+]/[H^+] + \beta_2' \cdot ([ImH^+]/[H^+])^2$ is the quadratic term and the principal complex formed is $Hg(Im)_2^{++}$.

Representative data analyzed in terms of the simple equation

$$E = E_0' - 0.0298 \log [\Sigma\ Hg^{II}] + 0.0596 \log \left\{\beta_2' \frac{[ImH^+]}{[H^+]}\right\} \quad (7)$$

are presented in Table I. In all cases from the actual potential, we know that $[\Sigma Hg^{II}]/[Hg^{++}] \geq 400$. The equilibrium constant for the reaction

$$Hg + Hg^{++} \rightleftharpoons Hg_2^{++} \quad (8)$$

has been measured as 130.[6] We have assumed that the system was at equilibrium with respect to this reaction, although we do not know that such is the case. With this assumption, $[HgIm_2^{++}] = [\Sigma\ Hg^{II}] = [\Sigma\ Hg] - [Hg_2^{++}]$ where $[\Sigma\ Hg]$ is the total amount of mercury added as Hg(II) in the solution and $[\Sigma\ Hg^{II}]$ is the total amount of Hg^{II}, *i.e.*, after correction for the mercurous ion formed. Then $[ImH^+] = [\Sigma\ ImH^+] - 2[HgIm_2^{++}]$. The corrections for the amount of Hg_2^{++} present and for the amount of imidazole tied up as $HgIm_2^{++}$ are small in all cases and negligible for high ratios $[ImH^+]/[\Sigma\ Hg]$, so errors in the corrections are not very important.

The constancy of the calculated values of β_2' in Table I with varying pH, mercury(II) concentration and imidazole concentration shows that the principal species is $Hg(Im)_2^{++}$.

TABLE I

POTENTIAL MEASUREMENTS OF Hg^{II}, ImH^+ SOLUTIONS

$-E$,[a] v.	pH	$[\Sigma\ Hg^{II}]$[b] F[c]	$[Hg^{++}]$ M	$[\Sigma\ ImH^+]$ F	$[ImH^+]$ M	log β_2'
0.369	2.03	3.85×10^{-4}	1.05×10^{-8}	0.0963	0.0955	2.53
.361	2.21	3.84×10^{-4}	5.49×10^{-9}	.0960	.0952	2.46
.317	2.91	3.82×10^{-4}	1.82×10^{-10}	.0954	.0946	2.54
.267	3.77	3.82×10^{-4}	3.80×10^{-12}	.0954	.0946	2.58
.243	4.17	3.82×10^{-4}	6.02×10^{-13}	.0954	.0946	2.50
.411	2.12	3.87×10^{-4}	2.52×10^{-7}	.0160	.0153	2.55
.394	2.12	4.08×10^{-4}	6.74×10^{-8}	.0317	.0309	2.54
.377	2.10	4.10×10^{-4}	1.81×10^{-8}	.0642	.0634	2.53
.366	2.10	3.88×10^{-4}	7.71×10^{-9}	.0972	.0965	2.51
.395	2.58	5.11×10^{-4}	7.76×10^{-8}	.0147	.0138	2.38
.352	2.60	5.26×10^{-4}	2.75×10^{-9}	.0696	.0686	2.40
.361	2.59	1.01×10^{-3}	5.49×10^{-9}	.0692	.0674	2.42
.388	2.60	6.44×10^{-3}	4.46×10^{-8}	.0684	.0567	2.46
				Av.	log β_2' =	2.50 ± 0.06

[a] As already emphasized, these are conventional oxidation–reduction potentials *vs.* s.c.e.; the electrode was electrically positive with respect to s.c.e. [b] $[\Sigma Hg^{II}]$ is the total (formal) concentration of Hg^{II}, corrected for Hg_2^{++}. [c] F and M are formula weights per liter and moles per liter, respectively.

On changing concentrations of reagents, the potentials usually were established to ± 0.5 mv. within a few minutes, although occasionally the potentials drifted for 10–30 minutes before becoming constant.

