

pertaining to the relationship between changes in physical properties and conformational changes are rather involved, however, and the reader is referred to the original paper. They are, at any rate, inconclusive and cannot be used to eliminate or substantiate the present picture. They do serve to emphasize

the tentative nature of the conclusions presented here and to point out the need for more extensive studies.

Acknowledgment.—The author wishes to acknowledge financial assistance from the National Institutes of Health (Grant GM 11071) during the course of this investigation.

[CONTRIBUTION NO. 3110 FROM THE GATES, CRELLIN, AND CHURCH LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Studies of the Chemistry of Mercury in Aqueous Solution. I. Mercury(I) and Mercury(II) Complexes of Aniline¹

BY THOMAS H. WIRTH AND NORMAN DAVIDSON

RECEIVED MAY 27, 1964

The formation constant of the 1:1 complex of Hg(II) with aniline in aqueous NaClO₄-HClO₄ solution has been determined spectrophotometrically. Potentiometric study of this system revealed that in addition to 1:1 and 2:1 complexes of aniline with Hg(II), a 1:1 aniline-Hg(I) complex exists. The ultraviolet absorption spectra of aniline-Hg(I) solutions confirmed the existence of the latter. This is the first confirmed case of a soluble mercurous complex with a nitrogen ligand. The equilibrium constants at 27°, $\mu = 1.0 M$ (NaClO₄), are: C₆H₅-NH₃⁺ + Hg⁺² = C₆H₅NH₂Hg⁺² + H⁺, $K_1 = 0.68$; C₆H₅NH₃⁻ + Hg₂⁺² = C₆H₅NH₂Hg₂⁺² + H⁺, $K_1^1 = 0.09$; and 2C₆H₅NH₃⁺ + Hg⁺² = (C₆H₅NH₂)₂Hg⁺² + 2H⁺, $K_2 = 0.45$.

Introduction

Mercury(II) shows an extremely strong affinity for organic nitrogen ligands; in aqueous solution the Hg(II) ion forms stronger complexes with nitrogen bases than do the transition metal ions or even the other ions of the d¹⁰ electronic configuration. Studies of the binding of Hg(II) by a variety of heterocyclic and aromatic nitrogen ligands have been carried out in this laboratory.²⁻⁴ Interest in the topic was stimulated in part by the role of Hg(II) in the study of biological macromolecules which contain basic nitrogen atoms such as the nucleic acids. That work showed that the interaction of Hg(II) with such ligands is neither straightforward nor easily characterized.

In the present work, the interaction of Hg(II) with the simplest aromatic amine, aniline, was studied to determine whether Hg(II) exhibits an unusually strong affinity for such compounds. Although aqueous, acidic Hg(II)-aniline solutions are not stable with time because of aromatic mercuration, it was possible to measure the stability constants of the labile C₆H₅NH₂Hg⁺² and (C₆H₅NH₂)₂Hg⁺² complexes by working rapidly and using appropriate extrapolations. The stability of the 2:1 complex was determined from the potential of a Hg(II) electrode in acidic solutions containing aniline in excess. However, unless the Hg⁺² ion is strongly complexed, a large fraction of the total Hg(II) reacts with the electrode to form Hg₂⁺².⁵ Therefore the 1:1 Hg(II)-aniline complex was studied by spectrophotometry in the presence of excess Hg⁺². In the potentiometric study, evidence for a Hg(I)-aniline complex, C₆H₅NH₂Hg₂⁺², was obtained. Independent spectrophotometric evidence confirmed the existence of this soluble mercurous-nitrogen complex.

Experimental

Materials.—All solutions were prepared from redistilled water. Perchloric acid, nitric acid, and sodium nitrate solutions were prepared from reagent grade chemicals. Carbonate-free sodium hydroxide was prepared from a 50% NaOH solution. Acids and bases were standardized by conventional methods. Mercuric perchlorate was prepared from weighed quantities of HgO and an excess of standardized 60% perchloric acid; filtration through sintered glass removed the slight residue. The Hg(II) concentration was determined by Volhard titration with KSCN using FeNH₄(SO₄)₂ indicator. The concentration of excess acid was determined by titration with standard base in the presence of a large excess of NaCl, using a glass electrode as indicator.

Sodium perchlorate was prepared by adding 50% NaOH to aliquots of standardized 60% HClO₄ until neutral when tested with pH paper, then diluting to volume. When necessary, NaClO₄ solutions were carefully titrated for excess acid or base using a glass electrode indicator and a NaNO₃ salt bridge.

