

soluble residue. Chemical analysis established the composition of the trichloride. Calcd. for $ZrCl_3$: Zr, 46.2; Cl, 53.8. Found: (1) Zr, 45.8; Cl, 54.2; (2) Zr, 46.0; Cl, 54.0. There was no indication of the brown color mentioned in the description of previous trichloride preparations^{2,3} but the blue-black compound changed to brown if left standing in an inert atmosphere to which traces of moist air were admitted.

Zirconium Tribromide.—This compound first appeared in the reduction zone as a light blue film at a generator temperature of 210°. Unreduced tetrabromide did not condense on the tube walls until the generator reached 250°, and 230° was adopted as a satisfactory working temperature. A hydrogen pressure of 3 mm. gave erratic results but consistent reproducibility was obtained when the pressure was raised to 4 mm. A temperature of 200° proved satisfactory for the subsequent purification of the tribromide.

Zirconium tribromide was obtained as a blue

powder, much lighter in color than the trichloride and chemical analysis established its composition. Calcd. for $ZrBr_3$: Zr, 27.6; Br, 72.4. Found: (1) Zr, 27.2; Br, 72.8; (2) Zr, 27.0; Br, 73.0.

Zirconium Triiodide.—The preparation of this compound did not follow the pattern of the trichloride and tribromide. At a generator temperature of 255° unreduced tetraiodide started to condense on the walls of the discharge tube. No reaction was apparent until the generator reached 290° at which temperature a green-black deposit formed in the reduction zone. As soon as this compound appeared it was found that the reduction proceeded in a normal fashion provided the generator temperature was reduced to 235°. The hydrogen pressure for the reaction was 4 mm. and the purification temperature was 260°. Chemical analysis established the composition of the greenish-black zirconium triiodide powder. Calcd. for ZrI_3 : Zr, 19.3; I, 80.7. Found: (1) Zr, 19.4; I, 80.6; (2) Zr, 19.1; I, 80.9.

[CONTRIBUTION NO. 1052 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Stabilities of Divalent Metal Complexes of 4-Hydroxybenzothiazole

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The acid dissociation constants of 4-hydroxybenzothiazole and the formation constants of its chelates with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Mg(II) have been determined potentiometrically in 50% v./v. dioxane-water. The order of decreasing stability of the metal chelates $Cu > Pb, Ni, Co > Zn > Cd > Mn > Mg$ is similar to the stability sequence generally obtained for divalent metals. The chelates of 4-hydroxybenzothiazole with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) have been prepared and their infrared spectra determined.

The reactions of divalent metal ions with 4-hydroxybenzothiazole have a marked resemblance to those with 8-hydroxyquinoline, with some noteworthy exceptions. The magnesium complex of 4-hydroxybenzothiazole is much more soluble in water than magnesium oxinate, and the copper, nickel and zinc complexes of 4-hydroxybenzothiazole are insoluble in chloroform in contrast to the corresponding oxinates.¹ The presence of the sulfur atom in the 4-hydroxybenzothiazole ring system undoubtedly will affect the basicities of the ligand and also give rise to resonance interactions which can cause the properties of the metal complexes to be drastically altered. The present study was initiated in order to obtain more information on the factors that cause certain metal chelates of 4-hydroxybenzothiazole to behave differently from the corresponding oxinates.

Experimental

Preparation of 4-Hydroxybenzothiazole.—4-Hydroxybenzothiazole was prepared by the method described by Erlenmeyer and Ueberwasser,² with several modifications.

123 g. of *o*-anisidine was dissolved in 93 ml. of HCl (d. 1.19) and 500 ml. water, to which was added 160 g. of ammonium thiocyanate in 3.5 l. of water. The resulting solution was heated in a 5 l. beaker on a hot plate for 8 hr., with constant addition of water to maintain a volume of about 2 l. On cooling, crystals of *o*-methoxyphenylthiourea separated

out. The crystals were filtered, washed thoroughly with water and recrystallized from water; yield 90%, m.p. 146°.

