

Log K , ΔH° , and ΔS° Values for the Stepwise Replacement of Cl^- in $\text{HgCl}_2(\text{aq})$ by Ethylenediamine, Glycinate Ion, and Methylamine at 25° ¹

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Abstract: The stepwise reaction of Y (Y = ethylenediamine, glycinate ion, or methylamine) with $\text{HgCl}_2(\text{aq})$ in dilute aqueous solution has been studied, and the thermodynamic quantities ΔG° , ΔH° , and ΔS° , valid at zero ionic strength and 25° , have been determined. The species formed and the corresponding log K values were determined from pH titration data. Calorimetric ΔH° values were obtained, and ΔS° values were calculated from these and corresponding ΔG° values. In each system the reactions between $\text{HgCl}_2(\text{aq})$ and Y were found to produce the species HgClY and HgY_2 .

In a previous paper² a method for investigating ligand replacement reactions was used to study the interaction of OH^- with $\text{HgCl}_2(\text{aq})$. A computer technique was employed in the selection of the correct reaction sequence from among several proposed sequences, and the thermodynamic quantities ΔG° , ΔH° , and ΔS° were determined for the established reactions. This study has now been extended to include the reaction of methylamine (MeNH_2), ethylenediamine (en), and glycinate ion (G^-) with $\text{HgCl}_2(\text{aq})$.

The choice of these ligands should allow interesting comparisons to be made of the thermodynamic quantities for N-N vs. N-O chelation, and for unidentate (MeNH_2) vs. bidentate (en) type complex formation. It is also of interest to observe the effect of imposing with en by chelate formation a (presumably) tetrahedral arrangement on $\text{Hg}(\text{II})$ and observing whether Cl^- is associated with the resulting $\text{Hg}(\text{en})_2^{2+}$ species. In this connection, it has been observed³ that the third Cl in the $\text{Hg}^{2+}-\text{Cl}^-$ system is very weakly associated with $\text{HgCl}_2(\text{aq})$. Further, it is well known that $\text{Hg}(\text{II})$ forms a very stable dicoordinated species with unidentate ligands, while the tri- and tetracoordinated species have greatly reduced stability with respect to dissociation of one and two ligands, respectively. The stability of HgX_2 has been shown,⁴ at least in the cases of X = CN^- , I^- , Br^- , Cl^- , to be primarily a ΔH effect. It is now of interest to study the interaction of bidentate ligands with $\text{Hg}(\text{II})$ to see whether complex stability in these cases is primarily a result of ΔH or ΔS changes.

No previous determinations of the thermodynamic quantities for the interaction in dilute aqueous solution of en, G^- , or MeNH_2 with $\text{HgCl}_2(\text{aq})$ have been reported. However, the reactions in aqueous solution between these ligands and Hg^{2+} have been studied as has the

reaction of en with HgCl_4^{2-} .⁵ Roe, *et al.*,⁶ in a polarographic study determined ΔG , ΔH , and ΔS values for the formation of $\text{Hg}(\text{en})_2^{2+}$ from Hg^{2+} and 2en at 25° and ionic strength, $\mu = 0.1$ (KNO_3). Watters and Mason⁷ have reported a polarographic investigation of Hg^{2+} -en interaction in aqueous 0.1 F KNO_3 solution. Loras and Flood⁸ have investigated the interaction of G^- with Hg^{2+} at 20° and $\mu = 0.5$ and report a log β_2 (K_1K_2) value for the formation of $\text{HgG}_2(\text{aq})$. Bjerrum⁹ reports log K_1 and log K_2 values for the interaction of Hg^{2+} and MeNH_2 in aqueous solution at 25° and $\mu = 0.5$. No ΔH or ΔS values have been reported for the $\text{Hg}^{2+}-\text{G}^-$ or $-\text{MeNH}_2$ systems.

Reported in this paper are the species formed in dilute aqueous solution, together with ΔG° , ΔH° , and ΔS° values, valid at 25° and $\mu = 0$, for the interaction of en, G^- , and MeNH_2 with $\text{HgCl}_2(\text{aq})$.

Experimental Section

Materials. Reagent grade HgCl_2 (Baker and Adamson), NaOH (Baker Analyzed), ethylenediamine (Eastman White Label, 98% in water), glycine (Calbiochem, Grade A), methylamine (Matheson Coleman and Bell), HClO_4 (Baker and Adamson), and freshly boiled, double-distilled water of pH 6.3 to 6.8 were used in the preparation of solutions for the determinations. All stock solutions were stored either under a nitrogen atmosphere or in bottles equipped with ascarite-filled drying tubes to prevent CO_2 absorption.

