soluble in 1 F HClO$_4$ than in 1 F NaClO$_4$ lends credence to these possibilities.

If either of the explanations is correct, the lower values of K_M correspond most closely to the conventional equilibrium constant. In the absence of more accurate data or independent evidence, however, it seems preferable to propose the average value.

We have determined, then, that the equilibrium quotient of reaction 1 is two orders of magnitude greater than that of reaction 2.

Therefore, equilibrium in the reaction

$$C_5H_5N^-Hg^+ + C_6H_6 \rightleftharpoons C_5H_5NH^+ + C_6H_5Hg^+ \quad (8)$$
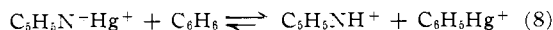
favors the products. While solvation effects have a strong influence on equilibria in aqueous solution, it seems likely the position of this equilibrium reflects relative strengths of aromatic carbon and aromatic nitrogen bonds with Hg(II).

From a practical point of view, this work points out that in aqueous solution, nonacidic aromatic hydrogens may in fact be replaced by Hg^{+2}. This is important in the study of the interaction of Hg(II) with complex nitrogen heterocycles, including those of biological significance.
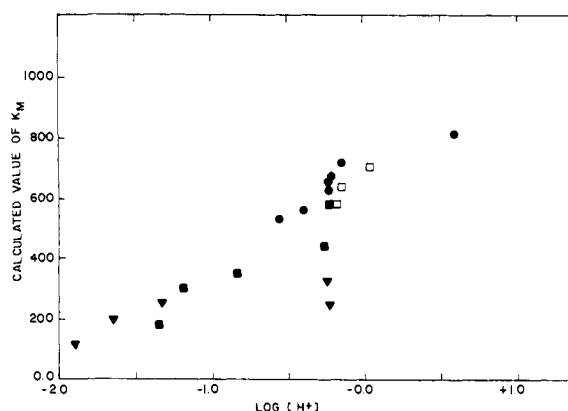

Fig. 3.—Variation of the equilibrium quotient for the mercuration of p-methoxyanisole with [H$^+$]: solid points, forward reaction; open points, reverse reaction; circles, squares, and triangles represent solutions of decreasing [Hg^{-2}] (1 × 10^{-5}–5 × 10^{-4} M).

Mercury(II) Complexes of Guanidine and Ammonia, and a General Discussion of the Complexing of Mercury(II) by Nitrogen Bases[1]

By THOMAS H. WIRTH AND NORMAN DAVIDSON

The stability constants of guanidine and ammonia complexes of Hg(II) have been measured potentiometrically. For guanidine, the reactions and equilibrium constants at 27°, μ = 1.0 M (NaClO$_4$), are: 2RH$^+$ + Hg^{+2} = R$_2$Hg^{+2} + 2H$^+$, K_2 = 7.4 × 10^{-3}; RH$^+$ + Hg^{+2} + H$_2$O = RHgOH + 2H$^+$, $K_1{}^H$ = 2.7 × 10^{-4} mole/l. [R = (H$_2$N)$_2$CNH]. The pK_A of the guanidinium ion was determined pectrophotometrically to be 13.54 at 27°, μ = 1.0 M. For complexing of Hg^{+2} by ammonia [25°, μ = 1.0 M NaClO$_4$)], 2NH$_4^+$ + Hg^{+2} = (NH$_3$)$_2$-Hg^{+2} + 2H$^+$, K_2 = 0.08 ± 0.02. The ammonia results are in good agreement with the classic measurements of Bjerrum. An extensive tabulation of the binding constants of nitrogen bases for Hg^{+2} and H$^+$ is presented and the approximate linear free energy relationship is discussed.

Introduction

For many organic nitrogen ligands and metal ions, a parallel exists between the basicity of the ligand and the stability of the metal–ligand complex.[2,3] Guanidine is among the strongest organic bases known.[4] It is therefore of interest to study its binding with metal ions in order to test this relationship over the widest possible range. Very little is known about the characteristics of guanidine as a ligand, however. Few solid guanidine complexes have been prepared. Wormser[5] studied the formation of the guanidine–Ag(I) complex in solution, but calculated no stability constants.

In this work, the potentiometric method was employed to study complexes of guanidine with Hg(II). The 2:1 complex was found to be stable enough that HgO does not precipitate in basic solutions containing guanidinium ion in excess. Evidence for a mixed complex, RHgOH, was obtained (R ≡ guanidine).

(1) This is the fourth and final paper in the series "Studies of the Chemistry of Mercury in Aqueous Solution."