In general a good way to investigate the possible influence of the first complex, $HgIm^{++}$ and the term $K_1'[ImH^+]/[H^+]$ is to start from the equation

$$\frac{\frac{[\Sigma Hg^{II}]}{[Hg^{++}]} - 1}{[ImH^+]/[H^+]} = K_1' + \beta_2' \frac{[ImH^+]}{[H^+]} \quad (9)$$

Plots of the function on the left of equation 9 *vs.* $[ImH^+]/[H^+]$ gave fairly good straight lines; however, it was not possible to obtain points close enough to the origin to result in a reliable extrapolation for K_1'. The difficulty is essentially this. To emphasize the contribution to the binding by $HgIm^{++}$, one should work at low $[ImH^+]/[H^+]$ ratios. This decreases the ratio $[\Sigma\ Hg^{II}]/[Hg^{++}]$; the amount of Hg_2^{++} according to equation 8 then becomes large relative to $[\Sigma\ Hg^{II}]$. Under these circumstances, the corrections involved in analyzing the data are too great to permit reliable interpretation. There was no evidence for the formation of $Hg(Im)_3^{++}$ or $Hg(Im)_4^{++}$ even at $[ImH^+] = 0.10\ M$ and pH 4.

The pK_a of imidazolium at 27° and $\mu = 0.15\ M$ was measured by a pH titration to be 7.12. This can be compared with Edsall's value[7] of 7.11 at 23°, $\mu = 0.16\ M$, and Tanford and Wagner's value[8] of 7.12 at 25°, $\mu = 0.15\ M$. Since

$$Hg^{++} + 2ImH^+ = HgIm_2^{++} + 2H^+, \qquad \beta_2' = 10^{2.50} \quad (10)$$

$$Hg^{++} + 2Im = HgIm_2^{++}, \qquad \beta_2 = \frac{[HgIm_2^{++}]}{[Hg^{++}][Im]^2} = 10^{16.74}\ M^{-2} \quad (11)$$

---

[4] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 509.

[5] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1956, p. 179.

[6] L. G. Sillén, A. Jonsson and I. Qvarfort, *Acta Chem. Scand.*, **1**, 461 (1947).

[7] J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, THIS JOURNAL, **76**, 3054 (1954).

[8] C. Tanford and M. L. Wagner, *ibid.*, **75**, 434 (1953).

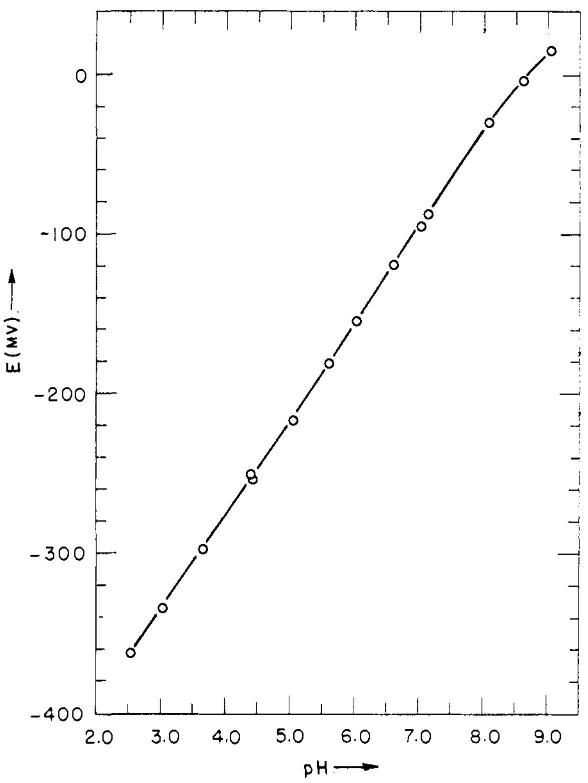


Fig. 1.—Potential *vs.* pH for fixed ΣHg^{II} and histidine concentrations. These concentrations, $[\Sigma Hg^{II}] = 3.80 \times 10^{-3}$ *F* and $[\Sigma L] = 0.095$ *F*, actually decreased slightly during the titration due to dilution; suitable corrections were made. A similar straight line, displaced as expected by the Nernst law, was obtained for $[\Sigma Hg^{II}] = 3.4 \times 10^{-4}$ *F*, $[\Sigma L] = 0.011$ *F*. The solid line is calculated from equation 15a and the values $\log \beta_{20} = 2.98$, $\log \beta_{21} = 9.18$, $\log \beta_{22} = 14.99$.

Insoluble $Hg(C_3H_3N_2)(ClO_4)\cdot H_2O$.—Both the imidazole and histidine complexes with mercury become insoluble as the pH is raised. The imidazole mercury complex precipitates copiously at pH's greater than 4.5, but the histidine complex is more soluble, solutions at very alkaline pH's (*ca.* 12–13) being just slightly cloudy.