A pH 4.008 buffer solution, prepared using potassium hydrogen phthalate (National Bureau of Standards [NBS] standard sample no. 185c), and a pH 6.865 buffer solution, prepared using KH_2PO_4 and Na_2HPO_4 (NBS samples 186-I-b and 186-II-b, respectively), were used in the pH determinations. The buffer solutions were prepared using instructions supplied by NBS and were stored under a CO_2 -free atmosphere.

Equilibrium Constant Determinations. The equilibrium constants were determined from pH titration data taken at 25° . The pH measurements were made with a Leeds and Northrup pH meter (catalog no. 7401) equipped with a 1000-ohm precision helipot introduced into the feedback circuit which increased the sensitivity and made the precision of the readings about ± 0.004 pH unit. The pH meter was calibrated using a Leeds and Northrup K-3 potentiometer and was equipped with Beckman glass and saturated calomel electrodes.

(1) (a) Supported by U. S. Atomic Energy Commission Contract AT(04-3)-299; presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, and in part at the First Western Regional Meeting, Los Angeles, Calif., Nov 1965; (b) taken from the Ph.D. dissertation of J. A. Partridge, Brigham Young University, May 1965.

(2) J. A. Partridge, R. M. Izatt, and J. J. Christensen, *J. Chem. Soc.*, 4231 (1965).

(3) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(4) (a) J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. D. Hale, *Inorg. Chem.*, **3**, 130 (1964); (b) J. J. Christensen, R. M. Izatt, and D. Eatough, *ibid.*, **4**, 1278 (1965).

(5) J. J. Wylegala, Ph.D. Dissertation, The Pennsylvania State University, University Park, Pa., 1956.

(6) D. K. Roe, D. B. Masson, and C. J. Nyman, *Anal. Chem.*, **33**, 1464 (1961).

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(8) V. Loras and H. V. Flood, *Tidsskr. Kemi, Bergvesen. Met.*, **5**, 83 (1945).

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The electrodes were calibrated immediately prior to each run using standard buffer solutions, and the calibration was checked immediately after the run. If the values before and after the run differed by more than 0.01 pH unit, the average of the two values was used for the standardization. In the very few cases in which the values differed by more than 0.03 pH unit, the runs were discarded.

For the HgCl_2 -en system, solutions 0.003998 and 0.001994 F in $\text{HgCl}_2(\text{aq})$ were titrated under a nitrogen atmosphere with aqueous solutions of en, and pH data were taken at appropriate intervals. For the HgCl_2 - G^- system, solutions containing HgCl_2 and G^- in a ratio of approximately 1:2.5 and having HgCl_2 concentrations ranging from 0.007996 to 0.002665 F were titrated with NaOH under a nitrogen atmosphere. For the HgCl_2 - MeNH_2 system, solutions of HgCl_2 and methylammonium perchlorate having HgCl_2 concentrations of 0.003463 and 0.002364 F were titrated under a nitrogen atmosphere with an aqueous solution of MeNH_2 . The affinity of the $\text{Hg}(\text{II})$ for MeNH_2 was much less than that for en, and the hydrolysis of $\text{HgCl}_2(\text{aq})$ was much more significant in the MeNH_2 system than in either the en or G^- systems. This problem was partially overcome in the $\text{HgCl}_2(\text{aq})$ - MeNH_2 study by adding methylammonium perchlorate to the solutions in order to increase the concentration of free MeNH_2 at a given pH value and, thus, enhance the amount of reaction between the $\text{Hg}(\text{II})$ and MeNH_2 .

Determination of ΔH° . The calorimeter¹⁰ and thermometric titration procedure¹¹ used to obtain the ΔH° values have been described. Solutions of (1) HgCl_2 and ethylenediamine, (2) HgCl_2 , methylammonium perchlorate, and methylamine, and (3) HgCl_2 , glycine, and NaOH were titrated with perchloric acid in the determinations.

Calculations. The calculation of correct equilibrium constant values requires a knowledge of the species formed during the pH titration. The method used in this study to determine the reactions occurring in the system has been described.² For a given HgCl_2 -ligand system, several possible reaction sequences are proposed which involve stepwise or nonstepwise addition of the ligand to $\text{Hg}(\text{II})$ accompanied by corresponding stepwise or nonstepwise release of Cl^- . Through computer analysis of the pH titration data in terms of \bar{n} , the average number of ligands (exclusive of Cl^-) bound per $\text{Hg}(\text{II})$, and free ligand concentration,^{15,12} the correct reaction sequence is selected. This selection is based on the premise that only when the correct reaction sequence is proposed will consistent thermodynamic equilibrium constants be obtained as a function of both \bar{n} and total metal concentration.