Aniline perchlorate and nitrate stock solutions for the potentiometric experiments were prepared by distilling aniline directly into an aqueous solution containing a known amount of the appropriate acid. The receiver was stirred continuously, and a nitrogen atmosphere was maintained; ultraviolet radiation was excluded. The amount of aniline added was computed from the weight of the receiver before and after the distillation. If stored in the dark, these acidic solutions are stable over long periods. The aniline perchlorate stock solution for spectrophotometric experiments was prepared from the solid compound. Reagent grade aniline (J. T. Baker) was added to excess 30% HClO₄, cooled, and filtered. The crude solid was precipitated from acetone solution with chloroform four times in succession and dried. A weighed sample of the pure, white product was dissolved in dilute perchloric acid and made up to known volume.

Mercurous perchlorate solutions were prepared by treating Hg(ClO₄)₂ solutions with metallic mercury. A mercurous nitrate solution was prepared from the reagent grade salt (Baker and Adamson). The acidic solutions were analyzed for total Hg by titration with KSCN after oxidation with KMnO₄ and removal of brown MnO₂ with aqueous FeSO₄. Analysis for the traces of Hg(II) in the Hg(I) solutions was accomplished potentiometrically with a Pt electrode.⁶

The Potentiometric Method.—A 200-ml. round-bottom flask with an inlet for nitrogen gas contained the experimental solutions. It was immersed in a constant-temperature bath, which was equipped with an underwater magnetic stirrer. The Hg⁺² concentration was determined from the potential of a J-type mercury electrode vs. a saturated calomel reference elec-

(1) This work is described in more detail in the Ph.D. Thesis of T. H. W., California Institute of Technology, 1964.

(2) P. Brooks and N. Davidson, *J. Am. Chem. Soc.*, **82**, 2118 (1960).

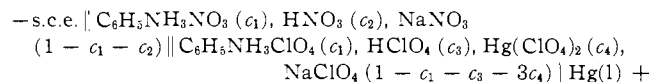
(3) R. Ferreira, E. Ben-Zvi, T. Yamane, J. Vasilevskis, and N. Davidson, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, pp. 457-462.

(4) J. Vasilevskis, Ph.D. Thesis, California Institute of Technology, 1963.

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

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

trode (Beckman No. 39970). A salt bridge isolated the calomel electrode from the reaction solution, contact with which was made through the frit junction from a Beckman 39071 reference electrode. The e.m.f. of the cell

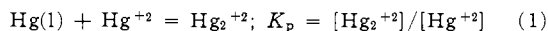


was measured with a Leeds and Northrup type K-2 potentiometer and a 0.02 μ a./mm. galvanometer. The composition of the salt bridge here is essentially that of the reaction solution with nitrate replacing perchlorate as the anion. In all cases, c_2 , c_3 , and c_4 were less than 0.01 M . The junction potentials change only very slightly with changing c_1 and are believed to be small since the mobilities of nitrate and perchlorate are almost the same.⁷

The pH of the solutions was monitored with a general purpose glass electrode (Beckman 40498) and a Beckman expanded scale pH meter in conjunction with the s.c.e. reference electrode already described. The potentiometric circuit was disconnected during pH measurements. Prior to each day's measurements, the pH meter was standardized by adjusting it to read the pH of a standard buffer in which the calomel and glass electrodes were immersed (omitting the salt bridge, which would now introduce a junction potential).

The glass and mercury electrodes were calibrated to read concentrations, not activities. Measurement of the apparent pH of solutions of known acidity and unit ionic strength using a 1.0 F $NaNO_3$ salt bridge permitted calibration of the pH meter-glass electrode combination. If the pH meter is standardized with Beckman No. 3506 buffer solution (pH 4.00) and a Beckman 40495 (Type E-2) glass electrode is used, we find that $-\log [H^+] = (pH)_{obsd} + 0.13$.

Because Hg(II) solutions react with a Hg(0) electrode, the apparent standard potential of the Hg(0)-Hg(II) couple was determined indirectly from the E° values of the Hg(0)-Hg(I) and the Hg(I)-Hg(II) couples. The potentials of a Hg(0) electrode immersed in standardized $Hg_2(NO_3)_2$ solutions and those of a Pt electrode immersed in $Hg_2(NO_3)_2$ - $Hg(ClO_4)_2$ solutions permitted calculation of the apparent E° values. The solutions and salt bridges contained 0.01 F acid, and a small correction for unrepressed hydrolysis was made. At 27° and $\mu = 1.0 M$, the apparent standard potentials of the half-reactions are: $2Hg(l) = Hg_2^{+2} + 2e$, $E^\circ = -0.5400$ v.; $Hg_2^{+2} = 2Hg^{+2} + 2e$, $E^\circ = -0.6733$ v.; $Hg(l) = Hg^{+2} + 2e$, $E^\circ = -0.6066$ v. (E° values are vs. s.c.e.). All calculated E° values were constant to within ± 1.3 mv. as the concentrations were varied by a factor of 10-20. From these potentials, the calculated equilibrium constant of the reaction



is $K_p = 172$ at 27°, $\mu = 1.0 M$. Equilibrium with respect to this reaction is attained almost immediately at the Hg electrode surface.⁶