(2) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

(3) R. J. Bruehlman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

(4) D. J. Cram and G. S. Hammond, "Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 173–174.

(5) Y. Wormser. *J. Chim. Phys.*, **46**, 658 (1949).

The complexes of Hg(II) with ammonia were also studied potentiometrically. This system has already been studied by Bjerrum[6] in his classical investigations of ammine complexes. Bjeruum himself pointed out, however, that his glass electrode method is less suitable for studying this system than the many other systems he investigated. Hg(II) is so strongly bound by amines—including ammonia—that the pH is not a sensitive measure of complex formation at the high acidities necessary to partially dissociate the complexes.

Experimental

Materials.—Guanidine perchlorate and nitrate were prepared by neutralizing a slurry of guanidine carbonate (Eastman Organic Chemicals) with the appropriate concentrated acid. The resulting mixtures were cooled and filtered. The perchlorate was recrystallized twice from absolute ethanol and dried in a vacuum desiccator using a Dry Ice–acetone trap. Heating at 105° for 1 hr. produced no weight loss. The melting point was 252–255°; lit. m.p. 240°.[7] The nitrate was recrystallized from water, dried, and dissolved in hot absolute methanol. The solution was evaporated to half its original volume and filtered. After drying in a vacuum desiccator over CaSO$_4$, the compound melted at 216–218°, which compared with literature values of

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Thesis, P. Haase and Son. Copenhagen, 1941, pp. 164–173.

(7) A. Glasner and A. Makovsky. *J. Chem. Soc.*, **182** (1953).

214.2°[8] and 217°.[9] One formal (1 F) stock solutions were prepared by dissolving weighed amounts of these salts in water and diluting to volume.

Ammonium perchlorate and ammonium nitrate stock solutions were prepared by roughly neutralizing aliquots of standardized acid with ammonium hydroxide (Du Pont). Solutions (1.0 F) were prepared by appropriate dilution. Aliquots of these solutions were titrated with acid using a glass electrode and a 1 F NaNO$_3$ salt bridge. From the results, the 1 F solutions remaining were accurately neutralized with standard acid. They were then analyzed by evaporating aliquots of solution and weighing the residues.

The preparation and standardization of Hg(ClO$_4$)$_2$, NaClO$_4$, NaNO$_3$, HClO$_4$, and NaOH solutions have already been described.[10]

Potentiometric Measurements.—With minor changes, the technique was the same as in part I. In any one run, solutions containing known amounts of Hg(II), acid, and amine were titrated with acid or base and the pH and free Hg^{+2} concentrations measured with glass and mercury electrodes. The initial concentrations of Hg(II) and amine were varied in different runs. Beckman Type E-2 glass electrodes were used. Before each separate ammonia experiment, the pH meter was recalibrated by titrating the NaClO$_4$-NH$_4$ClO$_4$ solution to be used in the experiment with standard acid. This was just prior to the addition of Hg(ClO$_4$)$_2$ and the Hg(0) electrode. Nitrogen gas was bubbled through the solutions except when free ammonia was present.

Guanidine experiments were carried out at 27°; ammonia experiments at 25°. For the latter series, the apparent standard potential of the Hg(0)-Hg(II) couple was redetermined at 25° as described in part I ($E°$ = −0.6054 v. vs. s.c.e.). All measurements were performed at ionic strength 1.0 M (NaClO$_4$).

Determination of pK_A Values.—In order to correlate basicity with complex stability, it was necessary to determine the basicity of ammonia and guanidine under the conditions employed here. The pK_A of ammonia was determined by titrating NH$_4$ClO$_4$ solutions of different concentrations with base after the pH meter had been calibrated as described above. The salt bridge, a solution of NaNO$_3$ and NH$_4$NO$_3$, was prepared to match the NH$_4^+$ concentration in the reaction vessel at half-equivalence.

A spectrophotometric method was chosen to determine the basicity of guanidine in order to avoid the difficulties of pH measurement in strong base. The intensity of the absorption of the guanidinium ion between 220 and 250 mμ increases greatly in alkali. The absorption of the hydroxide ion itself makes observation of the spectrum of free guanidine at wave lengths less than 225 mμ very difficult. The concentration of free guanidine can be determined from the absorbance in the 225–235 mμ region, however, even though the absorbance does not reach a maximum.