The \bar{n} values were calculated for the ligands other than Cl^- from the pH titration data. The equations used included the H^+ and OH^- balance equations and the several mass balance equations. Free Cl^- concentration was calculated from the charge balance equation at each experimental point for each reaction sequence considered. The effect of the hydrolysis of $\text{HgCl}_2(\text{aq})$ in each system studied was taken into account in the calculations using the results obtained in the previous study.²

Ionic strength effects were taken into account in the calculations using eq 1, where the several terms have their usual meaning.¹³

$$\log \gamma = \frac{-AZ^2\sqrt{\mu}}{1 + B\bar{a}\sqrt{\mu}} \quad (1)$$

Values of \bar{a} ranging from 4 to 7 Å were used in eq 1 to learn the effect of varying this parameter on the calculated $\log K$ values. The variation in the calculated $\log K$ values was found to be $<0.01 \log K$ unit indicating that in the low μ region studied the value used for \bar{a} was not critical. A value of 4 Å was used in the calculation of the results reported in this study. Activity coefficients thus obtained were used to convert pH, K_w (ion product of water), and the pK values of the ligands to the corresponding concentration quantities at each experimental point. This was done so that the quantities which were used in the equations for the

calculation of \bar{n} and the concentration quotients would be concentration terms and not a mixture of concentration and activity terms. The concentration quotients which were thus calculated for the $\text{HgCl}_2(\text{aq})$ -ligand interactions were then corrected to thermodynamic constants using activity coefficients. It was assumed that the activity coefficients were the same for all species of the same charge type and that the value was unity for a neutral species.

Since μ was not constant during a titration, it was calculated at each experimental point. In some cases this required a series of successive approximations since the concentrations of all the charged species were not known prior to the calculation of the equilibrium constants being determined. The computer programs were written such that recycling continued until successive approximations of μ agreed within 0.1%.

Calculation of the $\log K$ and ΔH° values for the reactions investigated in this study required a knowledge of the equilibrium constant and ΔH° values for the protonation of en, G^- , and MeNH_2 in solutions having low μ values. The pK and ΔH° (kcal/mole) values, respectively (valid at 25° and $\mu = 0$), used in this study were $\text{H}(\text{en})^+ = \text{H}^+ + \text{en}$ (9.91 ± 0.03 , 11.94 ± 0.06),¹⁴ $\text{H}_2(\text{en})^{2+} = \text{H}^+ + \text{H}(\text{en})^+$ (7.13 ± 0.03 , 11.03 ± 0.10),¹⁴ $\text{HG} = \text{H}^+ + \text{G}^-$ (9.780 ,¹⁵ 10.57 ± 0.07),¹⁴ $\text{H}_2\text{G}^+ = \text{H}^+ + \text{HG}$ (2.35 ,¹⁶ 0.97 ± 0.01),¹⁴ and $\text{MeNH}_3^+ = \text{H}^+ + \text{MeNH}_2$ (10.59 ± 0.01 , 13.25 ± 0.01).¹⁴ The uncertainties of these pK and ΔH° values are expressed as standard deviations. The ΔH° value for the ionization of water reported by Hale, *et al.*,¹⁶ was used in the calculations.

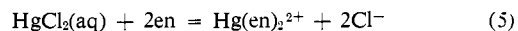
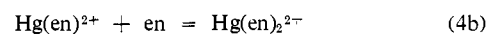
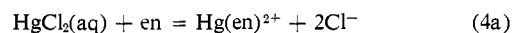
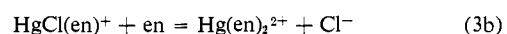
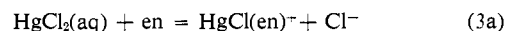
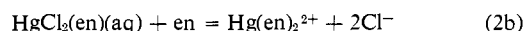
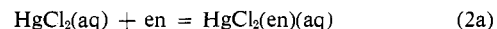
Heat of dilution data for the HClO_4 titrant were taken from the literature.¹⁷

The calculation of heats of reaction from thermometric titration data has been described.^{11,18}

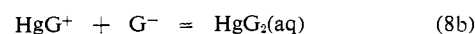
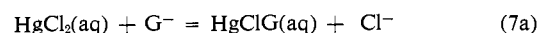
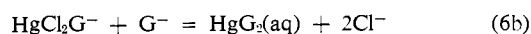
The solutions used in the calorimetric runs made in this study had μ values of about 0.01. Because of the observation in previous aqueous solution calorimetric studies^{16,19} in which ΔH values were obtained as a function of μ that the extrapolated ΔH values at $\mu = 0$ differed very little from those at $\mu = 0.01$, the heat of reaction values determined in this study are taken to be ΔH° values.