In the preparation of the reaction solution, salt bridge, and electrodes for each potentiometric aniline experiment, the $Hg(ClO_4)_2$ and Hg(0) electrode were omitted. After degassing and bringing the solution to temperature in the round-bottom flask, an aliquot of $Hg(ClO_4)_2$ solution was added, the Hg(0) electrode inserted, and the e.m.f. immediately measured. The pH was then determined.

In order to relate the basicity of aniline to the stability of its Hg(II) complexes, the K_A of $C_6H_5NH_3^+$ in $NaClO_4$ ($\mu = 1.0 M$) was determined at 27°. The pH of $C_6H_5NH_3ClO_4$ solutions during titrations with base was measured with a Type E-2 glass electrode (Beckman 41260). The salt bridge analogous to that described above was used; the $C_6H_5NH_3^+$ concentration matched that of the reaction solution at half-equivalence. The result was $pK_A = 4.78 \pm 0.02$. K_A is defined here in terms of concentrations, not activities.

For spectrophotometry, the components of Hg(II)-aniline solutions were brought to temperature and mixed rapidly. Immediately a sample of the solution was transferred to a 1-cm. spectrophotometer cell and the absorbances at 276 and 332 $m\mu$ were recorded alternately as functions of time with a Cary Model 14 instrument with a thermostated cell compartment. Both spectrophotometric and potentiometric measurements

were made at 27° on solutions made up to $\mu = 1.0 M$ with $NaClO_4$. Stock solutions of $Hg(ClO_4)_2$ and aniline salts were stored in the dark, and all reaction solutions were protected from unnecessary illumination.

Results

If only 1:1 and 2:1 aniline-Hg(II) complexes are formed

$$\frac{[Hg^{+2}]_0}{[Hg^{+2}]} = (1 + K_p) + K_1 \frac{[C_6H_5NH_3^+]}{[H^+]} + K_2 \left(\frac{[C_6H_5NH_3^+]}{[H^+]} \right)^2 \quad (2)$$

where $[Hg^{+2}]_0$ is the total Hg(II) concentration, and

$$K_1 = \frac{[C_6H_5NH_2Hg^{+2}][H^+]}{[Hg^{+2}][C_6H_5NH_3^+]} \quad (3)$$

$$K_2 = \frac{[(C_6H_5NH_2)_2Hg^{+2}][H^+]^2}{[Hg^{+2}][C_6H_5NH_3^+]^2} \quad (4)$$

Equation 2 can be rearranged to give

$$\left(\frac{[Hg^{+2}]_0}{[Hg^{+2}]} - 1 - K_p \right) \frac{[H^+]}{[C_6H_5NH_3^+]} = K_1 + K_2 \frac{[C_6H_5NH_3^+]}{[H^+]} \quad (5)$$

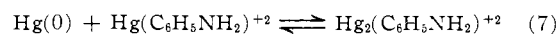
From "conservation of protons"

$$[H^+]_0 - [OH^-]_0 + [C_6H_5NH_3^+]_0 = [C_6H_5NH_3^+] + [H^+] \quad (6)$$

in acidic solution; $[H^+]_0$, $[OH^-]_0$, and $[C_6H_5NH_3^+]_0$ are the formal concentrations of acid, base, and aniline perchlorate, respectively. From this, $[C_6H_5NH_3^+]$ can be computed.

In Fig. 1 a plot of the quantity on the left of eq. 5 vs. $[C_6H_5NH_3^+]/[H^+]$ is shown.⁸ The intercept in Fig. 1 is 16; the slope is 0.45. This intercept is a very unreasonable value for K_1 , since $K_2 \cong (K_1)^2$ for most complexes of Hg(II).

We propose that this large apparent value of K_1 is due to the reaction



which is at equilibrium close to the surface of the electrode. If K_1^I is the formation constant of the 1:1 mercurous complex analogous to K_1 , and K_p is the equilibrium constant for eq. 1, eq. 2 becomes

$$\frac{[Hg^{+2}]_0}{[Hg^{+2}]} = (1 + K_p) + (K_1 + K_p K_1^I) \frac{[C_6H_5NH_3^+]}{[H^+]} + K_2 \left(\frac{[C_6H_5NH_3^+]}{[H^+]} \right)^2 \quad (8)$$

Thus the existence of a mercurous complex at equilibrium does not change the functional dependence of the potential on $[C_6H_5NH_3^+]$, $[H^+]$, or $[Hg^{+2}]_0$.