A solution of 82 g. of bromine in 200 ml. of chloroform was added slowly and with shaking to a suspension of 90 g. *o*-methoxyphenylthiourea in 400 ml. of dry chloroform in a 3 l. round-bottomed flask. The temperature of the mixture was kept below 30°. After all the bromine was added, a red liquid layer was formed at the bottom of the vessel. This mixture was refluxed for about an hour until the evolution of HBr ceased. The solution was cooled, the supernatant chloroform layer decanted and a fresh 200 ml. portion of chloroform added and refluxed again for another hour. This sequence of operations, of cooling, decantation, addition of a fresh portion of chloroform and finally refluxing, was repeated several times until a solid, 2-amino-4-methoxybenzothiazole, was obtained. At this stage the chloroform in the flask was decanted and the small amount of chloroform remaining in the solid was removed by means of a vacuum pump. The solid was transferred to a beaker with a small amount of sulfurous acid, stirred thoroughly and neutralized with a dilute solution of sodium hydroxide, filtered and recrystallized from water; yield 70%, m.p. 144°.

Forty-five g. of 2-amino-4-methoxybenzothiazole was dissolved in 225 ml. of phosphoric acid (88–92%), the mixture cooled to 0°, and 64 ml. of nitric acid added with stirring, keeping the temperature at 0°. A solution of 18 g. of sodium nitrite in 25 ml. of water was added very slowly to this mixture with constant stirring when a dark red viscous solution was obtained. This diazotized mixture was added slowly and with constant stirring to a solution containing 100 g. of copper in 500 ml. of HCl (d. 1.19). The mixture was allowed to stand for an hour, diluted to 2 l. with water and allowed to stand overnight. The solid, 2-chloro-4-methoxybenzothiazole, obtained was filtered, washed thoroughly with water and recrystallized from a methanol–water mixture; yield 60%, m.p. 140°.

Twenty g. of 2-chloro-4-methoxybenzothiazole was refluxed with 6 g. of red phosphorus and 100 ml. of hydriodic

(1) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 192.

(2) H. Erlenmeyer and H. Ueberwasser, *Helv. Chim. Acta*, **25**, 515 (1942).

acid (d. 1.7) and 20 ml. of glacial acetic acid for about 7 hr. The solution was diluted with about 100 ml. of water and the red phosphorus filtered off on a sintered glass funnel. The resulting solution was neutralized with sodium bicarbonate and the 4-hydroxybenzothiazole which precipitated out was filtered and recrystallized from ethanol. The compound finally was purified chromatographically on a column of 60–100 mesh Florisil using chloroform as the eluent. The final product was colorless; yield 16%, m.p. 143°.

Acid Dissociation Constants.—The acid dissociation constants of 4-hydroxybenzothiazole were determined at $25 \pm 0.1^\circ$, by titrating potentiometrically in an atmosphere of nitrogen, a weighed quantity of 4-hydroxybenzothiazole and 50 ml. of 0.01 *M* perchloric acid in a 50% v./v. dioxane-water medium, against carbonate-free sodium hydroxide. With each increment of sodium hydroxide, an equal volume of 1,4-dioxane was added throughout the titration. A Beckman Model G pH meter equipped with a glass-saturated calomel electrode pair and standardized with buffer solutions at pH 4.00 and 7.00 was used to determine the pH during the course of the titration. Carbide and Carbon 1,4-dioxane was purified by refluxing with sodium metal for 12 hr. and then fractionated through a four-foot column packed with glass helices. Since the pH-hydrogen ion correspondence in 50% v./v. aqueous dioxane can be determined at 25° , the observed pH values were corrected by a predetermined factor in the calculation of the acid dissociation constants. Table I gives the results obtained.

Chelate Formation Constants.—The Calvin-Bjerrum³ potentiometric technique was used in this work. Fifty ml. of 0.01 *M* perchloric acid, 52 ml. dioxane, 2 ml. of a standard metal perchlorate solution and weighed quantities of 4-hydroxybenzothiazole were added to a titration vessel maintained at $25 \pm 0.1^\circ$. Prepurified nitrogen gas was passed through the solution and an atmosphere of nitrogen was maintained above the solution, throughout the course of the titration. The standard carbonate-free sodium hydroxide solution was added in small increments together with equal volumes of dioxane to the stirred solution. All pH measurements were made with a Model G Beckman pH meter. Approximately 0.01 *M* stock solutions of metal ions were prepared by dissolving the reagent grade metal perchlorate in water. The copper(II) and cobalt(II) solutions were standardized by electrodeposition; the nickel(II) solution was standardized by precipitation with dimethylglyoxime and the zinc(II), manganese(II) and cadmium(II) solutions were standardized gravimetrically as ZnNH_4PO_4 , $\text{Mn}_2\text{P}_2\text{O}_7$ and CdNH_4PO_4 , respectively.