The calculations were aided by an IBM 7040 electronic computer.

Proposed Reaction Sequences. For the $\text{HgCl}_2(\text{aq})$ -en system, reaction sequences 2-5 were proposed as possible descriptions of the reactions occurring in the solution. In addition to these, sequences involving the formation of polynuclear species were proposed and tested.



For the $\text{HgCl}_2(\text{aq})$ -glycinate system, reaction sequences 6-8 were proposed as possible descriptions of the reactions occurring in the solutions.



For the $\text{HgCl}_2(\text{aq})$ - MeNH_2 system it was assumed that since

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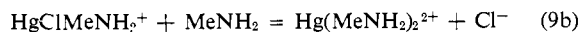
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MeNH₂ is a unidentate ligand the reactions were analogous to the HgCl₂(aq)-OH⁻ system, and log *K* values were calculated for reactions 9a and 9b only.



Results

The pH titration data together with calculated \bar{n} values are given in Table I. Log *K* values were cal-

Table I. Representative pH Titration Data for the HgCl₂(aq)-en, -G⁻, and -MeNH₂ Systems

Titrant, ml	pH	\bar{n}	Titrant, ml	pH	\bar{n}
HgCl₂(aq)-en System (titrant, 0.04504 F en; initial volume 49.98 ml)					
Initial [HgCl ₂] = 0.001994 F			Initial [HgCl ₂] = 0.003998 F		
0.904	6.103	0.347	1.684	6.156	0.340
1.060	6.198	0.420	1.953	6.248	0.400
1.182	6.273	0.475	2.208	6.328	0.458
1.346	6.368	0.549	2.416	6.388	0.505
1.468	6.438	0.605	2.626	6.449	0.553
1.588	6.504	0.660	2.842	6.611	0.602
2.967	7.239	1.298	6.165	7.440	1.361
3.200	7.372	1.405	6.450	7.523	1.426
3.415	7.500	1.504	6.696	7.607	1.482
3.619	7.644	1.596	6.938	7.688	1.537
3.752	7.751	1.657	7.228	7.792	1.602
3.860	7.849	1.706	7.450	7.882	1.653
HgCl₂(aq)-G⁻ System (initial volume, 49.98 ml)					
Titrant, 0.04051 F NaOH			Titrant, 0.04045 F NaOH		
Initial [HgCl ₂] = 0.002997 F			Initial [HgCl ₂] = 0.007996 F		
Initial [G ⁻] = 0.007948 F			Initial [G ⁻] = 0.01920 F		
1.321	5.172	0.347	3.422	5.201	0.342
1.432	5.259	0.376	4.225	5.430	0.421
1.618	5.390	0.424	5.922	5.843	0.590
1.810	5.542	0.472	6.647	5.999	0.661
1.990	5.655	0.519	7.405	6.147	0.736
2.241	5.802	0.584	14.176	7.387	1.403
5.238	7.238	1.361	14.974	7.531	1.482
5.461	7.344	1.417	15.986	7.745	1.578
5.587	7.405	1.446	16.735	7.902	1.648
5.738	7.475	1.487	17.202	7.997	1.690
5.906	7.560	1.525			
6.170	7.701	1.589			
HgCl₂(aq)-MeNH₂ System (titrant, 0.09141 F MeNH₂)					
Initial Volume, 211.0 ml			Initial Volume, 216.0 ml		
Initial [HgCl ₂] = 0.002364 F			Initial [HgCl ₂] = 0.003463 F		
Initial [MeNH ₂] = 0.03028 F			Initial [MeNH ₂] = 0.02958 F		
Initial [HClO ₄] = 0.02976 F			Initial [HClO ₄] = 0.02907 F		
0.634	5.896	0.226	2.600	6.300	0.330
0.981	6.056	0.270	3.596	6.520	0.416
1.390	6.207	0.319	4.298	6.653	0.482
2.110	6.446	0.414	4.955	6.764	0.533
2.700	6.606	0.497	5.505	6.855	0.571
3.622	6.832	0.623	7.500	7.159	0.750
4.988	7.127	0.820	11.740	7.770	1.120
7.878	7.789	1.190	12.351	7.872	1.150
9.248	8.281	1.290			

culated using the data in Table I for each of the reaction sequences proposed. The reaction sequences for which consistent log *K* values were obtained for the HgCl₂(aq)-en and G⁻ systems were 3 and 7, respectively, establishing these as the correct descriptions of the reactions occurring in these systems. Typical log *K* results as a function of \bar{n} and total Hg(II) concentration are given in Table II.