The intercept in Fig. 1, then, is $K_1 + K_p K_1^I$. From the spectrophotometric experiments, $K_1 = 0.68$. Since $K_p = 172$, $K_1^I = 0.09$. From the slope, $K_2 = 0.45$.

Hg(I) Complexes.—In Fig. 2, the spectrum of an $Hg_2(ClO_4)_2$ - $C_6H_5NH_3ClO_4$ solution is compared with those of the components. There was no turbidity

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, p. 452.

(8) The numerical data are tabulated in ref. 1, p. 25.

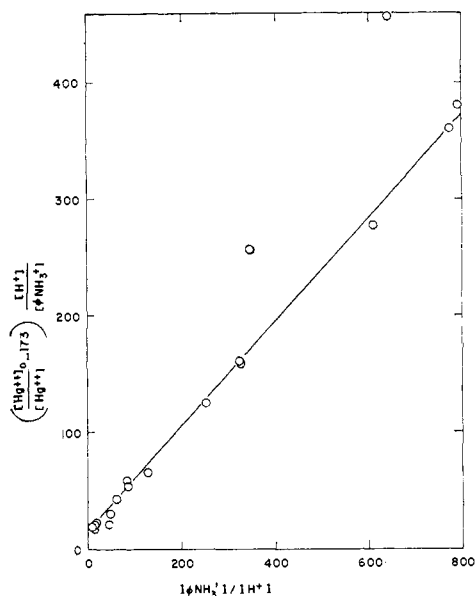


Fig. 1.—Potentiometric experiments with aniline-mercury solutions.

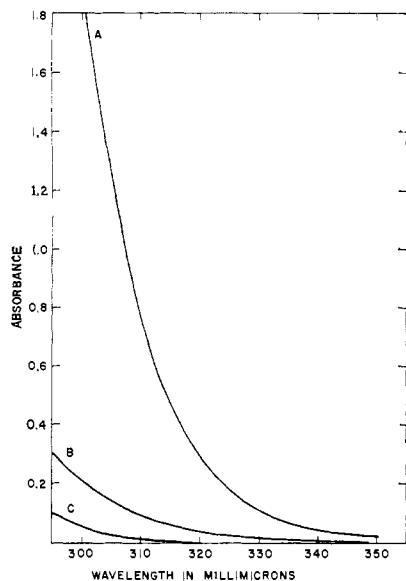


Fig. 2.—(A) Absorption spectrum of an Hg(I)-aniline solution $9.3 \times 10^{-3} F \text{ Hg}_2(\text{ClO}_4)_2$, $9.4 \times 10^{-3} F \text{ C}_6\text{H}_5\text{NH}_3\text{ClO}_4$, $6.6 \times 10^{-5} F \text{ Hg}(\text{ClO}_4)_2$, $1.8 \times 10^{-3} F \text{ HClO}_4$; (B) Hg(I) blank, $9.3 \times 10^{-3} F \text{ Hg}_2(\text{ClO}_4)_2$, $6.6 \times 10^{-5} F \text{ Hg}(\text{ClO}_4)_2$, $1.2 \times 10^{-3} F \text{ HClO}_4$; (C) aniline-Hg(II) blank, $9.4 \times 10^{-3} F \text{ C}_6\text{H}_5\text{NH}_3\text{ClO}_4$, $6.6 \times 10^{-5} F \text{ Hg}(\text{ClO}_4)_2$, $1.6 \times 10^{-3} F \text{ HClO}_4$.

due to disproportionation to Hg(0) and Hg(II). The increased absorbance is a clear qualitative demonstration of the formation of a mercurous aniline complex. The spectral changes can be reversed by the addition of acid. The solution was titrated with acid and the spectrum recorded after each addition. The aniline-Hg(II) background, due to unprotonated aniline and minute amounts of aniline-Hg(II) complex, was determined as a function of acidity from a similar titration. For a trial value of K_1^I , the equation

$$K_1^I = \frac{[\text{C}_1^I]([\text{H}^+]_0 + [\text{C}_1^I])}{([\text{C}_6\text{H}_5\text{NH}_3^+]_0 - [\text{C}_1^I])([\text{Hg}_2^{+2}]_0 - [\text{C}_1^I])} \quad (9)$$

can be solved for $[\text{C}_1^I]$, the concentration of the mercurous complex. Figure 3 shows that the absorbance,