Solutions containing guanidine perchlorate (0.006–0.02 F), sodium perchlorate (0.03–0.87 F), and sodium hydroxide (0.12–0.96 F) at unit ionic strength were prepared and brought to constant temperature. The spectra of three successive samples of each solution were recorded on a Cary Model 14 spectrophotometer with a thermostated cell compartment with air in the reference beam. The spectra of fresh samples were identical; however, absorption of CO$_2$ changed the spectra of solutions exposed to the air. Blank solutions containing only NaOH were prepared and their spectra recorded; all unnecessary exposure to the air was avoided.

The concentration of free guanidine in each solution was determined from the absorbance at 227.0, 229.0, and 231.0 mμ. At the concentrations used, protonated guanidine does not absorb at these wave lengths. The absorbances were corrected for NaOH background. The concentration of guanidine never exceeded 5% of that of NaOH; therefore, corrections to [NaOH] for reaction were not made. Under these conditions

$$\frac{[RH^+]_0}{X} = \frac{1}{\epsilon_X} + \frac{K_B}{\epsilon_X}\left(\frac{1}{[OH^-]}\right) \qquad (1)$$

where X is the corrected absorbance, ϵ_X the molar absorptivity of (H$_2$N)$_2$C=NH at that wave length, [RH$^+$]$_0$ the formal guani-

dine concentration, and

$$K_B = \frac{[RH^+][OH^-]}{[R]} \qquad (2)$$

RH$^+$ and R represent C(NH$_2$)$_3^+$ and (H$_2$N)$_2$C=NH, respectively.

The value of pK_W is necessary in order to find the K_A of the guanidinium ion from this spectrophotometric K_B. pK_W was determined from the apparent pH of solutions of known [OH$^-$] after calibration of the pH meter on solutions of known [H$^+$].

Results

Basicity of Guanidine.—The average K_B, from data at 231.0, 229.0, and 227.0 mμ, is

$$K_B = 0.72 \pm 0.06 \ M \ (27.2°, \mu = 1.0 \ M) \qquad (3)$$

The molar absorptivity of free guanidine at each wave length is 54, 92, and 150 l./mole-cm., respectively. K_W, defined here as the concentration product [H$^+$]·[OH$^-$], was determined as

$$pK_W = 13.68 \pm 0.04 \ (27.2°, \mu = 1.0 \ M) \qquad (4)$$

From eq. 3 and 4, the pK_A of the guanidinium ion is

$$pK_A = 13.54 \pm 0.06 \ (27.2°, \mu = 1.0 \ M) \qquad (5)$$

Using a hydrogen electrode, Hall and Sprinkle[11] found the pK_A to be 13.59 ± 0.05 in 2 N KCl at 24.2°.

Basicity of Ammonia.—The pK_a of the ammonium ion was measured as 9.47 ± 0.02 at μ = 1.0 M (NaClO$_4$), 25.0°.

Guanidine–Hg(II) Complexes.—The quantitative analysis of the results indicates that, in addition to the ion Hg(NHC(NH$_2$)$_2$)$_2^{+2}$, there is a species, the formation of which involves release of two protons and the addition of only one guanidine to Hg^{+2}. A likely species of this type is (H$_2$N)$_2$CNHHgOH$^+$, written here as RHgOH$^+$.

The equilibria considered are

$$K = 170 = [Hg_2^{+2}]/[Hg^{+2}] \ \text{(at the electrode)}^{12,13a} \qquad (6)$$
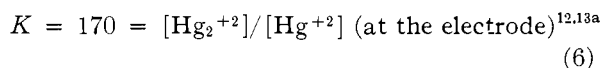
$$K_{2H} = 10^{-63} = [Hg(OH)_2][H^+]^2/[Hg^{+2}]^{13b} \qquad (7)$$

$$K_2 = [HgR_2^{+2}][H^+]^2/[Hg^{+2}][RH^+]^2 \qquad (8)$$

$$K_1^H = [RHgOH^+][H^+]^2/[Hg^{+2}][RH^+] \qquad (9)$$

These equilibria lead to the equation

$$\frac{[Hg^{+2}]_0}{[Hg^{+2}]} = 1 + K + \frac{K_{2H}}{[H^+]^2} + K_2\frac{[RH^+]^2}{[H^+]^2} + K_1^H\frac{[RH^+]}{[H^+]^2} \qquad (10)$$

from which

$$\left(\frac{[Hg^{+2}]_0}{[Hg^{+2}]} - 1 - K - \frac{K_{2H}}{[H^+]^2}\right)\left(\frac{[H^+]}{[RH^+]}\right)^2 = K_2 + \frac{K_1^H}{[RH^+]} \qquad (11)$$

The quantity on the left of eq. 11 will be designated Q_1. In Fig. 1, the experimental results are presented in the form of a plot of Q_1 vs. 1/[RH$^+$]. The results represent variation over wide concentration ranges ([RH$^+$]$_0$ = 0.015–0.38 F; [Hg^{+2}]$_0$ = 1 × 10^{-4}–6 × 10^{-3} F; pH 2.6–5.1).