The log *K* values calculated for each of the other sequences proposed for the en and G⁻ systems had trends as a function of \bar{n} and/or total Hg(II) concentration,

Table II. Log *K*₁ and Log *K*₂ Values as a Function of \bar{n} and Total Hg(II) Concentration Involving Reaction Sequences 3 and 7

\bar{n}	Log <i>K</i> ₁	\bar{n}	Log <i>K</i> ₂	\bar{n}	Log <i>K</i> ₁	\bar{n}	Log <i>K</i> ₂
Reaction Sequence 3, HgCl₂-en System							
0.0020 F HgCl ₂				0.0040 F HgCl ₂			
0.24	5.55	1.24	4.18	0.26	5.56	1.21	4.17
0.33	5.55	1.34	4.18	0.34	5.56	1.31	4.17
0.39	5.55	1.41	4.17	0.40	5.55	1.43	4.17
0.46	5.55	1.55	4.17	0.46	5.54	1.54	4.16
0.53	5.55	1.61	4.17	0.55	5.54	1.60	4.16
0.60	5.54	1.71	4.17	0.60	5.53	1.65	4.16
Reaction Sequence 7, HgCl₂-G⁻ System							
0.0080 F HgCl ₂				0.0030 F HgCl ₂			
0.34	3.44	1.40	2.55	0.30	3.43	1.34	2.59
0.42	3.44	1.48	2.56	0.41	3.44	1.40	2.60
0.59	3.43	1.58	2.57	0.50	3.43	1.50	2.62
0.66	3.40	1.65	2.60	0.63	3.41	1.60	2.64

thus eliminating them as representing the main reactions in these systems. A typical set of such log *K* results as a function of \bar{n} and total Hg(II) concentration for sequences 4 and 8 are given in Table III. Results similar to these were obtained for sequences 2, 5, and all those involving polynuclear species in the en system, as well as sequence 6 for the HgCl₂(aq)-G⁻ system.

Table III. Log *K*₁ and Log *K*₂ Values as a Function of \bar{n} and Total Hg(II) Concentration Calculated Assuming (4) and (8) to Represent the Correct Reaction Sequences for the HgCl₂(aq)-en and HgCl₂(aq)-G⁻ Systems, Respectively

\bar{n}	Log <i>K</i> ₁	\bar{n}	Log <i>K</i> ₂	\bar{n}	Log <i>K</i> ₁	\bar{n}	Log <i>K</i> ₂
Reaction Sequence 4, HgCl₂-en System							
0.0020 F HgCl ₂				0.0040 F HgCl ₂			
0.25	2.97	1.26	7.11	0.25	3.35	1.24	6.97
0.42	3.27	1.43	7.05	0.42	3.56	1.44	6.88
0.63	3.46	1.56	7.02	0.52	3.64	1.54	6.88
0.73	3.54	1.73	7.02	0.67	3.73	1.64	6.86
Reaction Sequence 8, HgCl₂-G⁻ System							
0.34	1.41	1.33	4.66	0.32	1.02	1.30	5.08
0.42	1.49	1.40	4.75	0.48	1.16	1.50	5.03
0.59	1.60	1.49	4.68	0.53	1.20	1.54	5.03
0.67	1.62	1.58	4.66	0.60	1.24	1.61	5.03

The log *K* values determined in this study for the correct reaction sequence in each of the HgCl₂(aq)-ligand systems investigated are summarized in Table IV.

Table IV. Log *K*₁ and Log *K*₂ Values Valid at 25° and $\mu = 0$ for the Interaction of en, G⁻, and MeNH₂ with HgCl₂(aq)

	en	G ⁻	MeNH ₂
Log <i>K</i> ₁ ^a	5.54 ± 0.01	3.42 ± 0.01	2.40 ± 0.07
Log <i>K</i> ₂ ^a	4.19 ± 0.04	2.61 ± 0.02	2.21 ± 0.05
Reaction sequence	3	7	9

^a Uncertainties are given as standard deviations. The \bar{n} region covered for each system was 0.3-0.7 and 1.3-1.7 for log *K*₁ and log *K*₂, respectively, except in the case of MeNH₂ where the highest \bar{n} value obtained was approximately 1.3.