To *ca.* 150 ml. of solution containing 10 mmoles of Hg^{II}, 45 mmoles of Im, 35 mmoles of H^+, was added about 13 mmoles of NaOH. About half the mercury precipitated as a white precipitate and the pH was 6.1. The precipitate was dried in a vacuum desiccator over $CaSO_4$ for several days and then analyzed.

The analysis for mercury was carried out in 6 *N* $HClO_4$ with NaSCN by a Volhard titration. About 60% of the NaSCN was added prior to the titration to dissolve the complex. The analyses for carbon, hydrogen, nitrogen and chlorine were done commercially by Dr. A. Elek.

Element	% Present	Relative molar amount
Hg	51.12	1.00
Cl	9.41	1.04
N	7.63	2.13
H	1.21	4.71
C	9.75	3.18
O (by difference)	20.88	5.08

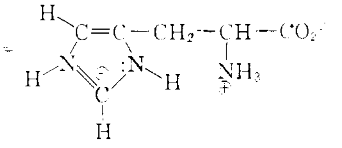
This corresponds approximately to the formula $Hg(ClO_4)(C_3H_3N_2)\cdot H_2O$.

L-Histidine.—The ionization equilibria of histidine are

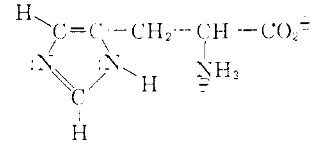
$$H_2L^+ \underset{K_a}{\rightleftarrows} HL + H^+ \underset{K_a'}{\rightleftarrows} L^- + 2H^+ \qquad (12)$$

where

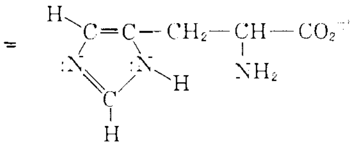
H_2L^+ =



HL =



L^- =



Our measurements give $pK_a = 6.08$, $pK_a' = 9.12$; in good agreement with other results (Albert,[9] 6.08, 9.20, 20°, $\mu = 0.01$ *M*; Li and Manning,[10] 6.05, 9.12, 25°, $\mu = 0.15$ *M*).

In a solution with constant ΣHg^{II} concentration and a constant, rather large $[\Sigma L]$ (where $[\Sigma L] = [H_2L^+] + [HL] + [L^-]$) the potential was observed to be a linear function of pH over the pH range 2.5 to 9, with a slope of 0.060 v. per pH unit, as displayed in Fig. 1. The linear relation is rather surprising since the transformation $H_2L^+ \rightleftarrows HL + H^+$ has $pK_a \approx 6.0$. It is necessary to suppose therefore that the complexes also can be protonated and we propose the following equilibria. It is convenient for the analysis to write all equilibria terms of the species HL.

$$\begin{array}{lll} Hg^{++} + HL \rightleftarrows HgL^+ + H^+ & \beta_{10} & (13) \\ Hg^{++} + HL \rightleftarrows HgHL^{++} & \beta_{11} & \\ Hg^{++} + 2HL \rightleftarrows HgL_2 + 2H^+ & \beta_{20} & \\ Hg^{++} + 2HL \rightleftarrows HgL(HL)^+ + H^+ & \beta_{21} & \\ Hg^{++} + 2HL \rightleftarrows Hg(HL)_2^{++} & \beta_{22} & \end{array}$$

The measurements used for quantitative interpretation were in the pH range 9–3, so that it is necessary to consider the three histidine species, L^-, HL and H_2L^+. (We can neglect H_3L^{++}, which has a pK_a of 1.8).[9] We write ΣL for the total uncomplexed histidine

$$[\Sigma L] = [L^-] + [HL] + [H_2L^+]$$

understanding that any significant corrections for the amount complexed have been made (if necessary, by a successive approximation procedure). Then, from equation 12

$$\frac{[\Sigma L]}{[HL]} = 1 + \frac{[H^+]}{K_a} + \frac{K_a'}{[H^+]} = \frac{1}{f(H^+)} \qquad (14)$$

---

[9] A. Albert, *Biochem. J.*, **50**, 690 (1952).

[10] N. C. Li and R. A. Manning, THIS JOURNAL, **77**, 5225 (1955).