(8) C. R. Witschonke, *Anal. Chem.*, **26**, 562 (1954).

(9) C. B. L. Smith, "Inorganic Syntheses," Vol. I, J. C. Booth, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 96.

(10) Paper I of this series: T. H. Wirth and N. Davidson, *J. Am. Chem. Soc.*, **86**, 4314 (1964).

(11) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

(12) T. H. Wirth, Ph.D. Thesis, California Institute of Technology, 1964, p. 20.

(13) (a) S. Hietanen and L. G. Sillén, *Arkiv Kemi*, **10**, 103 (1956); (b) *Acta Chem. Scand.*, **6**, 747 (1952).

Points for which $[\text{Hg}^{+2}]_0/[\text{Hg}^{+2}]$ was less than 300 were excluded. Under conditions where this ratio is less than 300, $[\text{Hg}_2{}^{+2}]$ represents a large fraction of $[\text{Hg}^{+2}]_0$, and little information about Hg(II) complexes can be obtained.[14]

The experiments in Fig. 1 were conducted in acidic solution. The pH-e.m.f. behavior is essentially similar in basic solution; there is no evidence for the formation of additional complexes. Irreversible changes in the solutions occur at high basicity, however. Since the results in basic solution were also less precise, they were not included in the equilibrium constant calculations. From Fig. 1

$$K_2 = 7.4 \times 10^{-3}, \; K_1{}^H = 2.7 \times 10^{-4} \text{ mole/l.} \quad (12)$$

at $27.2°$, $\mu = 1.0 \; M$. From K_2 and K_A

$$\beta_2 = \frac{[\text{HgR}_2{}^{+2}]}{[\text{Hg}^{+2}][\text{R}]^2} = K_2/K_A{}^2 = 10^{24.95} \; \text{l.}^2/\text{mole}^2 \quad (13)$$

It is of interest to consider the equilibrium constant of the reaction

$$\text{HgR}_2{}^{+2} + \text{Hg(OH)}_2 \rightleftharpoons 2\text{RHgOH}^+ \quad (14)$$
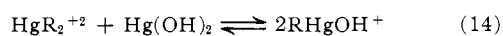
$$K_{15} = \frac{[\text{RHgOH}^+]^2}{[\text{HgR}_2{}^{+2}][\text{Hg(OH)}_2]} = \frac{(K_1{}^H)^2}{K_{2H}K_2} = 20 \quad (15)$$

This is greater than the statistical value of 4, but it corresponds to an equilibrium value of $[\text{RHgOH}^+]$ only about twice as great as the statistical. Marcus[15] observed a similar stabilization of mixed complexes in his study of the mixed halides of mercury(II).

Ammonia–Hg(II) Complexes.—K_{2}, defined as in eq. 8, with $\text{R} \equiv \text{NH}_3$, can be computed from eq. 16 if no other ammine complexes are present

$$K_2 = \left(\frac{[\text{H}^+]}{[\text{RH}^+]}\right)^2 \left(\frac{[\text{Hg}^{+2}]_0}{[\text{Hg}^{+2}]} - 1 - K - \frac{10^{-6.3}}{[\text{H}^+]^2}\right) \quad (16)$$

As is true with guanidine, this value of K_2 is not constant as the total ligand concentration is changed. However, the relationship between $[\text{NH}_4{}^+]$ and the calculated K_2 is not simple; indeed, K_2 goes through a minimum.

In Table I, the average value of K_2 from each of six

TABLE I
VALUES FOR THE STABILITY CONSTANT OF THE
$\text{Hg(NH}_3)_2{}^{+2}$ COMPLEX

No.	$[\text{NH}_4{}^+]$	$[\text{Hg(ClO}_4)_2]_0$	Average K_2
6	0.74	2.9×10^{-3}	0.098 ± 0.005
1	0.38–0.42	5×10^{-3}	0.089 ± 0.012
2	0.185–0.189	1.2×10^{-4}	0.066 ± 0.006
4	0.075–0.078	6.1×10^{-4}	0.080 ± 0.007
5	0.019–0.023	1.2×10^{-4}	0.101 ± 0.006
7	0.0066–0.0072	1.2×10^{-4}	0.15 ± 0.01

separate titrations is given. Values where $[\text{Hg}^{+2}]_0/[\text{Hg}^{+2}] < 300$ are excluded. Also excluded are values where $[\text{NH}_4{}^+]/[\text{H}^+] > 10^7$. From the stability constants determined by Bjerrum, it is possible to calculate that if this ratio exceeds 10^7, $\text{Hg(NH}_3)_3{}^{+2}$ begins to form in significant concentration. We observed that the apparent K_2 does indeed increase above this point.