In Table V is given for typical runs the measured heat change in the calorimeter together with corrections for heat of stirring, heat of dilution of titrant, and the heat due to reactions occurring in the calorimeter for which

Table V. Representative Calorimetric Data for HgCl₂(aq)-Ligand Systems^a

Data point	Titrant, moles × 10 ³	ΔQT	ΔQ1	ΔQ2	ΔQ3	ΔQ4	ΔQ5	ΔQC	Δn ₁ , moles × 10 ³	Δn ₂ , moles × 10 ³
HgCl ₂ (aq)-en System (titrant 0.3931 F HClO ₄)										
1	0.02503	-0.1956	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.6213	-4.2873	6.7193	0.1398	0.0108	-0.0232	0.0039	2.7589	0.2356	-0.2696
3	0.7049	-4.9308	7.7346	0.0892	0.0108	-0.0282	0.0039	3.0751	0.2471	-0.2953
4	1.3660	-9.7205	15.6409	-0.2066	0.0111	-0.0655	0.0039	5.8590	0.0924	-0.3777
5	1.5317	-10.8925	17.5704	-0.2553	0.0113	-0.0681	0.0039	6.5653	0.0172	-0.3800
HgCl ₂ (aq)-G ⁻ System (titrant 0.1361 F HClO ₄)										
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.2503	-2.0418	0.0003	2.5136	0.3101	0.0326	0.0011	0.8159	0.0928	-0.1563
3	0.2926	-2.3414	0.0005	2.9638	0.3193	0.0490	0.0012	0.9923	0.0904	-0.1750
4	0.5950	-4.1645	0.0757	6.0450	0.3361	0.1773	0.0012	2.4708	-0.0622	-0.2386
5	0.7269	-4.4814	0.7239	5.9562	0.3363	0.1947	0.0012	2.7308	-0.0994	-0.2400
HgCl ₂ (aq)-MeNH ₂ System (titrant 0.1361 F HClO ₄)										
1	0.00315	-0.0316	0.0000	...	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.1538	-1.4759	1.8020	...	0.1675	0.0086	0.0002	0.5341	0.0000	-0.0675
3	0.1888	-1.8103	2.1995	...	0.1969	0.0391	0.0002	0.6569	-0.0054	-0.0780
4	0.3393	-3.1274	3.7895	...	0.2763	0.3133	0.0003	1.2835	-0.0568	-0.1140
5	0.3637	-3.3194	3.9883	...	0.2800	0.3746	0.0003	1.3552	-0.0685	-0.1157

^a All ΔQ and Δn values are differences taken between the indicated and first data points. All ΔQ values are given in calories. ΔQT = actual heat evolved in the calorimeter corrected for heat losses, stirring, and heat of dilution; ΔQ1 = heat resulting from ionization of two (en, G⁻) or one (MeNH₂) proton from H₂(en²⁺), H₂G⁺, or MeNH₃⁺; ^{14,15} ΔQ2 = heat resulting from ionization of one proton from H(en)⁺ or Hg⁺; ^{14,15} ΔQ3 = heat resulting from the reaction Hg(OH)₂(aq) + 2Cl⁻ = HgCl₂(aq) + 2OH⁻, ΔH° = -24.26 kcal/mole;² ΔQ4 = heat resulting from the reaction HgClOH(aq) + Cl⁻ = HgCl₂(aq) + OH⁻, ΔH° = -12.13 kcal/mole;² ΔQ5 = heat resulting from the reaction H₂O(aq) = H⁺ + OH⁻, ΔH° = 13.360 kcal/mole;¹⁶ ΔQC = heat evolved (ΔQT) corrected for heats of reactions ΔQ1, ΔQ2, ΔQ3, ΔQ4, and ΔQ5; Δn₁ = change in number of moles of HgCl(en⁺), HgClG, or HgClMeNH₂⁺; Δn₂ = change in number of moles of Hg(en)²⁺, HgG₂(aq), or Hg(MeNH₂)₂²⁺.

ΔH° values are known (*i.e.*, H₂O formation, protonation of free ligand, and HgCl₂(aq) hydrolysis) as a function of moles of titrant added. Also included in Table V are values for the change in the number of moles of HgClY and HgY₂ (Y = en, G⁻, or MeNH₂) as a function of moles of titrant added.