If K_1 and K_2 are the stepwise formation constants of the metal chelates, (R^-) the concentration of the anion species of 4-hydroxybenzothiazole, and \bar{n} the average number of ligand molecules per metal ion, a plot of $\frac{(R^-)^2 (\bar{n} - 2)}{\bar{n}}$ against $\frac{(R^-) (\bar{n} - 1)}{\bar{n}}$ gives a straight line of slope $1/K_1$ and intercept $1/K_1 K_2$.⁴ Table II gives the values of K_1 and K_2 obtained.

Preparation of Chelates.—A 2% ethanolic solution of 4-hydroxybenzothiazole was added in slight excess to a solution of the metal perchlorate. The pH of the solution was raised slowly with continuous stirring until precipitation occurred. The solution was warmed on a water-bath until the precipitate coagulated. The solution containing the metal chelate was cooled, filtered and the precipitate washed thoroughly with water. The chelates were finally dried in a vacuum desiccator to constant weight and analyzed for the metal content.

Infrared Spectra.—All the spectra were recorded with a Perkin-Elmer Model 21 double-beam spectrophotometer equipped with sodium chloride optics, employing Nujol mulls of 4-hydroxybenzothiazole and its metal chelates.

Results and Discussion

It is of interest to compare the acid dissociation constants of a number of related heterocyclic compounds before attempting to evaluate the acid

TABLE I
ACID DISSOCIATION CONSTANTS OF 4-HYDROXYBENZOTHIAZOLE AND 8-HYDROXYQUINOLINE

	In aqueous solution	
	pK_{NH}	pK_{OH}
8-Hydroxyquinoline ⁵	5.13	9.89
4-Hydroxybenzothiazole ⁶	1.2	8.85
	In 50% v./v. dioxane-water	
8-Hydroxyquinoline ⁷	3.97	11.54
4-Hydroxybenzothiazole	<2	10.75

TABLE II
CHELATE FORMATION CONSTANTS OF 4-HYDROXYBENZOTHIAZOLE AND 8-HYDROXYQUINOLINE AT 25° IN 50% v./v. AQUEOUS DIOXANE

	4-Hydroxybenzothiazole		8-Hydroxyquinoline ⁵	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Cu(II)	9.28	8.15	(13.49)	12.73
Pb(II)	7.73	5.69	10.61	8.09
Ni(II)	7.35	6.11	11.44	9.94
Co(II)	6.88	6.60	10.55	9.11
Zn(II)	6.90	5.92	9.96	8.90
Cd(II)	6.66	5.30	9.43	7.68
Mn(II)	5.36	4.88	8.28	7.17
Mg(II)	4.54	4.00	6.38	5.43

dissociation constants obtained for 4-hydroxybenzothiazole. The pK_{NH} of pyridine is 5.23, quinoline 4.94, thiazole 2.53 and benzothiazole 1.2.⁸ Hence it is apparent that the fusion of a benzene ring to a pyridine or thiazole ring decreases the pK_{NH} value of pyridine or thiazole as a result of an increase in resonance interactions, which involve the unshared pair of electrons on the nitrogen atom in pyridine or thiazole. In general, the effect of a second heteroatom in a ring system is to decrease the base strength markedly. This is the case with thiazole and benzothiazole which are much weaker bases than pyridine and quinoline, respectively. The introduction of a hydroxyl group in peri-position to the nitrogen atom in quinoline and benzothiazole gives rise to the molecules 8-hydroxyquinoline and 4-hydroxybenzothiazole, in which weak hydrogen bonding can take place as a result of internal chelation. Therefore, the pK_{NH} and pK_{OH} values of these two compounds should be affected by the extent to which intramolecular hydrogen bonding occurs in these molecules. However, the pK_{NH} and pK_{OH} values of 8-hydroxyquinoline are not very different from the pK_{NH} of quinoline and the pK_{OH} of 1-naphthol⁹; also, the pK_{NH} of 4-hydroxybenzothiazole and of benzothiazole are nearly the same. This seems to indicate that intramolecular hydrogen bonding does not play an important part in determining the acid-base strengths of 8-hydroxyquinoline and 4-hydroxybenzothiazole. The lowering of the pK_{OH} of 4-hydroxybenzothiazole by about 1 pK unit with respect to the pK_{OH} of 8-hydroxyquinoline can be attributed to the electron-withdrawing effect of the sulfur atom, which is present in the heterocyclic ring system.

(5) A. Albert, *Biochem. J.*, **54**, 646 (1953).