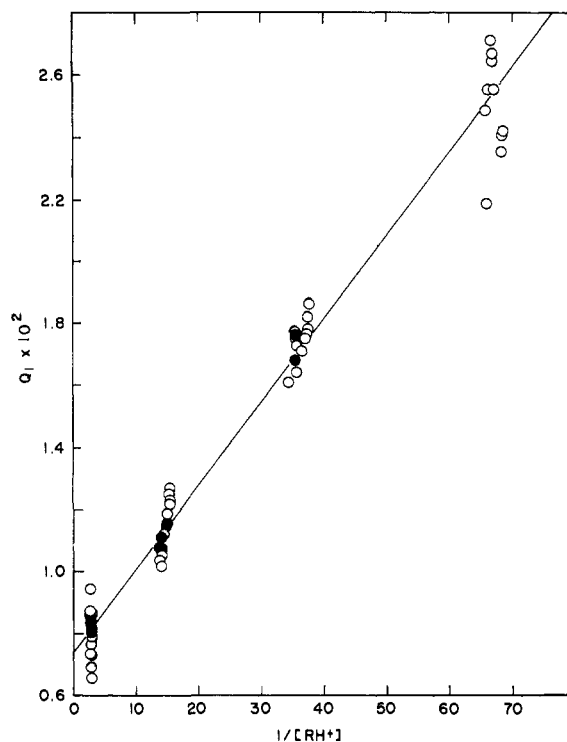Each average value of K_2 represents a wide variation of pH (between 3 and 7) at approximately constant

(14) Reference 12, p. 135.
(15) Y. Marcus, *Acta Chem. Scand.*, **11**, 611 (1957).

Fig. 1.—Guanidine–Hg(II), variation of Q_1 with $1/[\text{RH}^+]$.

$[\text{NH}_4{}^+]$. The variation in K_2 with $[\text{NH}_4{}^+]$ is small but significant. It is evidently related to $[\text{NH}_4\text{ClO}_4]$, not to $[\text{Hg(ClO}_4)_2]_0$.

The increase in K_2 as $[\text{NH}_4\text{ClO}_4]$ decreases below $0.2 \; M$ might be attributed to a $\text{HOHgNH}_3{}^+$ complex similar to that formed in the Hg(II)–guanidine system. The contribution of such a complex to the mercury binding increases as $\text{NH}_4{}^+$ decreases; thus run 7 is the most important one in this respect. We felt that it was not practical to push conditions to the point where the possible contribution of $\text{HOHgNH}_3{}^+$ to the binding was more pronounced because of the precipitation of basic salts; the trend in K_2 in Table I is not sufficient to warrant a confident conclusion that $\text{HOHgNH}_3{}^+$ exists. The small increase in K_2 at very high $\text{NH}_4{}^+$ concentration can be attributed to activity coefficient effects due to the replacement of Na^+ by $\text{NH}_4{}^+$ in large amounts.

Rather than obtaining a value of K_2 by extrapolating a graph of Q_1 vs. $1/[\text{RH}^+]$ to $1/[\text{RH}^+] = 0$ and ignoring the experiments where $[\text{NH}_4{}^+] > 0.2$, it seems preferable to adopt an appropriate mean. The median of the average K_2 values seems suitable. Experiment 7 can be excluded from the group of acceptable measures of K_2, however. We have, then

$$K_2 = 0.08 \pm 0.02 \; (25.0°, \; \mu = 1.0) \quad (17)$$

From the pK_A of ammonia

$$\beta_2 = \frac{[\text{Hg(NH}_3)_2{}^{+2}]}{[\text{Hg}^{+2}][\text{NH}_3]^2} =$$

$$K_2/K_A{}^2 = 10^{17.8 \pm 0.1} \; (\text{l./mole})^2 \quad (18)$$

The value obtained by Bjerrum was $\log \beta_2 = 17.5$ in $2 \; M \; \text{NH}_4\text{NO}_3$ at approximately $22°$.

In more basic solution, the complexes $\text{Hg(NH}_3)_3{}^{+2}$ and $\text{Hg(NH}_3)_4{}^{+2}$ form. The presence of free ammonia in such solutions makes a number of changes in procedure necessary in order to obtain accurate constants.