In Table VI are summarized the ΔG°, ΔH°, ΔS°, and TΔS° values determined in this study for the replacement of Cl⁻ from HgCl₂(aq) by en, G⁻, and MeNH₂, (reactions 3, 7, and 9, respectively).

Table VI. ΔG°, ΔH°, ΔS°, and TΔS° Values^a Valid at 25° and μ = 0 for the Stepwise Replacement of Cl⁻ from HgCl₂(aq) by en, G⁻, and MeNH₂

Ligand, reaction	ΔG°, kcal/mole	ΔH°, kcal/mole	ΔS°, eu	TΔS°, kcal/mole
en				
3a	-7.56 ± 0.01	-8.66 ± 0.17	-3.7	-1.1
3b	-5.72 ± 0.06	-9.03 ± 0.13	-11.1	-3.3
G ⁻				
7a	-4.67 ± 0.02	-6.10 ± 0.07	-4.8	-1.4
7b	-3.56 ± 0.03	-2.94 ± 0.06	2.1	0.62
MeNH ₂				
9a	-3.3 ± 0.1	-6.8 ± 0.2	-11.7	-3.5
9b	-3.0 ± 0.1	-1.0 ± 0.3	6.7	2.0

^a Uncertainties in the ΔH° values are given as standard deviations. The uncertainties in the ΔG° values are estimated from the uncertainties in the corresponding log K values (Table IV).

Discussion

The results in Tables II and III show the necessity of making equilibrium constant determinations under a number of experimental conditions since "equilibrium constants" can be calculated for any reaction or reaction sequence proposed for a given system. Through analysis of data obtained under a number of experimental

conditions, one can eliminate incorrect choices in the reactions proposed for a system. However, one must also be sure that trends in the results are not due to errors, systematic or otherwise, in the data.

Watters and Mason⁷ report evidence for aqueous Hg(II)-en complexes containing the ligands OH⁻ and enH⁺ in addition to en. No evidence was found in the present study for any Hg(II)-en species containing either OH⁻ or enH⁺; however, it should be pointed out that the two studies were carried out under quite different experimental conditions. If such species were present in the solutions used in the present study, they existed in negligible concentrations since the presence (in appreciable concentration) of species not taken into account in the equations prevents the calculation of consistent log K values for the reactions. Failure to include in the equations species accounting for as little as 3-5% of the total mercury present results in calculation of inconsistent log K values. This was learned early in this study when attempts were made to calculate log K values for the HgCl₂(aq)-en and -G⁻ interactions without taking the hydrolysis of HgCl₂(aq) into account in the equations.

No equilibrium constant or heat of reaction data have been reported previously for the systems studied here; therefore, no data comparisons are possible. However, the log β₂ values for the interaction of the ligands en, G⁻, and MeNH₂ with HgCl₂(aq) should differ from those for the interaction of the same ligands with Hg²⁺ by an amount equal to the log β₂ value for the formation of HgCl₂(aq) from Hg²⁺ and 2Cl⁻. Unfortunately, log β₂ values valid at 25° and μ = 0 are not available for the Hg²⁺-en, -G⁻, -MeNH₂, or -Cl⁻ systems. Thus, no better than fair agreement would be expected between the log β₂ values determined in the present study and those obtained from a combination of reported

values for the $\text{Hg}^{2+}\text{-Cl}^-$ systems and the other Hg^{2+} -ligand systems. Sillén²⁰ reports a $\log \beta_2$ value of 13.2 for the formation of $\text{HgCl}_2(\text{aq})$ from Hg^{2+} and 2Cl^- at 25° and $\mu = 0.5$. Combination of this value with the $\log \beta_2$ value of 23.2 reported by Roe, *et al.*,⁶ for the formation of $\text{Hg}(\text{en})_2^{2+}$ from Hg^{2+} and 2en at $\mu = 0.1$ gives a $\log \beta_2$ value of 10.0 for the reaction of $\text{HgCl}_2(\text{aq})$ with 2en . Considering the differences in μ values between the two studies, this β_2 value is in good agreement with the $\log \beta_2$ value of 9.73 obtained in the present study. A similar combination of Sillén's $\log \beta_2$ value for $\text{HgCl}_2(\text{aq})$ with the $\log \beta_2$ value of 19.2 reported by Loras and Flood⁸ for the formation of $\text{HgG}_2(\text{aq})$ from Hg^{2+} and 2G^- (20° , $\mu = 0.5$) gives a $\log \beta_2$ value of 6.0 for the reaction of $\text{HgCl}_2(\text{aq})$ with 2G^- . The agreement between this value and that obtained in the present study, 6.03, is probably fortuitous, since the two studies were carried out under different conditions of temperature and μ . Combination of Sillén's $\log \beta_2$ value for HgCl_2 with that of Bjerrum⁹ for $\text{Hg}(\text{MeNH}_2)_2^{2+}$ gives a $\log \beta_2$ value of 4.7 for the reaction of $\text{HgCl}_2(\text{aq})$ with 2MeNH_2 which is in good agreement with the $\log \beta_2$ value, 4.61, obtained in the present study.

