[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Steric Effects and the Stability of Complex Compounds. I. The Chelating Tendencies of N-Alkylethylenediamines, with Copper(II) and Nickel(II) Ions[1]

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The effect of steric hindrance on the chelating tendencies of diamines with copper(II) and nickel(II) ions has been illustrated using N-alkylethylenediamines. The stepwise formation constants of these two metal ions with $\mathrm{RNHCH_2CH_2NH_2}$- (R = H, Me, Et, *n*-Pr, *n*-Bu and *i*-Pr) have been determined at 0 and 25° and from these data the thermodynamic quantities ΔF, ΔH, and ΔS were calculated. Except for the *n*-butyl derivative, there is a general decrease in complex stability with increase in chain length of the straight chained alkyl groups. However complexes with N-*i*-propylethylenediamine are less stable than those of the straight chained alkyl derivatives. The steric effect on complexes of copper(II) and nickel(II) was much the same at a coördination number of four, but appreciably greater with nickel(II) at a coördination number of six.

The stepwise formation constants of numerous metal ammines have been determined using the now familiar technique employed originally by Bjerrum.[2] An excellent summary of much of this work done prior to 1950 is available in a review article on the tendency of metal ions toward complex formation.[3] The data collected by various investigators are tabulated here[3] in such a manner as to emphasize the rather good correlation between the hydrogen-ion affinity of particular ligands and their tendency toward complex formation. However, in a few isolated instances the correlation breaks down and these discrepancies can apparently be attributed to steric factors. It would therefore appear that a systematic study of the steric effect is desirable and this paper is the first of a series of such investigations.

Reported here are the results obtained on the chelating tendencies of N-alkylethylenediamines with copper(II) and nickel(II) ions at 0 and 25° in 0.50 *M* potassium nitrate solution. This particular choice of N-alkylethylenediamines was made as it was expected that they would have very nearly the same base strengths.[4] These two metal ions were chosen in an attempt to arrive at the effect of steric hindrance on three different configurations; copper(II) complexes with a coordination number of four are planar, Ni(II) complexes of this type at a coördination number of four are probably tetrahedral,[5] whereas at a coordination number of six they are octahedral.

Experimental

Calculation of Formation Constants.—The concentration formation constants for equilibria of the type $\mathrm{MA}_{(n-1)} + \mathrm{A} \rightleftarrows \mathrm{MA}_n$ are designated by the expression

$$K_n = [\mathrm{MA}_n]/[\mathrm{MA}_{(n-1)}][\mathrm{A}]$$

These constants may be found by measuring the *p*H of solutions prepared by adding a standard solution of amine to a solution containing known amounts of the metal ion plus hydrogen ions and a large amount of a non-complexing electrolyte. Suitable calculations give the consecutive concentration constants. The maximum value of *n* for systems investigated here was three, and the development due to Bjerrum,[3] modified by Verhoek,[6] was used with suitable simplifications in our case. If one assumes that in the range of $\bar{n} \sim 0.5$ the *p*H is not below 4.5, then by substitution in the formulas of Verhoek[6] it follows that

$$\bar{n}_{\mathrm{A}} = f_1/f_2;/[\mathrm{A}] = k_3/f_1V_{\mathrm{T}};\ \bar{n} = \frac{V}{V_0}\,k_1 - \frac{k_2}{\bar{n}_{\mathrm{A}}}$$

where

$f_1 = k_{\mathrm{AH}_2^{+2}}\mathrm{H}^+ + 2[\mathrm{H}^+]^2$

$f_2 = k_{\mathrm{AH}_2^{+2}}k_{\mathrm{AH}^{+1}} + k_{\mathrm{AH}_2^{+2}}[\mathrm{H}^+] + [\mathrm{H}^+]^2$

$k_1 = \dfrac{\text{molarity of amine}}{\text{molarity of metal ions}} = \dfrac{M_{\mathrm{A}}}{M_{\mathrm{M}}}$

$k_2 = \dfrac{\text{molarity of hydrogen ions}}{\text{molarity of metal ions}} = \dfrac{M_{\mathrm{H^+}}}{M_{\mathrm{M}}}$