TABLE II

SLOPE AND INTERCEPT OF EQUATION 15b FOR EXPERIMENTS AT FIXED *p*H

*p*H	5.00	5.20	6.08	6.20	7.00
Intercept[a]	$4.93(\pm 1) \times 10^{9}$	$1.30(\pm 1.3) \times 10^{10}$	$6.90(\pm 2) \times 10^{11}$	$4.87(\pm 3) \times 10^{11}$	$2.42(\pm 1.5) \times 10^{13}$
Slope[b]	$5.46(\pm 0.1) \times 10^{12}$	$1.84(\pm 0.1) \times 10^{13}$	$1.42(\pm 0.2) \times 10^{15}$	$2.46(\pm 0.2) \times 10^{15}$	$9.75(\pm 0.1) \times 10^{16}$

[a] Intercept $= \frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}(\beta_{10} + \beta_{11}[\mathrm{H}^+])$. [b] Slope $= \left\{\frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}\right\}^2(\beta_{20} + \beta_{21}[\mathrm{H}^+] + \beta_{22}[\mathrm{H}^+]^2)$.

where the function $f(\mathrm{H}^+)$ is defined by the second equality.

The total mercury(II) concentration is given by the relation: $[\Sigma\mathrm{Hg^{II}}] = [\mathrm{Hg^{++}}] + [\mathrm{HgL^+}] + [\mathrm{HgHL^{++}}] + [\mathrm{HgL_2}] + [\mathrm{HgL(HL)^+}] + [\mathrm{Hg(HL)_2^{++}}]$. $[\mathrm{HL}] = [\Sigma\mathrm{L}]f(\mathrm{H}^+)$ from equation 14. The equilibria 13 then permit us to express the quantities $[\mathrm{HgL^+}]$, $[\mathrm{Hg(HL)_2^{++}}]$, etc., in terms of $[\mathrm{Hg^{++}}]$, $[\mathrm{H^+}]$ and $[\Sigma\mathrm{L}]$; for example, $[\mathrm{HgL(HL)^+}] = \beta_{21}\,[\mathrm{Hg^{++}}]\,[\Sigma\mathrm{L}]^2(f(\mathrm{H}^+))^2/[\mathrm{H}^+]$. By substitution of these relations into the equation for $[\Sigma\mathrm{Hg^{II}}]$ we obtain

$$\frac{\frac{[\Sigma\mathrm{Hg^{II}}]}{[\mathrm{Hg^{++}}]} - 1}{[\Sigma\mathrm{L}]} = \frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}(\beta_{10} + \beta_{11}[\mathrm{H}^+]) + \left\{\frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}\right\}^2(\beta_{20} + \beta_{21}[\mathrm{H}^+] + \beta_{22}[\mathrm{H}^+]^2)[\Sigma\mathrm{L}] \quad (15a)$$

$$= \frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}\bar{\beta}_1 + \left\{\frac{f(\mathrm{H}^+)}{[\mathrm{H}^+]}\right\}^2\bar{\beta}_2[\Sigma\mathrm{L}] \quad (15b)$$

where $\bar{\beta}_1$ and $\bar{\beta}_2$ are implicitly defined by comparison of (15a) and (15b). The term on the left of (15) was plotted *vs.* $[\Sigma\mathrm{L}]$ for experiments at several fixed values of the *p*H with varying $[\Sigma\mathrm{L}]$. One of the best plots is shown in Fig. 2. The values of the intercepts and slopes are collected in Table II.

Examination of the plots, such as Fig. 2, strongly suggests that there is a significant contribution by the $\bar{\beta}_1$ term, but the intercept cannot be estimated accurately, as we have tried to suggest by the estimated uncertainties in the table. The two best intercepts for *p*H 7 and 5 give $\bar{\beta}_1 = 2.6 \times 10^6$ at *p*H 7.00 and $\bar{\beta}_1 = 6.5 \times 10^5$ at *p*H 5.00. According to our formulation, $\bar{\beta}_1$ should increase with decreasing *p*H. It is quite possible that there is another complex such as HgL(OH), but we believe the data are not sufficiently good to warrant such a conclusion. We provisionally conclude only that there is a complex with one histidine per mercury, $\mathrm{HgL^+}$, that probably $\beta_{10} \approx 10^6$ and that in the 5 to 7 *p*H range there is not much of a contribution by $\mathrm{Hg(HL)^{++}}$.