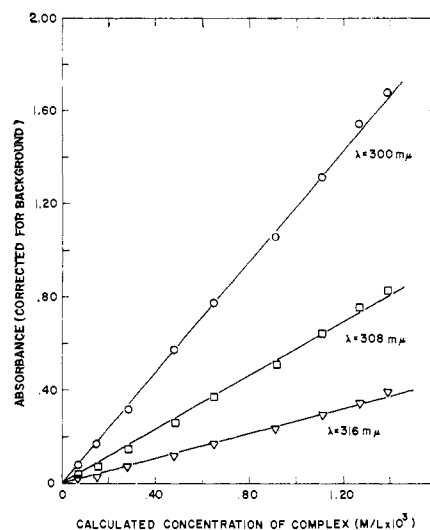


Fig. 3.—Absorbance of an Hg(I)-aniline solution, corrected for Hg(I) and $\text{C}_6\text{H}_5\text{NH}_3^+ - \text{Hg}^{+2}$ background, as a function of the concentration of 1:1 complex, computed from a trial value of $K_1^I = 0.07$; the aniline-Hg(II) correction never exceeded 5%.

corrected for background, is proportional to the calculated concentration of complex at three different wave lengths for a trial K_1^I of 0.07. Noticeable deviations from linearity result from trial values of K_1^I of 0.075 or 0.060.

An unsuccessful attempt was made to detect a 2:1 aniline-Hg(I) complex. A solution containing Hg(II) strongly complexed by aniline was treated with metallic mercury. The solution, and a control solution untreated with Hg(0), were assayed for Hg(I) by diluting into acid and recording the ultraviolet spectra. Any mercurous complex would be dissociated to release Hg_2^{+2} ions by the excess acid. The Hg_2^{+2} ion has a molar absorptivity of 2.8×10^4 l./mole-cm. at $236.5 \text{ m}\mu$.⁹ The absorbance of Hg^{+2} at this wave length is 2.3×10^1 .¹⁰ The absorbance due to $\text{C}_6\text{H}_5\text{NH}_3^+$ is small and constant. Therefore, any reduction of Hg(II) to Hg(I) is accompanied by an increase in absorbance in the assay solutions. No such increase occurred; if even 10% of the total Hg(II) had reacted, it would have been detected.

The 1:1 Aniline-Hg(II) Complex.—In Fig. 4, the spectrum of an acidic $\text{C}_6\text{H}_5\text{NH}_3\text{ClO}_4 - \text{Hg}(\text{ClO}_4)_2$ solution is compared with the spectra of the components. For quantitative study of the complex, the absorbance of $\text{C}_6\text{H}_5\text{NH}_3\text{ClO}_4 - \text{Hg}(\text{ClO}_4)_2$ solutions at $276 \text{ m}\mu$, which increases linearly with time, was extrapolated to the time of mixing.¹¹

If the complex $\text{C}_6\text{H}_5\text{NH}_2\text{Hg}^{+2}$ has a molar absorptivity ϵ_1 at a given wave length, then

$$[\text{C}_6\text{H}_5\text{NH}_2\text{Hg}^{+2}] = Y/\epsilon_1 \quad (10)$$

where Y is the absorbance at that wave length. If $\text{C}_6\text{H}_5\text{NH}_2\text{Hg}^{+2}$ is the only complex formed in solutions containing excess Hg^{+2}

$$[\text{C}_6\text{H}_5\text{NH}_3^+]_0 = [\text{C}_6\text{H}_5\text{NH}_3^+] + [\text{C}_6\text{H}_5\text{NH}_2\text{Hg}^{+2}] \quad (11)$$

From eq. 3, 10, and 11

$$\frac{[\text{C}_6\text{H}_5\text{NH}_3^+]_0}{Y} = \frac{1}{\epsilon_1} + \frac{1}{\epsilon_1 K_1^I} \frac{[\text{H}^+]}{[\text{Hg}^{+2}]} \quad (12)$$

(9) W. C. E. Higginson, *J. Chem. Soc.*, 1438 (1951).

(10) T. H. Wirth, unpublished results.

(11) Results are tabulated in ref. 1, p. 55.