The precision of the $\log K$ and ΔH° data for the $\text{HgCl}_2(\text{aq})\text{-MeNH}_2$ system was not nearly as good as that for the other systems in this study. As already mentioned, the problem of $\text{HgCl}_2(\text{aq})$ hydrolysis was much more significant in this system. This decreased the accuracy with which the equilibrium constants could be determined. Since the equilibrium constants are used in the analysis of the thermometric titration data, this also decreased the accuracy in the corresponding ΔH° values.

The data in Table VI for the $\text{HgCl}_2(\text{aq})\text{-en}$ and -G^- systems show that the main driving force for each of the reactions in these systems is the change in enthalpy. In fact, in the *en* system ΔH° and ΔS° oppose each other in each stepwise reaction. It is observed that the ΔH° values for the $\text{HgCl}_2(\text{aq})\text{-en}$ system are larger than the corresponding values for the $\text{HgCl}_2(\text{aq})\text{-G}^-$ system. As pointed out by Schwarzenbach,²¹ the affinity of group B type metal ions for N donor atoms is greater than that for O donor atoms leading to the expectation that the reaction of *en* (N-N bonding) with $\text{Hg}(\text{II})$ would be more exothermic than the corresponding reaction between G^- (O-N bonding) and $\text{Hg}(\text{II})$. A different explanation for the larger ΔH° values in the

$\text{HgCl}_2(\text{aq})\text{-en}$ system is that the ionic species formed in the *en* system would have a higher affinity for water molecules than the uncharged species formed in the reaction of G^- with $\text{HgCl}_2(\text{aq})$.

The data in Table VI show that the values of the thermodynamic quantities for the $\text{HgCl}_2(\text{aq})\text{-en}$ interaction differ markedly from those for the $\text{HgCl}_2(\text{aq})\text{-MeNH}_2$ interaction. Values of ΔH°_i for the *en* system are significantly more negative than the corresponding ΔH°_i values for the MeNH_2 system, indicating that both nitrogens are coordinated to the mercury in $\text{HgCl}(\text{en})^+$. The similar stabilities of $\text{HgCl}(\text{en})^+$ and $\text{Hg}(\text{en})^{2+}$ are interesting in light of the stabilities of known complexes of $\text{Hg}(\text{II})$ with unidentate ligands. For example, for the stepwise reaction of Cl^- , Br^- , I^- , NH_3 , SCN^- , or CN^- ^{3,4,22} with Hg^{2+} the stability constants for the first two species with each ligand are large, while the stepwise stability constants for the third and fourth species are many orders of magnitude smaller. This decrease in stability is accompanied by a change in configuration²³ from the linear HgX_2 species to the HgX_3^- and the tetrahedral HgX_4^{2-} species. When $\text{Hg}(\text{II})$ forms a chelate with bidentate *en* the large stability difference between two-coordinate and higher-coordinate $\text{Hg}(\text{II})$ disappears, probably because in the case of *en* there is no configuration change between two-coordinate and higher-coordinate $\text{Hg}(\text{II})$ since the two donor atoms of the *en* cannot coordinate *trans* to each other. Thus, there has been imposed on the $\text{Hg}(\text{II})$ a configuration other than linear by the first *en* molecule to coordinate.

The results of the present study do not establish whether G^- is uni- or bidentate in its interaction with $\text{HgCl}_2(\text{aq})$.

Using the values of ΔS° from Table VI, the entropy of $\text{Cl}^-(\text{aq})$ (13.2 eu),²⁴ the entropy of $\text{G}^-(\text{aq})$ (31.7 eu) reported by Brannan, *et al.*,²⁵ and the entropy of $\text{HgCl}_2(\text{aq})$ (39 eu) reported by Christensen, *et al.*,^{4a} entropy values of 53 and 73 eu are calculated for the $\text{HgClG}(\text{aq})$ and $\text{HgG}_2(\text{aq})$ species, respectively.

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