$k_3 = k_{\mathrm{AH}_2^{+2}}k_{\mathrm{AH}^+}V_0M_{\mathrm{H}^+}$

V = volume of amine added

V_0 = initial volume of metal ion solution

$V_{\mathrm{T}} = V + V_0$

$k_{\mathrm{AH}_2^{+2}}$ and $k_{\mathrm{AH}^{+1}}$ = acid dissociation constants of the amine

At no time during these titrations did the *p*H fall below 4.5 at $\bar{n} \sim 0.5$. When $\bar{n}$ = 0.5, 1.5 and 2.5, there are about equal amounts of MA_{n-1} and MA_n, then, as a first approximation, $\log K_{\mathrm{metalammine}} = -\log\,[\mathrm{A}]$. At $\bar{n}$ nearly equal to the above numbers a correction factor Δ was added, $\Delta = \log\,[(\bar{n} - (n-1)]/n - \bar{n})$, which at no time exceeded 0.4 log *K* unit. With this correction a series of formation constants were obtained, which did not vary by more than 0.03 log *K* unit, in each titration. This represents a simpler method of calculating the formation constants without any loss in accuracy.

Each of the constants were measured at two temperatures, 0 and 25°. By using the equation

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\,\frac{(T_2 - T_1)}{(T_2T_1)}$$

the ΔH quantities (enthalpy changes) were evaluated. This equation is valid at constant ΔH and it was therefore necessary to show (Fig. 4) that ΔH was essentially constant over the short range of temperature employed in these studies. Bonding energies for each reaction step can conveniently be expressed in terms of changes in free energy, ΔF, as calculated from the equation $\Delta F = -RT\ln K$. The change in entropy was in turn calculated using the equation $\Delta F = \Delta H - T\Delta S$.

Reagents.—Ethylenediamine was obtained commercially and redistilled after drying over sodium hydroxide. The diamines N-Meen, N-Eten, N-*n*-Buen, and N-*i*-Pren[7] were prepared by the method of O'Gee and Woodburn.[8] N-*n*-Propylethylenediamine was obtained by the courtesy of Dr. H. M. Woodburn at the University of Buffalo.

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[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[3] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[4] F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 2373 (1952).

[5] D. P. Mellor, *Chem. Revs.*, **33**, 137 (1943).

[6] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 134 (1945).

[7] The diamines discussed here are designated as follows: en = ethylenediamine; N-Meen = N-methylethylenediamine; N-Eten = N-ethylethylenediamine; N-*n*-Pren = N-*n*-propylethylenediamine; N-*n*-Buen = N-*n*-butylethylenediamine; N-*i*-Pren = N-*i*-propylethylenediamine.

[8] R. C. O'Gee and H. M. Woodburn, THIS JOURNAL, **73**, 1370 (1951).

The properties of these amines are described in a previous note.[4]

Standard Solutions.—The amines were diluted with distilled water until approximately 5 molar and then titrated with standard hydrochloric acid by conductometric and *p*H titration. Both methods gave the same result and the molarity of the amines was known with an accuracy of 2 parts per thousand (p.p.t.).

The copper standard solution, approximately 0.1 *M* nitric acid, 0.05 *M* copper nitrate and 0.50 *M* potassium nitrate, was standardized; the copper by electrode position, the nitric acid by titration against standard base. The primary standard for all acid-base titrations was a sample of potassium acid phthalate obtained from the Bureau of Standards. The molarity of the copper was known to 2 p.p.t. and that of the nitric acid 1 p.p.t.

The nickel nitrate standard solution was made up to approximately 0.1 *N* nitric acid, 0.05 *M* nickel nitrate and 0.50 *M* in potassium nitrate. The nickel concentration was determined by electrodeposition and by dimethylglyoxime precipitation, the nitric acid concentration by titration with standard base. The nickel molarity was known to 2 p.p.t. and the nitric acid concentration to 1 p.p.t.

All chemicals used were of the analytical reagent grade and the nitric acid was boiled before use to expel the oxides of nitrogen.

Measurements of *p*H were made with a Beckman *p*H meter, model G, equipped with a model 1190-90 glass electrode which was useful over a temperature range −5 to 100° and to a *p*H of 11 in the absence of sodium ion. None of the solutions measured contained any appreciable concentration of sodium ion or had a *p*H over 11. A saturated calomel electrode, model E, was used in conjunction with the glass electrode.

The solutions were maintained at a constant temperature by means of a constant temperature bath at 25 ± 0.1° and by means of an intimate mixture of ice and water at 0 ± 0.1°.