TABLE II
ASSOCIATION CONSTANTS OF NITROGEN-CONTAINING LIGANDS WITH Hg(II)

Ligand	Complex[a]	log K_H[a]	log K_{Hg}[a]	Temp., °C.	Method	Medium	Ref.
Ammonia (L)	HgL_2^{+2}	9.61	8.75	22	pH	2 M NH_4NO_3	b
	HgL_2^{+2}	9.47	8.9	25	Hg	1 M $NaClO_4$	c
Methylamine (L)	HgL_2^{+2}	10.72	8.95	25	pH	0.5 M $HLNO_3$	d
n-Butylamine (L)	HgL_2^{+2}	10.71	9.05	25	pH	0.5 M $HLNO_3$	d
Ethylenediamine (L)	HgL_2^{+2}	10.18	11.71	25	pH	1 M KNO_3	d
	HgL_2^{+2}	10.00	11.65	25	Hg	0.1 M $NaClO_4$	e
	HgL_2^{+2}	10.00	11.59	25	Polarography	0.1 M KNO_3	f
	$Hg(HL)_2^{+2}$	7.20	6.45	25	Hg	0.1 M $NaClO_4$	e
2-Methoxyethylamine (L)	HgL_2^{+2}	9.30	8.92	30	pH	1 M $NaClO_4$	g
Aminoacetic acid (HL)	HgL_2	9.76	9.6	20	pH	0.5 M KNO_3	h
Ethanolamine (L)	HgL_2^{+2}	9.60	8.66	25	pH	0.4 M KNO_3	d
2-Amino-2'-hydroxydiethyl sulfide (L)	HgL_2^{+2}	9.18	9.13	30	pH	1 M $NaClO_4$	g
Pyridine (L)	HgL_2^{+2}	5.21	5.0	25	pH	0.5 M $HLNO_3$	d
Aniline (L)	HgL_2^{+2}	4.78	4.60	27	Hg	1 M $NaClO_4$	i
Piperidine (L)	HgL_2^{+2}	11.12	8.72	25	pH	0.5 M KNO_3	d
Diethanolamine (L)	HgL_2^{+2}	9.00	7.83	25	pH	0.5 M KNO_3	j
Triethylamine (L)	HgL_2^{+2}	10.77	7.80	25	pH	0.4 M $HLNO_3$	d
Triethanolamine (L)	HgL_2^{+2}	7.90	6.54	25	pH	0.5 M KNO_3	d
Guanidine (L)	HgL_2^{+2}	13.54	12.48	27	Hg	1 M $NaClO_4$	c
d-Cycloserine (HL)	$Hg(HL)_2^{+2}$	4.57	7.04	25	Hg	0.4 M KNO_3	k
	HgL_2	7.40	8.77	25	Hg	0.4 M KNO_3	k
Imidazole (L)	HgL_2^{+2}	7.12	8.37	27	Hg	0.15 M $NaClO_4$	l
Histidine (HL)	$Hg(HL)_2^{+2}$	6.08	7.50	27	Hg	0.15 M $NaClO$	l
	HgL_2	9.12	10.61	27	Hg	0.15 M $NaClO_4$	l
Adenosine (L)	HgL_2^{+2}	3.5	4.25	27	Hg	0.1 M $NaClO$	m
Cytosine (L)	HgL_2^{+2}	4.5	5.45	27	Hg	0.1 M $NaClO_4$	m
Thymidine (HL)	HgL_2	9.6	10.6	27	Hg	0.1 M $NaClO_4$	m
Thymine (HL)	HgL_2	9.8	10.6	27	Hg	0.1 M $NaClO_4$	m

[a] If the complex is HgR_2, $K_H \equiv [HR^+]/[H^+][R]$, $\beta_2 \equiv [HgR_2^{+2}]/[Hg^{+2}][R]^2$, $K_{Hg} \equiv \sqrt{\beta_2}$. [b] See ref. 6. [c] Present work. [d] Ref. 2. [e] J. I. Watters and J. G. Mason, *J. Am. Chem. Soc.*, **78**, 285 (1956). [f] C. J. Nyman, D. K. Roe, and D. B. Masson, *ibid.*, **77**, 4191 (1955). [g] J. Lotz, unpublished; from G. H. McIntyre, Dissertation, Pennsylvania State College, 1952. [h] H. V. Flood and V. Loräs, *Tidskr. Kjemi Bergvesen Met.*, **5**, 83 (1945). [i] Part I of this series. [j] J. Bjerrum and S. Refn, *Suomen Kemistilehti*, **B29**, 68 (1956). [k] N. G. Lordi, *J. Pharm. Sci.*, **52**, 397 (1963). [l] P. Brooks and N. Davidson, *J. Am. Chem. Soc.*, **82**, 2118 (1960). [m] R. Ferreira, E. Ben-Zvi, T. Yamane, J. Vasilevskis, and N. Davidson, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, pp. 457–462.