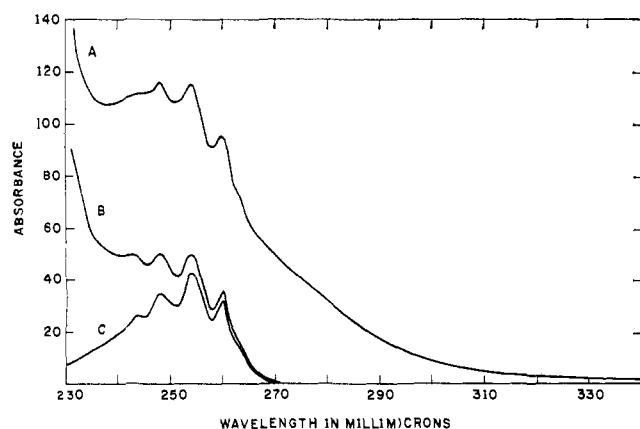


Fig. 4.—Aniline-Hg(II) spectra in aqueous perchloric acid: (A) 0.019 F $Hg(ClO_4)_2$, 0.0026 F $C_6H_5NH_3ClO_4$, 0.25 F $HClO_4$, 0.73 F $NaClO_4$; (B) spectrum C + spectrum of 0.019 F $Hg(ClO_4)_2$; (C) 0.0026 F $C_6H_5NH_3ClO_4$, 0.25 F $HClO_4$, 0.19 F $NaClO_4$.

Since $[C_6H_5NH_3^+]_0 \ll [Hg^{+2}]_0$ and $[H^+]_0$, the latter concentrations are nearly equal to $[Hg^{+2}]$ and $[H^+]$, respectively. Figure 5 is a plot of $[C_6H_5NH_3^+]_0/Y$ vs. $[H^+]_0/[Hg^{+2}]_0$. From the slope and intercept, $\epsilon_1 = 2.44 \times 10^3$ l./mole-cm. at $\lambda = 276.0$ m μ ; $K_1 = 0.68$.

Knowledge of ϵ_1 allows determination of the concentration of $C_6H_5NH_2Hg^{+2}$ responsible for the spectrum in Fig. 4. The absorption due to unreacted $C_6H_5NH_3^+$ and Hg^{+2} can be subtracted out; the resulting spectrum of $C_6H_5NH_2Hg^{+2}$ is displayed in Fig. 6.

Discussion

In part IV^{12a} of this series, the stabilities of Hg(II)-amine complexes are discussed in terms of ligand basicity. It will be seen that aniline, with an unshared pair of π -electrons, shows no special affinity for Hg^{+2} as compared to other nitrogen bases with σ -electron pairs. The binding of DNA and the nucleotides by Hg(II) has been studied in this laboratory^{3,12b}; determination of the binding site is very difficult. In the absence of contrary evidence, it was thought that aromatic amino groups might bind Hg(II) preferentially. The present work shows that this is not the case.

This is the first quantitative investigation of a Hg(I) complex with a nitrogen ligand. As a rule, these bases cause Hg(I) salts to disproportionate, forming Hg(II) complexes and metallic mercury.^{13,14} Many workers have reported solid products from this type of reaction¹⁵⁻¹⁷; in most cases, they are black, indicating the presence of Hg(0). Mercurous diacetylhydrazide is the only mercurous-nitrogen complex which has been characterized unequivocally.¹⁷ A soluble complex of triethanolamine with Hg(I) has been reported,¹⁸

(12) (a) T. H. Wirth and N. Davidson, *J. Am. Chem. Soc.*, **86**, 4325 (1964); (b) T. Yamane and N. Davidson, *ibid.*, **83**, 2599 (1961).

(13) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, pp. 295-296.

(14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers (John Wiley and Sons, Inc.), New York, N. Y., 1962, pp. 483 and 486.

(15) "Gmelin's Handbuch der Anorganischen Chemie, Quecksilber" (System No. 34). Teil A, Lieferung 2, Verlag Chemie, Weinheim, 1962, p. 832 ff.

(16) K. A. Hofmann and E. C. Marburg, *Ann. Chem.*, 305, 191 (1899).

(17) K. Brodersen and L. Kunkel, *Chem. Ber.*, **91**, 2698 (1958).

(18) I. P. Ryazanov and V. D. Chistota, *Sb. Nauchn. Tr. Magnitogor. Gorno-Met. Institut.*, **16**, 146 (1958); *Chem. Abstr.*, **53**, 6874i (1959).

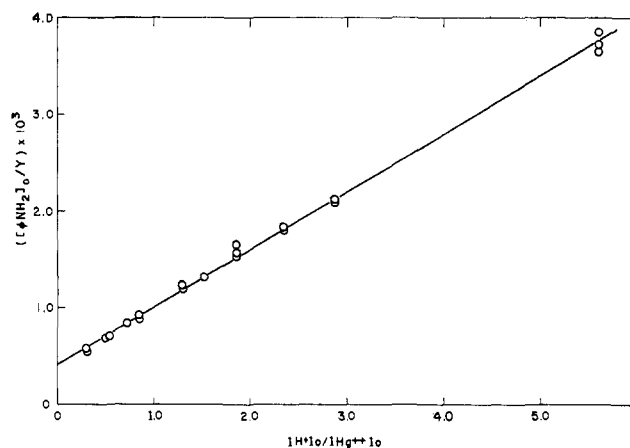


Fig. 5.—Aniline-Hg(II): stability of the 1:1 complex.