Results.—The acid dissociation constants have been previously reported[5] except for ethylenediamine. These were determined in exactly the same manner as described previously and the following results were obtained.

	$pK_{AH_2^{+2}}$	pK_{AH^+}
0°	7.98	10.73
25°	7.47	10.18

A portion of the experimental data for the determination of the formation constants of nickel are given in Table I. The first column gives the volume of amine added to 50.00-ml. portions of the standard nickel nitrate solution. The second column shows the *p*H of the resulting solution while the data in the other columns are calculated from the equations designated previously. In most cases $\bar{n}$ was plotted against *p*[A] and formation curves were obtained as shown in Fig. 1. At least two titrations were made for each temperature and in the case of en, N-Eten, N-*i*-Pren, N-*n*-Pren, two different samples of amine were used. The formation constants obtained agreed within ±0.02 log *K* unit for different titrations and ±0.03 log *K* unit between different samples of amine. All measurements were made in 0.5 potassium nitrate to keep the ionic strength almost constant.

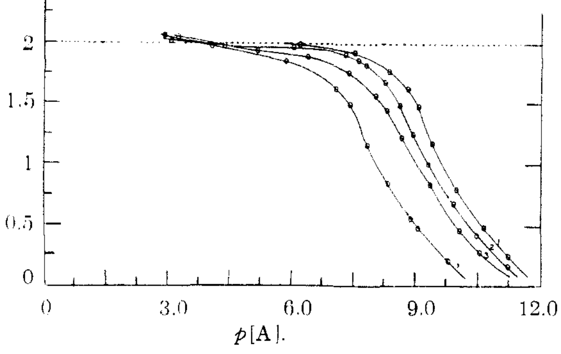

Fig. 1.—Formation curves of copper(II) with N-alkylethylenediamines (25°): 1, en; 2, N-Meen; 3, N-Eten; 4, N-*i*-Pren.

Tables II and III contain the formation constants for nickel(II) and copper(II) complexes, respectively, and these are represented graphically in Figs. 2 and 3. Additional thermodynamic quantities calculated from these data are summarized in Tables IV and V.

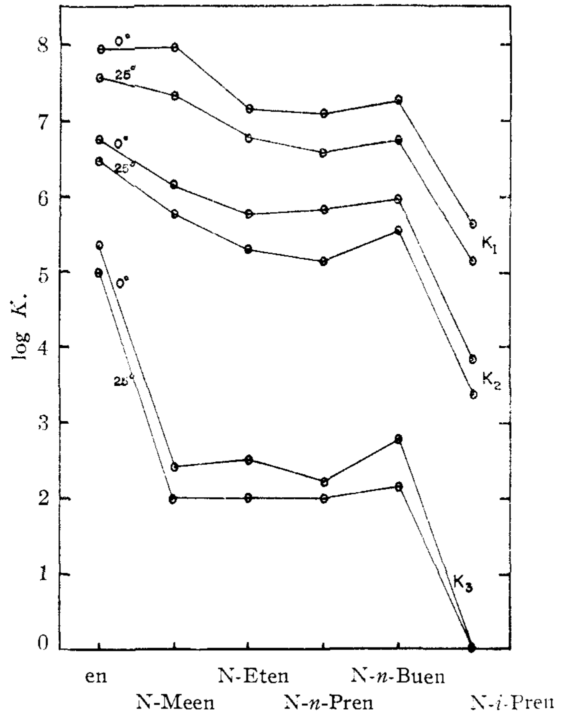

Fig. 2.—Formation constants of nickel(II) with N-alkylethylenediamines (0 and 25°).

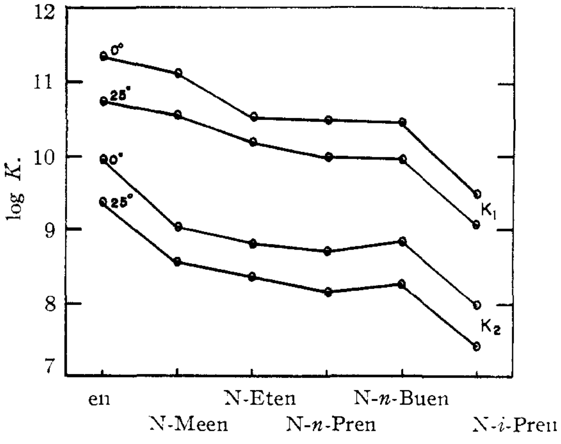

Fig. 3.—Formation constants of copper(II) with N-alkylethylenediamines (0 and 25°).