Titration with acid or base is no longer useful, because large changes in $[NH_4^+]$ result. The method of Bjerrum is suitable for study of these complexes; therefore, the constants were not redetermined.

These results confirm those of Bjerrum. It is somewhat disappointing that K_2 is so sensitive to the nature of the medium. Such variations make it difficult to define a constant of general validity. A constant useful in all 1 F perchlorate solutions evidently cannot be more precisely determined than the K_2 given here.

Complex Stability and Ligand Basicity

The base strength of an electron donor can be discussed in terms of its tendency to bind protons, metal ions, or any other Lewis acid. For a series of sufficiently similar donors, one expects a correlation to exist between basicities measured on different scales. Bruehlman and Verhoek[3] showed that the equation

$$\log K_{Ag} = a \log K_H + b \qquad (19)$$

is obeyed for several amines. K_{Ag} is the equilibrium constant of the reaction

$$Ag^+ + R \rightleftharpoons AgR^+ \qquad (20)$$

and K_H that of

$$H^+ + R \rightleftharpoons HR^+ \qquad (21)$$
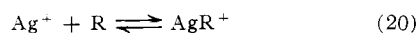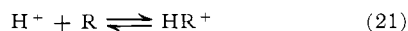
R being an amine. In order to investigate the corresponding correlation, we have compiled the known stability constants of Hg(II) complexes with nitrogen bases in Table II.

The listed value of each K_{Hg} is a "mean complexity constant"—the square root of the over-all association constants of the 2:1 complex (HgL_2^{+2}). The first and second stepwise formation constants are usually similar.[2] Therefore, K_{Hg} approximates β_1, the association constant of the 1:1 complex, which is not always measured separately from the over-all constant. The β_1 of many mercury complexes is particularly difficult to determine. In Fig. 2, log K_{Hg} is displayed as a function of log K_H.

One must be cautious in interpreting plots such as that presented here. There is likely to be some scatter due to different conditions of measurement and experimental error. It appears, however, that there is a rough correlation, but only a rough correlation, between log K_H and log K_{Hg}.

The most striking and obvious feature of this rough correlation, as displayed in Fig. 2, is the fact that the slopes of the lines in the equation log $K_{Hg} = a \log K_H + b$ are relatively large; $a = 0.93$ (lower line) and $a = 1.15$ (upper line). For silver, the corresponding slope is about 0.3. We have not made a careful study of other metal ions, but for Cu^{+2}, considering ammonia and pyridine as ligands, we find $a \approx 0.45$. The large value of the slope for Hg^{+2} correlates with the high strength of the Hg–N bond compared to other metal to nitrogen bonds.

Several additional qualitative generalizations emerge from Fig. 2, however. Alkylamines, primary, second-

ary, and tertiary, bind Hg(II) less well relative to protons than do other nitrogen bases. Bruehlman and Verhoek[3] noted a similar effect with Ag(I) and secondary and tertiary amines.

Heterocyclic nitrogen compounds such as the purines, pyrimidines, and imidazole derivatives bind particularly strongly. However, other π-electron systems, such as aniline and pyridine, do not. The strong binding by the heterocycles may be due to donation of d-electrons from Hg^{+2} into the π-electron system of the ring to place negative charge on the other nitrogen atoms. A similar but smaller effect would have been expected, but is not observed, for guanidine.

The slightly high value for ethylenediamine may be due to a small contribution from the formation of third and fourth bonds to Hg^{+2}. It is clear, however, that such chelate effects are very weak for Hg^{+2} as compared to, say Cu^{+2}, because of the tendency of Hg^{+2} to form two strong collinear bonds. The case of cycloserine may be complicated because there are two nonequivalent basic nitrogens in this molecule (in any case, the complex surely contains mercury–nitrogen bonds rather than mercury–oxygen bonds as suggested in ref. k of Table II).

We have drawn two lines in Fig. 2. The lower line is our suggestion as to the best correlation for typical amines without bulky alkyl substituents, and the upper line is for heterocyclic nitrogen compounds.