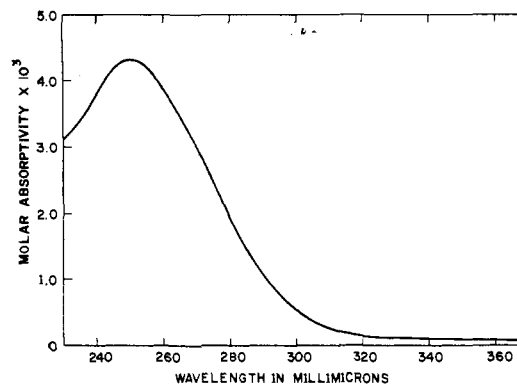


Fig. 6.—Spectrum of the $C_6H_5NH_2Hg^{+2}$ complex.

but the conclusiveness of the work cannot be judged on the basis of available abstracts.

In Table I, the stability of the Hg(I)-aniline complex is compared with that of other complexes of aniline. Although Hg(I) binds aniline less well than Hg(II), both oxidation states form far more stable complexes than Ag(I) or Ni(II). It appears, then, that the scarcity of mercurous complexes indeed results from the very high stability of Hg(II) complexes rather than lack of complexing tendency on the part of Hg(I). But the margin of stability seems smaller than was previously believed.

TABLE I

STABILITY CONSTANTS OF 1:1 METAL-ANILINE COMPLEXES

M	log β_1^a	Temp., °C.	Medium	Method	Ref.
Hg ⁺²	4.60	27	1 M $NaClO_4$	Spectrophotometric	<i>b</i>
Hg ₂ ⁺²	3.71	27	1 M $NaClO_4$	Potentiometric	<i>b</i>
Ag ⁺	1.44	25	1 M KNO_3	Distribution	<i>c</i>
Ni ⁺²	0.09	..	85% EtOH	Spectrophotometric	<i>d</i>

^a $\beta_1 \equiv [C_6H_5NH_2M]/[C_6H_5NH_2][M]$ in l./mole. ^b Present work. ^c C. Golumbic, *J. Am. Chem. Soc.*, **74**, 5777 (1952).

^d A. V. Ablov and L. V. Nazarova, *Zh. Neorgan. Khim.*, **5**, 1735 (1960).

The 1:1 Hg(I)-aniline complex may owe its existence to the unique character of aniline as a ligand, but it seems likely that other Hg(I) complexes exist in solution and simply have not been observed. Few mercury electrode studies have been made on nitrogen ligands. The region of stability of such complexes is small. The value of the 1:1 stability constant cannot be less

than 0.04 that of the corresponding Hg(II) complex if it is to be detectable potentiometrically.¹⁹ Spectrophotometric detection requires ligands, the spectra of which change considerably on complexing. The high ultraviolet absorbance of Hg₂⁺² and the absorbance of Hg(II) complexes increase the difficulty of observation.

Therefore, it is not surprising that more Hg(I)-nitrogen complexes have not been detected, even if they exist. However, neither Hg(I)-ammonia nor

(19) Reference I, pp. 29-31.

Hg(I)-guanidine complexes are stable enough to be detected potentiometrically.^{12a} Hg(I) complex stability may increase less strongly with increasing ligand basicity than the stability of Hg(II) complexes. It should then be possible to detect other Hg(I) complexes with amines of low basicity, but none with amines of high basicity.

Acknowledgment.—This research has been supported by the Atomic Energy Commission under Contract AT(11-1)-188. T. H. W. was a Woodrow Wilson Fellow in 1959-1960.

[CONTRIBUTION NO. 3112 FROM THE GATES, CRELLIN, AND CHURCH LABORATORIES OF CHEMISTRY, PASADENA, CALIFORNIA]

The Mercuration of Aniline in Acidic Solution. Mercury(II) Complexes with Mercurated Aniline Derivatives^{1,2}