TABLE I

SAMPLE DATA FOR THE DETERMINATION OF FORMATION CONSTANTS

Nickel(II) nitrate, 0.04084 *M*; N-*n*-propylethylenediamine, 5.932 *M*; nitric acid, 0.1001 *M*; potassium nitrate, 0.500 *M*; V_0 = 50.00 cc.; $k_1 = 145.2$; $k_2 = 2.449$; $k_3 = 2.606 \times 10^{-19}$; $pK_{\mathrm{AH}^{+2}} = 8.24$; $pK_{\mathrm{AH}^+} = 11.04$.

Ml.	*p*H	f_1	f_2	V/V_0	$\bar{n}_A$	$\bar{n}$	*p*[A]	Δ	log *K*
0.569	6.66	9.629×10^{-14}	4.877×10^{-14}	0.01138	1.974	0.411	7.26	−0.16	7.10
.680	6.70	8.034×10^{-14}	4.074×10^{-14}	.01160	1.972	.442	7.19	− .10	7.09
.591	6.72	7.329×10^{-14}	3.719×10^{-14}	.01182	1.971	.473	7.15	− .05	7.10
.602	6.75	6.368×10^{-14}	3.235×10^{-14}	.01204	1.968	.504	7.09	+ .01	7.10
								Av. log K_1	7.10
0.944	7.36	4.034×10^{-15}	2.142×10^{-15}	0.01888	1.883	1.440	5.90	−0.10	5.80
.967	7.40	3.396×10^{-15}	1.812×10^{-15}	.01934	1.874	1.501	5.82	+ .00	5.82
.994	7.44	2.828×10^{-15}	1.518×10^{-15}	.01988	1.863	1.572	5.73	+ .12	5.85
								Av. log K_2	5.82
1.718	9.79	9.784×10^{-19}	10.045×10^{-19}	0.03436	0.974	2.475	2.29	−0.04	2.25
1.743	9.84	8.271×10^{-19}	8.603×10^{-19}	.03486	.961	2.514	2.21	+ .03	2.24
1.768	9.90	7.520×10^{-19}	7.883×10^{-19}	.03536	.954	2.567	2.17	+ .12	2.29
1.792	9.97	6.372×10^{-19}	6.778×10^{-19}	.03584	.940	2.599	2.10	+ .17	2.27
								Av. log K_3	2.26

TABLE II

FORMATION CONSTANTS OF NICKEL(II) WITH N-ALKYL ETHYLENEDIAMINES

0°	en	N-Meen	N-Eten	N-*n*-Pren	N-*n*-Buen	N-*i*-Pren
log K_1	7.92	7.95	7.19	7.10	7.25	5.62
log K_2	6.77	6.15	5.78	5.82	5.97	3.84
log K_3	5.36	2.41	2.51	2.26	2.79	..
log K_t	20.05	16.51	15.48	15.18	16.01	9.46
$\log \frac{K_1}{K_2}$	1.15	1.80	1.41	1.28	1.28	1.78
$\log \frac{K_2}{K_3}$	1.41	3.74	3.27	3.36	3.18	3.84
$\frac{\log K_{\mathrm{Ni}^{+2}}\text{ (av.)}}{\log K_{\mathrm{AH}^+}}$	0.62	0.51	0.46	0.46	0.49	0.28
25°						
log K_1	7.60	7.36	6.78	6.60	6.73	5.17
log K_2	6.48	5.74	5.30	5.16	5.56	3.47
log K_3	5.03	2.01	2.00	2.00	2.20	..
log K_t	19.11	15.11	14.08	13.76	14.49	8.64
$\log \frac{K_1}{K_2}$	1.12	1.62	1.48	1.44	1.17	1.70
$\log \frac{K_2}{K_3}$	1.45	3.73	3.30	3.16	3.36	3.47
$\frac{\log K_{\mathrm{Ni}^{+2}}\text{ (av.)}}{\log K_{\mathrm{AH}^+}}$	0.63	0.48	0.44	0.43	0.47	0.27