A plot of $\bar{\beta}_2$ *vs.* *p*H is shown in Fig. 3. In addition to the results in Table II, we have used the data of Fig. 1 where the *p*H was varied at a constant high $\Sigma\mathrm{L}$ concentration; at this high concentration, only the $\bar{\beta}_2$ term is important. The solid lines in Figs. 1 and 3 are calculated from the values

$$\log \beta_{20} = 2.98$$
$$\log \beta_{21}(M^{-1}) = 9.18$$
$$\log \beta_{22}(M^{-2}) = 14.99$$

The good agreement justifies the interpretation given. Incidentally, since different $\Sigma\mathrm{Hg^{II}}$ concentrations were used in different experiments, the fact that the complexes are monomeric as regards mercury has been demonstrated. (The constants β_{20}, β_{21}, β_{22} were actually derived from the measurements in the *p*H range 8–3; the data at 9 and 2.5 are also predicted fairly satisfactorily.)

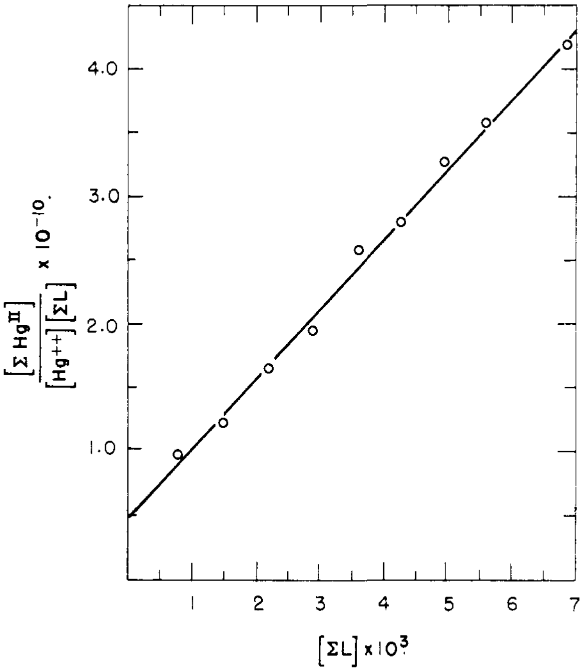


Fig. 2.—Plot of eq. 15b for the determination of $\bar{\beta}_1$ and $\bar{\beta}_2$; *p*H = 5.00 ± 0.01, $[\Sigma\mathrm{Hg^{II}}] \approx 1.4 \times 10^{-4}$ *F*.

As already remarked, the fact that the variation of potential with *p*H is quite linear with a slope of $RT/\mathfrak{F}$ in the *p*H 3–8 range (Fig. 1) was not to be expected in general. Reference to equation 15a shows that this linearity requires that the function $\log\{[f(\mathrm{H}^+)]^2(\beta_{20} + \beta_{21}[\mathrm{H}^+] + \beta_{22}[\mathrm{H}^+]^2)\}$ should be constant. For *p*H<8 where the K_a' term can be neglected, this is equivalent to the constancy of

$$\frac{\beta_{20} + \beta_{21}[\mathrm{H}^+] + \beta_{22}[\mathrm{H}^+]^2}{K_\mathrm{a}^2 + 2K_\mathrm{a}[\mathrm{H}^+] + [\mathrm{H}^+]^2}$$

which requires that $(\beta_{20}/\beta_{21}) = K_\mathrm{a}/2$; and $(\beta_{21}/\beta_{22}) = 2K_\mathrm{a}$. With the chosen values of the β's we have

$$\frac{\beta_{20}}{\beta_{21}} = 10^{-6.20}, \frac{K_\mathrm{a}}{2} = 10^{-6.38}, \frac{\beta_{21}}{\beta_{22}} = 10^{-5.81}, 2K_\mathrm{a} = 10^{-5.78}$$

Discussion

The binding constants analogous to β_2 of several nitrogen bases for various metal ions are displayed in Table III.

Several significant trends are evident in Table III. In the first place, as has been previously noted[7,8,12,13] the binding constants of imidazole and ammonia for complexing metals are approximately equal but the pK_a of imidazolium is less

---

(12) N. C. Li, T. L. Chu, C. T. Fuji and J. M. White, THIS JOURNAL, **77**, 859 (1955).

(13) R. B. Martin and J. T. Edsall, *ibid.*, **80**, 5033 (1958).