(6) Q. Fernando and T. Thirunamachandran, *Anal. Chim. Acta*, **17**, 417 (1957).

(7) W. D. Johnston and H. Freiser, *This Journal*, **74**, 5239 (1952).

(8) A. Albert, R. Goldacre and J. Phillips, *J. Chem. Soc.*, 2240 (1948).

(9) H. Scheunel, *Experientia*, **4**, 383 (1948).

(3) (a) M. Calvin and K. W. Wilson, *This Journal*, **67**, 2003 (1945).
(b) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(4) W. R. C. Crimmin, *Anal. Chim. Acta*, **16**, 50 (1957).

TABLE III
 INFRARED SPECTRA OF 4-HYDROXYBENZOTHAZOLE AND ITS METAL CHELATES (CM.⁻¹)

	Strong	Medium	Weak
4-Hydroxybenzothiazole	1570, 1238, 938, 875, 733	1308, 1300, 1286, 1164, 797, 780	1194, 1140, 1042, 953, 845
Ni(II) chelate	1568, 948, 765, 731	1329, 1308, 1282, 1148, 817, 797	1038, 844
Cu(II) chelate	1572, 946, 771, 765, 742, 733	1335, 1328, 1286, 805	1143, 1037, 900, 812
Pb(II) chelate	1545, 1258, 932, 768, 735	1310, 1287, 1145, 800	1180, 1062, 942, 870, 823
Cd(II) chelate	1560, 766, 731	1312, 1275, 1148, 828	1184, 947, 885, 848
Mn(II) chelate	1562, 767, 730	1314, 1274, 1143	1183, 945
Co(II) chelate	1568, 768	1325, 1300, 1277, 1150	946
Zn(II) chelate	1568, 762, 731	1316, 1282, 1143	943, 862, 820

Table II lists the stability constants of the chelates of 4-hydroxybenzothiazole and also those of 8-hydroxyquinoline for purposes of comparison. The stabilities of the 4-hydroxybenzothiazole chelates are smaller than those of 8-hydroxyquinoline by a factor of 5–9 $\log \beta_2$ units, where $\log \beta_2 = \log K_1 + \log K_2$. This decrease in stability is largely attributable to the decrease in the basic strength of the nitrogen atom as well as to the increase in the acidic strength of the hydroxyl group in 4-hydroxybenzothiazole.

The stability sequence for the metal chelates of 4-hydroxybenzothiazole is $\text{Cu} > \text{Pb}, \text{Ni}, \text{Co} > \text{Zn} > \text{Cd} > \text{Mn} > \text{Mg}$. This is essentially the same as that found for 8-hydroxyquinoline, as well as other chelating agents, such as ethylenediamine and salicylaldehyde.¹⁰ The Pb(II), Ni(II) and Co(II) chelates of 4-hydroxybenzothiazole have almost identical values for $\log \beta_2$ and in this respect are somewhat unusual, since in the case of 8-hydroxyquinoline these chelates have a decreasing order of stability, $\text{Ni} > \text{Co} > \text{Pb}$.

The differences between $\log K_1$ and $\log K_2$ for the metal chelates vary widely. In general, the value of $(\log K_1 - \log K_2)$ is much larger for the chelates of 8-hydroxyquinoline than for those of 4-hydroxybenzothiazole. Therefore, the ring system of 4-hydroxybenzothiazole is such that the tendency for chelate formation to occur by the stepwise addition of ligand molecules is diminished, thereby increasing the possibility of simultaneously adding two 4-hydroxybenzothiazole molecules to a metal ion.

Recently a method of comparing the metal chelate stability constants involving a wide variety of ligands has been proposed, in which the $\log \beta_2$ values for Ni(II) are plotted against those for Zn(II).¹¹ This correlation is a useful frame of reference for assessing any special ligand effects that may be present in 4-hydroxybenzothiazole chelates. The plot of $\log \beta_2$ for Ni(II) against $\log \beta_2$ for Zn(II) gives a straight line, $\log \beta_{\text{Ni}} = 1.13 \log \beta_{\text{Zn}} (1)$ to within 0.5 $\log K$ units for a large number of chelating agents including 8-quinolinols, salicylaldehydes and β -diketones. According to equation 1, the $\log \beta_2$ value for the nickel chelate of 4-hydroxybenzothiazole is low by about 1 $\log K$ unit. This lowering of the nickel chelate stability, although not as pronounced as in cases where steric hindrance to chelate formation is obtained, e.g., in 2-methyl-8-hydroxyquinoline,¹² is sufficiently

large to indicate that either resonance effects on the π -bonds in the nickel 4-hydroxybenzothiazole chelate, or distortion of the planar configuration of nickel, may play an important part in determining chelate stability. It would be of interest to determine the heats and entropies of formation of 4-hydroxybenzothiazole chelates in order to investigate this effect further.