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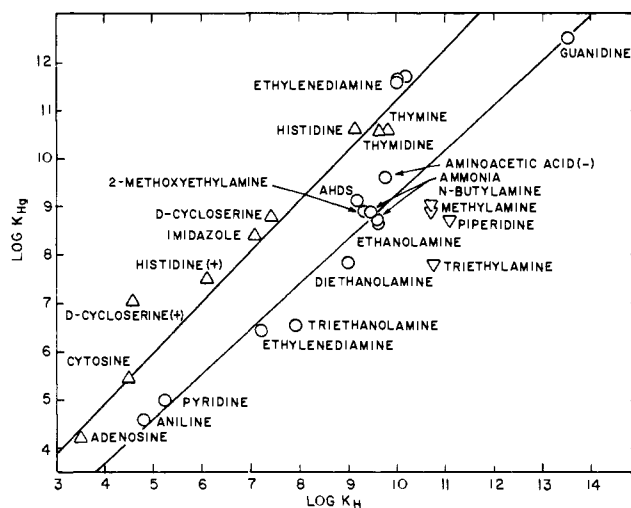

Fig. 2.— Complexes of Hg(II) with nitrogen bases; mean association constant (K_{Hg}) vs. proton affinity of the ligand (K_H) (AHDS = 2-amino-2'-hydroxydiethyl sulfide). Note that one of the points labeled ethylenediamine is for the singly protonated form. The two straight lines represent our suggestions for the best correlations for typical amines without bulky alkyl substituents (lower line) and for heterocyclic nitrogen compounds (upper line).

AT(11-1)-188. T. H. W. was a Woodrow Wilson Fellow in 1959–1960. We are indebted to Professor George S. Hammond for his optimistic attitude and helpful advice with regard to the interpretation of Fig. 2.

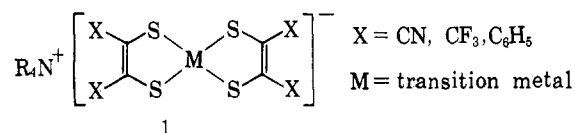# 1,2-Dicyanoethylene-1,2-dithiolate Chelates

BY J. F. WEIHER, L. R. MELBY, AND R. E. BENSON

Chelates derived from 1,2-dicyanoethylene-1,2-dithiol and certain transition metal ions exhibit singlet–triplet magnetic behavior which is attributed to spin interactions between pairs of metal ions through the sulfur atoms of adjacent ligands.

Dithiolate chelates **1** have been the subjects of

$$R_4N^+ \left[\begin{array}{c} X \\ \\ X \end{array} {>\!\!<}_S^S {>}M{<}_S^S {>\!\!<} \begin{array}{c} X \\ \\ X \end{array} \right]^-$$

1

X = CN, CF$_3$, C$_6$H$_5$

M = transition metal

recent publications.[1-3] The work reported here deals with the solid-state magnetic properties of bis(1,2-dicyanoethylene-1,2-dithiolato) chelates (**2**) wherein

$$(CH_3CH_2)_4N^+ \left[\begin{array}{c} NC \\ \\ NC \end{array} {>\!\!<}_S^S {>}M \right]_2$$

2
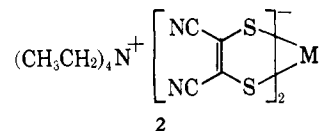
the metal ion formally has an odd-numbered d-electron configuration (M = Fe, Ni, Pd, or Pt). From studies of the temperature dependence of their magnetic susceptibilities, we find that these complexes exist in a singlet ground state with a corresponding low-

lying triplet state. These studies, together with X-ray data on **2** (M = Ni) suggest that spin correlation occurs through sulfur atom d-orbital interaction with the metal ion of an adjacent chelate molecule.

The nickel monoanion (**2**, M = Ni) has been reported[2] to exist in a doublet state (spin = $^1/_2$) in acetone solution. However, in the solid state the low magnetic moment ($\sim$1.0 B.M. at room tempreature) indicated significant exchange demagnetization. The platinum chelate (**2**, M = Pt), in the solid state, was shown to be weakly paramagnetic ($\sim$1.1 B.M. at room temperature).[2]

The temperature dependence of the magnetic susceptibility for a system of doublet spins coupled into pairs by an antiferromagnetic interaction is given[4] by

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \left[\frac{1}{3} e^{J/kT} + 1 \right]^{-1} + \chi_M{}^d + N\alpha \quad (1)$$

where J is the exchange coupling constant, g is the effective average splitting factor, $\chi_M{}^d$ is the underlying diamagnetic susceptibility, $N\alpha$ is the susceptibility due to temperature independent paramagnetism, β

(1) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

(2) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(4) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).