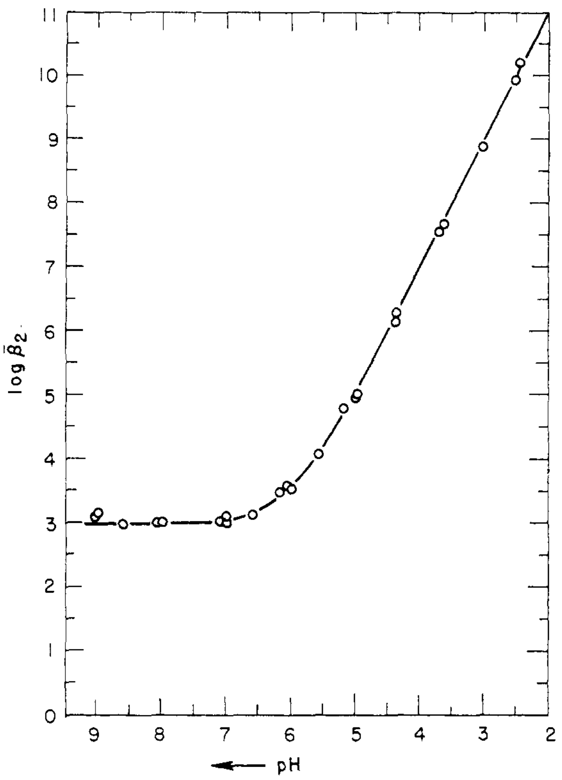


Fig. 3.—Log β_2 *vs.* pH; the circles are calculated directly from the experiments using 15b; the solid line curve is calculated from 15a and the values log β_{20} = 2.98, log β_{21} = 9.18, log β_{22} = 14.99.

than that of ammonia. Thus, relative to ammonia imidazole shows a preference for binding transition metal ions rather than protons.

TABLE III

β_2 FORMATION CONSTANTS OF COMPLEX IONS[a]

Metal/ligand	Imidazole ($C_3H_4N_2$)	NH_3[1]	Histidine (L^-)
H^{+}[b]	14.28	18.48	18.24
Zn^{++}	4.17[1]	4.43	11.78[1]
Cd^{++}	4.90[1]	4.47	11.10[1]
Hg^{++}	16.74	17.5	21.22
Ni^{++}	5.95[1]	4.79	15.84[11]
Cu^{++}	7.15[1]	7.33	18.60[11]

[a] The values listed are β_2's; *i.e.*, equilibrium constants for the reaction $Cu^{++} + 2Im \rightleftarrows CuIm_2^{++}$. [b] To compare with the β_2 values, we list twice the pK_a of the ligand, for example, the equilibrium constant of the reaction

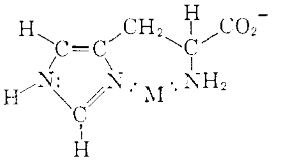
$$2H^+ + 2NH_3 \rightleftharpoons 2NH_4^+, \text{ etc.}$$

As is well known, Hg^{++} ion typically binds two ligands very strongly in a linear configuration and shows only a small tendency to form a third and a fourth coördinate bond. The other metals in Table III generally have coördination numbers of 4 or 6, with, typically, only a small gradual decrease in the intrinsic binding constants

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

(where L here is any monodentate ligand and *not* histidine) as n increases from 1 to 4 or 6.

The increase in binding from imidazole to the negative histidine anion (L^-) is very marked for the metals Zn^{++}, Cd^{++}, Ni^{++} and Cu^{++}, whereas it is rather small for Hg^{++}. In fact the ratios $p\beta_2(L^-)/p\beta_2(Im)$ for these five metals are 2.8, 2.3, 2.7, 2.6 and 1.3, respectively. For the first four metals, chelate formation with the probable structures[9]



undoubtedly contributes very significantly to the binding. Because of the tendency to form only two strong linear bonds, chelate formation contributes only slightly to the ligand binding for Hg^{++}.

This point can be illustrated further by these equilibria which can be calculated from data already given.

$$Hg^{++} + 2L^- \rightleftharpoons HgL_2 \qquad K = 10^{21.22}\ M^{-2} \quad (16a)$$

$$Hg^{++} + L^- + HL \rightleftharpoons HgL(HL)^+ \qquad K = 10^{18.40}\ M^{-2} \quad (16b)$$

$$Hg^{++} + 2HL \rightleftharpoons Hg(HL)_2^{++} \qquad K = 10^{14.99}\ M^{-2} \quad (16c)$$

The binding constant of HL by Hg^{++}, presumably *via* the imidazole group, is less than the binding constant of imidazole for Hg^{++} by about 10^2, which is just about what would be predicted from the differences in proton binding.