BY THOMAS H. WIRTH AND NORMAN DAVIDSON

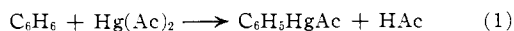
RECEIVED MAY 27, 1964

Spectrophotometric studies of acidic Hg(ClO₄)₂ solutions containing small amounts of aniline or *p*-acetoxymercurianiline indicate that aniline is mercurated in such solutions, and that the mercuration products form labile complexes with Hg⁺². These complexes are characterized by an intense ultraviolet absorption band between 330 and 335 mμ, the molar absorptivity of which ranges from 10³ to 10⁴ l./mole-cm., depending on the degree of mercuration. The equilibrium constant of the reaction *p*-⁺HgC₆H₄NH₃⁺ + Hg⁺² = *p*-⁻HgC₆H₄NH₂Hg⁺² + H⁺ is 1.5 at 27°, μ = 1.0 M (NaClO₄). The value of this constant changes only slightly as the number of mercury atoms on the ring varies. The molar absorptivity of the *p*-⁻HgC₆H₄NH₂Hg⁺² complex is 1.1 × 10³ l./mole-cm. at 331 mμ. An explosive, crystalline compound of simplest formula C₆NH₃Hg₂(ClO₄)₂·4H₂O has been isolated from acidic solutions 2 F in Hg(ClO₄)₂ and 0.1 F in C₆H₅NH₂ClO₄.

Introduction

Potentiometric and spectrophotometric studies of Hg(ClO₄)₂-C₆H₅NH₂ClO₄ solutions in aqueous perchloric acid³ reveal that slow reactions occur in such solutions and are accompanied by spectral changes, drifting potentials, and eventually by the formation of precipitates. These reactions can be distinguished sharply from the instantaneous formation of labile Hg-N complexes. The present paper deals with spectrophotometric studies and with the isolation of a crystalline aniline-mercury-perchlorate compound, which indicate that the slow reactions are aromatic mercuration.

Mercuration is a well-known example of electrophilic substitution.⁴ Hg(II) salts, particularly mercuric acetate, react with aromatic substrates



Carmack,⁵ Westheimer,⁶⁻⁹ and their co-workers have directed attention to mercuration by Hg(NO₃)₂ and Hg(ClO₄)₂ in aqueous solution.

Aromatic amines are easily mercurated; aniline is mercurated in aqueous solution at room temperature by mercuric acetate.¹⁰ The voluminous early work on compounds of mercury with aromatic amines has been surveyed by Whitmore.¹¹ The effect of HAc,

NaAc, HClO₄, NaClO₄, and HNO₃ on the rate of mercuration of aniline by Hg(Ac)₂ in aqueous solution was recently studied by Wronski.¹² He found that the rate is decreased by acids. This is to be expected, since free aniline is a much better substrate in aromatic substitution than is the anilinium ion. Unfortunately, the studies were not sufficiently complete to permit quantitative interpretation, for the rate of mercuration is sensitive to salt concentration,^{8,9} as well as to mercury(II)-acetate complex formation.

Experimental

Materials.—Solutions of acids, bases, inorganic salts, C₆H₅-NH₂ClO₄, and Hg(ClO₄)₂-C₆H₅NH₂ClO₄ solutions containing excess Hg(II) were prepared as in part I.³

p-Acetoxymercurianiline was prepared by the method of Dimroth.¹⁰ It was recrystallized by dissolving it in an ammoniacal NH₄Ac solution, adding decolorizing charcoal, and filtering. After the solution was neutralized with HAc, the compound precipitated slowly. This method was adapted from that used by Vecchiotti for 2,4-diacetoxymercurianiline.¹³ After drying in a vacuum desiccator, the crystals melted at 166-167.5°; lit. m.p. 167°. A stock solution of *para*-mercurated aniline was prepared by dissolving a weighed sample in an HClO₄-NaClO₄ solution and diluting to known volume.

The *p*-⁺HgC₆H₄NH₂ Complex with Hg(II).—The spectrophotometric procedure used to study the Hg(II) complex of aniline³ was also employed here. The absorbance at 331.0 mμ, where the 1:1 complex is the only absorbing species initially present, was recorded as a function of time. Occasionally 10-cm. cells were used. Data were obtained at 27°, μ = 1.0 M

The Crystalline Mercuration Product.—Several weeks after preparation, a yellow, crystalline compound precipitated copiously from a solution 2 F in Hg(ClO₄)₂, 0.1 F in C₆H₅NH₂ClO₄, and 0.5 F in HClO₄. (Single crystals can be obtained in 1-2.5 weeks if a small sample of the solution is seeded.) The solid was filtered off and washed, first with concentrated Hg(ClO₄)₂ solution, then with large amounts of water. If the supernatant is diluted by a factor of 2 or 3 with water, a yellowish white precipitate forms.

(1) Paper II in the series "Studies of the Chemistry of Mercury in Aqueous Solution."

(2) This work is described in more detail in the Ph.D. Thesis by T. H. W., California Institute of Technology, 1964.

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