TABLE III

FORMATION CONSTANTS OF COPPER(II) WITH N-ALKYLETHYLENEDIAMINES

0°	en	N-Meen	N-Eten	N-*n*-Pren	N-*n*-Buen	N-*i*-Pren
log K_1	11.34	11.12	10.55	10.49	10.47	9.46
log K_2	9.95	9.03	8.81	8.70	8.82	8.00
log K_t	21.29	20.15	19.36	19.19	19.29	17.46
$\log \frac{K_1}{K_2}$	1.39	2.09	1.74	1.79	1.65	1.46
$\frac{\log K_{\mathrm{Cu}^{+2}}\text{ (av.)}}{\log K_{\mathrm{AH}^+}}$	0.99	0.93	0.87	0.87	0.88	0.78
25°						
log K_1	10.76	10.55	10.19	9.98	9.94	9.07
log K_2	9.37	8.56	8.38	8.16	8.27	7.45
log K_t	20.13	19.11	18.57	18.14	18.21	16.52
$\log \frac{K_1}{K_2}$	1.39	1.99	1.81	1.82	1.67	1.62
$\frac{\log K_{\mathrm{Cu}^{+2}}\text{(av.)}}{\log K_{\mathrm{AH}^+}}$	1.04	0.92	0.88	0.88	0.88	0.78

TABLE IV

THERMODYNAMIC QUANTITIES FOR THE FORMATION OF NICKEL(II) COMPLEXES AT 0°

Δ*F* and Δ*H*, kcal.; Δ*S*, cal./deg.

	en	N-Meen	N-Eten	N-*n*-Pren	N-*n*-Buen	N-*i*-Pren
ΔF_1	− 9.89	− 9.93	− 8.98	− 8.87	− 9.06	− 7.02
ΔF_2	− 8.46	− 7.68	− 7.22	− 7.27	− 7.46	− 4.80
ΔF_3	− 6.69	− 3.01	− 3.13	− 2.82	− 3.48	.....
ΔF_t	−25.04	−20.62	−19.33	−18.96	−20.00	−11.82
ΔH_1	− 4.8	− 8.8	− 6.1	− 7.5	− 7.8	− 6.7
ΔH_2	− 4.3	− 6.1	− 7.2	− 9.9	− 6.1	− 5.5
ΔH_3	− 4.9	− 6.0	− 7.6	− 3.9	− 8.8	.....
ΔH_t	−14.0	−20.9	−20.9	−21.3	−22.7	−12.2
ΔS_1	+19	+ 4.0	+10.6	+ 5.1	+ 4.8	+ 1.1
ΔS_2	+15	+ 5.9	+ 0.4	− 9.5	+ 5.1	− 2.6
ΔS_3	+ 7	−11.0	−16.5	− 4.0	−19.4	.....
ΔS_t	+41	− 1.1	− 5.5	− 8.4	− 9.5	− 1.5

TABLE V

THERMODYNAMIC QUANTITIES FOR THE FORMATION OF COPPER(II) COMPLEXES AT 0°

Δ*F* and Δ*H*, kcal; Δ*S*, cal./deg.

	en	N-Meen	N-Eten	N-*n*-Pren	N-*n*-Buen	N-*i*-Pren
ΔF_1	−14.16	−13.89	−13.18	−13.10	−13.08	−11.82
ΔF_2	−12.43	−11.28	−11.00	−10.87	−11.02	− 9.99
ΔF_t	−26.59	−25.17	−24.18	−23.97	−24.10	−21.81
ΔH_1	− 8.6	− 8.5	− 5.4	− 7.6	− 8.0	− 5.8
ΔH_2	− 8.6	− 7.0	− 6.4	− 8.0	− 8.2	− 8.2
ΔH_t	−17.2	−15.5	−11.8	−15.6	−16.2	−14.0
ΔS_1	+21	+20	+29	+20	+19	+22
ΔS_2	+14	+16	+17	+11	+12	+ 7
ΔS_t	+35	+36	+46	+31	+31	+29

The acid dissociation constants of N-*n*-PrenH_2^{+2} were determined at five different temperatures in the range 0–40° and a straight line plot of log *K* *vs.* 1/*T* was obtained. This was extended to the formation constants for copper(II) complexes as shown in Fig. 4.