The small increase in binding constants in the series of reactions 16c, 16b and 16a may be partly due to chelate formation; it is also partly due to charge effects.

It is instructive to write out the acid ionization equilibria

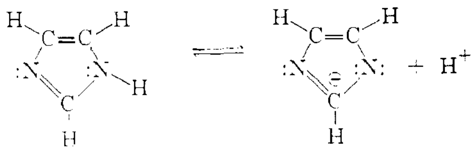
$$HL \rightleftharpoons H^+ + L^- \qquad K = 10^{-9.12}$$

$$Hg(HL)_2^{++} \rightleftharpoons Hg(HL)L^+ + H^+ \qquad K = 10^{-5.81}$$

$$Hg(HL)L^+ \rightleftharpoons HgL_2 + H^+ \qquad K = 10^{-6.20}$$

In each case, the protonated amino group is ionizing; coördination of Hg^{++} to the imidazole group increases the ionization constant by a factor of only 10^3; a much larger factor would be expected if chelation by L^- were very significant.

In addition to its basic properties, imidazole is also a weak acid.

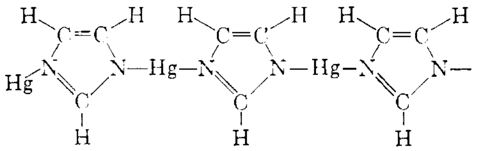


The pK for this reaction has been estimated as 14.2.[14] We presume that the insoluble mercury compound, $Hg(C_3H_3N_2)ClO_4 \cdot H_2O$, contains the linear polymer

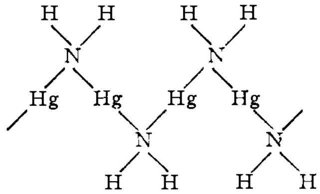
---

(11) N. C. Li, Br. E. Doody and J. M. White, THIS JOURNAL, 79, 5859 (1957).

(14) H. Walba and R. W. Isensee, *ibid.* 77, 5488 (1955).



with one positive charge per polymer unit. A similar substance $Hg(C_3H_3N_2)Cl$ has been reported.[15] The structure proposed above is similar to that which occurs in $Hg(NH_2)Br$[16] and $Hg(NH_2)Cl$.[17]



Acknowledgments.—Mr. Tetsuo Yamane designed and developed the cell and potentiometric techniques which we have used. We have profited also from his advice and criticism regarding other features of this research. We are grateful to the AEC for support of this work via the contract AT-(11-1)-188.

PASADENA, CALIFORNIA

---

[15] K. Böttcher, *Chem. Zentralblatt*, **102**, II, 2757 (1931).

[16] L. Nijssen and W. N. Lipscomb, *Acta Cryst.*, **5**, 604 (1952).

[17] W. N. Lipscomb, *ibid.*, **4**, 266 (1951).

[CONTRIBUTION NO. 2522 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Complexes of Mercury(I) with Polyphosphate and Dicarboxylate Anions and Mercury (II) Pyrophosphate Complexes[1]