For these chelate formulas, $\text{Zn}(\text{C}_7\text{H}_4\text{NOS})_2$, $\text{Co}(\text{C}_7\text{H}_4\text{NOS})_2$, $\text{Pb}(\text{C}_7\text{H}_4\text{NOS})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{C}_7\text{H}_4\text{NOS})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{C}_7\text{H}_4\text{NOS})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{C}_7\text{H}_4\text{NOS})_2 \cdot 4\text{H}_2\text{O}$, the percentage of metal found was within 0.61% of the metal calculated, this value being 2.5% of the calculated value. The chelates of 4-hydroxybenzothiazole could not be purified since they were very insoluble in all the solvents that were tried. Attempts were made to dry these chelates at 105°, but many of them especially the copper chelate darkened in color and had a tendency to decompose. The Mn(II) chelate was also prepared but a reliable analysis could not be obtained due to the difficulty in removing the large amount of water that was associated with the chelate. In each case the analytical data represent the results of three to five preparations and determinations.

Table III summarizes the infrared spectra of 4-hydroxybenzothiazole and its chelates. In general, the infrared spectra of the 4-hydroxybenzothiazole chelates are similar to one another. The most striking differences are present in the spectra of the copper and lead chelates. However, there are a number of minor differences in the spectra of these metal chelates, which may prove useful for purposes of identification.

It has been observed in several infrared studies on metal chelates, notably of salicylaldehydes and acetylacetones, that the carbonyl group usually gives rise to two sets of frequencies between 1608 and 1524 cm^{-1} and 1390–1309 cm^{-1} .¹³ There are three peaks that occur in these frequency regions in the spectra of 4-hydroxybenzothiazole, as well as in all its chelates. The strong absorption band at 1570 cm^{-1} in the reagent spectrum can be attributed to C–O vibrations in the reagent molecule. On replacing the hydrogen atom of the hydroxyl group with metal atoms of the first transition series to form chelates, this frequency shifts to a very small extent, the Mn(II) chelate showing the largest shift. The Pb(II) and Cd(II) chelates show a marked shift.

(10) L. E. Maley and D. P. Mellor, *Australian J. Sci. Research*, **2**, 92 (1949).

(11) H. Freiser, Q. Fernando and G. E. Cheney, *J. Phys. Chem.*, **63**, 250 (1959).

(12) W. D. Johnston and H. Freiser, *THIS JOURNAL*, **74**, 5239 (1952).

(13) L. G. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

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 ($\log \beta_2$) 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).

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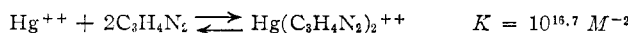
[CONTRIBUTION NO. 2496 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, PASADENA, CALIFORNIA]

Mercury(II) Complexes of Imidazole and Histidine

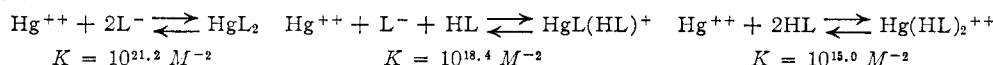
BY PHILIP BROOKS AND NORMAN DAVIDSON

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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



A solid substance, $\text{Hg}(\text{C}_3\text{H}_3\text{N}_2)\text{ClO}_4 \cdot \text{H}_2\text{O}$, precipitates from solutions at $\text{pH} > 4$. It probably contains an infinite chain: $(\text{C}_3\text{H}_3\text{N}_2\text{Hg}^-)_n^{+n}$. For histidine, the main results are:



where $\text{L}^- = (\text{C}_3\text{H}_3\text{N}_2)\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2^-$ and $\text{HL} = (\text{C}_3\text{H}_3\text{N}_2)\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$. 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. $88-90^\circ$, 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*.

(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.

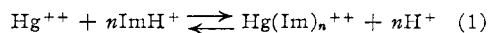
(2) F. R. N. Gurd and D. S. Goodman, *THIS JOURNAL*, **74**, 670 (1952).

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

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 $27.0 \pm 0.1^\circ$, 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



lies far to the right except for rather acid solutions with $\text{pH} \leq 2$. 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

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