BY TETSUO YAMANE AND NORMAN DAVIDSON

RECEIVED OCTOBER 30, 1959

It has been discovered that mercurous mercury forms complexes with pyrophosphate, tripolyphosphate, oxalate, α-dimethylmalonate and succinate. These complexes are stable toward disproportionation to mercury(II) complexes and mercury. If L^{-q} is the anion, the principal complexes are $Hg_2L_2^{-2q+2}$ and $Hg_2L(OH)^{-q+1}$. The formation constants determined from the potential of a mercury–mercurous electrode in ligand solutions are: $Hg_2(P_2O_7)_2^{-6}$, $(2.4 \pm 0.6)10^{12}$ M^{-2}; $Hg_2(OH)P_2O_7^{-3}$, $(4.4 \pm 0.6)10^{15}$ M^{-2}; $Hg_2(P_3O_{10})_2^{-8}$, $(1.7 \pm 0.3)10^{11}$; $Hg_2(OH)P_3O_{10}^{-4}$, $(1.0 \pm 0.2)10^{15}$; $Hg_2(C_2O_4)_2^{-2}$, $(9.5 \pm 0.2)10^{6}$; $Hg_2(OH)C_2O_4^{-1}$, $(1.1 \pm 0.2)10^{13}$; $Hg_2[(CH_3)_2C(CO_2)_2]_2^{-2}$, $(3.3 \pm 0.6)10^{7}$; $Hg_2(OH)[(CH_3)_2C(CO_2)_2]^{-1}$, $(3.8 \pm 0.5)10^{13}$; $Hg_2[(CH_2)_2(CO_2)_2]_2^{-2}$, $(1.9 \pm 0.3)10^{7}$; $Hg_2(OH)[(CH_2)_2(CO_2)_2]^{-1}$, $(2.8 \pm 0.6)10^{13}$. (The ionic strength was 0.75 M ($NaNO_3$), except for oxalate and succinate, where it was 2.5 M ($NaNO_3$).) The mercurous compounds have a characteristic ultraviolet spectrum. Theory and experiment agree that mercurous complexes of ligands (such as NH_3 and CN^-) which form strong covalent bonds to mercury are unstable toward disproportionation to give mercuric complexes but "ionic" chelating ligands can form stable mercurous complexes. The mercury(II) pyrophosphate complex was studied from the potential of a Pt electrode in Hg_2^{I}, Hg^{II}, pyrophosphate solutions at *p*H 7–10. The principal species is $Hg(OH)(P_2O_7)^{-3}$, with a formation constant of $(2.8 \pm 0.6)10^{17}$ M^{-2}.

The equilibrium constant for the formation of mercurous ion from elementary mercury and mercuric ion is 130 in 0.5 M $NaClO_4$.[2]

$$Hg + Hg^{++} = Hg_2^{++}, K = \frac{(Hg_2^{++})}{(Hg^{++})} = 130 \quad (1)$$

The equilibrium is readily reversible. When a complexing ligand is added to a mercurous solution, the usual reaction that occurs is disproportionation of the mercurous ion to give elementary mercury and a complexed mercuric ion. This occurs, for example, with the complexing ligands, CN^- and NH_3. It is due to the relatively greater stability of the mercuric complexes. The same situation occurs for many insoluble compounds. Thus, mercurous ion is unstable in basic solutions and in the presence of sulfide ion. Compounds such as "mercurous sulfide" or "mercurous oxide" reported in the past have been shown to be a mixture of mercury and the corresponding mercuric compound.[3,4]

The general impression conveyed by textbooks and by the chemical literature is that there are no known stable complexes of mercurous ion. Sillén and co-workers have suggested, on the basis of potentiometric evidence, that there are weak complexes of Hg_2^{++} formed by nitrate, sulfate and perchlorate anions, with formation constants of: 2.5 M^{-1} ($Hg_2NO_3^+$), 0.5 M^{-2} ($Hg_2(NO_3)_2$), 20 M^{-1} (Hg_2SO_4), 250 M^{-2} ($Hg_2(SO_4)_2^{-2}$) and 0.9 M^{-1} ($Hg_2ClO_4^+$).[2,5] This presumably is mainly ion-pair association. It is also possible that the assumption of constant activity coefficients at constant ionic strength is not sufficiently reliable to enable one to identify such weak complexes with certainty by potentiometric experiments.

However some time ago, Stromeyer[6] and then Brand[7] reported that when sodium pyrophosphate solution is added to a mercurous solution, a white precipitate forms and then redissolves in excess of the reagent, which suggests the formation of a strong, stable complex.

We have confirmed and extended these observations and have now found that mercurous ion forms stable complexes with pyrophosphate (Py^{-4}), tripolyphosphate (Tp^{-5}), oxalate (Ox^{-2}), α-di-

[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[2] S. Hietanen and L. G. Sillén, *Arkiv Kemi*, **10**, 103 (1956).

[3] R. Fricke and P. Ackermann, *Z. anorg. Chem.*, **211**, 233 (1933).

[4] W. N. Lipscomb, THIS JOURNAL, **73**, 1015 (1951).

[5] G. Infeldt and L. G. Sillén, *Svensk kem. Tidskr.*, **58**, 104 (1946).

[6] F. Stromeyer, *Schweigger's Journal*, **58**, 130 (1830); as reported in J. W. Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longman, Greens & Co., London, 1923, p. 1003.

[7] Brand, *Z. anal. Chem.*, **28**, 592 (1889).