Discussion

According to Bjerrum[4] the ratio log $K_{\mathrm{M}^{+2}}$/log K_{H^+} decreases whereas the difference between successive formation constants increases whenever steric factors affect the affinity of a base for the metal ion. Therefore the results obtained (Tables II and III) give evidence for steric hindrance during the formation of nickel(II) and copper(II) complexes in going from ethylenediamine to the N-alkylethylenediamines. Similarly Figs. 2 and 3 show that there is very little difference between the straight chain alkyl groups but the complexes

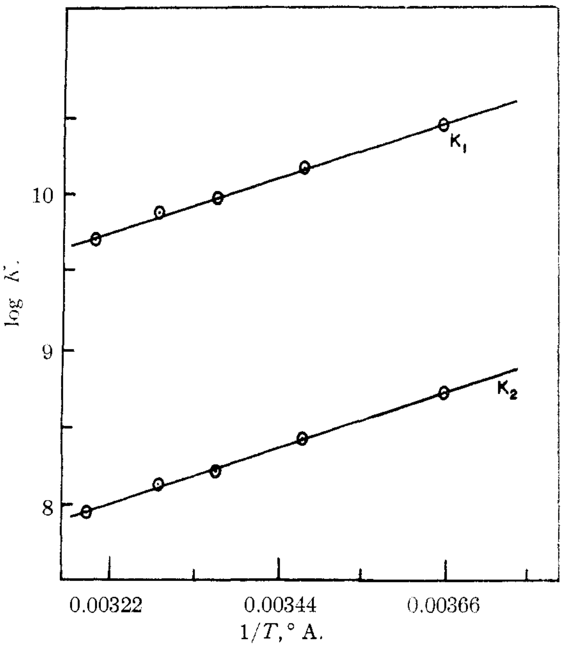

Fig. 4.—Temperature *vs.* log *K*: Cu^{+2} with N-*n*-propylethylenediamine at 0, 15, 25, 32 and 40°.

containing the isopropyl derivative are appreciably less stable. It should also be mentioned that although the complex stabilities in general decrease slightly from the methyl to the *n*-propyl substituted derivatives, this is always followed by an increase at the N-*n*-Buen. The enhanced stability at this point may possibly be attributed to the fact that a four-carbon chain can conveniently coil itself around in such a way as to shield the central atom and render it less accessible to contacts with the solvent. A similar interpretation[9] has been given recently to account for the increasing stability of *β*-diketone complexes which contain larger end groups on the diketone.

The generalizations made above apply both for the planar configuration of copper(II) complexes and the tetrahedral nickel(II) compounds. A consideration of molecular models likewise shows that the steric factors involved here are much the same for both structures. Of course there is also a good chance that the bis-(diamine)-nickel(II) complexes, $[Ni(AA)_2]^{+2}$, actually contain two molecules of water and have an octahedral structure of the type $[Ni(AA)_2(H_2O)_2]^{+2}$. In such a case if the water molecules are *trans* to each other then the chelate rings will be coplanar and the steric consideration would be essentially analogous to those of the copper(II) complexes. The steric effect, as expected, is considerably greater with the formation of the tris-(diamine)-nickel(II) compounds of an octahedral configuration.

That ΔH is constant between the temperatures 0–40° is shown by the linear plot of log *K* *vs.* $1/T$ in Fig. 4. The calculated values for heats of formation and entropy (Tables IV and V) are therefore believed to be reliable at these conditions. The N-alkylethylenediamine complexes of nickel(II) of the type $[Ni(AA)_2]^{+2}$ have ΔH values of approximately −13 kcal. and ΔS of +5 cal./deg. as compared to ΔH of −15 kcal. and ΔS of +30 cal./deg. for the $[Cu(AA)_2]^{+2}$ complexes. The greater free energy changes with copper(II) as compared to nickel(II) are primarily an entropy effect. It is not readily apparent why there should be such an appreciable difference in the entropy terms of these two systems.

There is little difference between the heats of formation and entropy changes between the reaction of ethylenediamine with copper(II) and its complex formation with the substituted diamines. However, a considerable difference was observed with the chelations of nickel(II). The explanation of Frank and Evans[10] for the large differences in entropy observed with the formation of $(Ni(CH_3NH_2)_6]^{+2}$ as compared to $[Ni(NH_3)_6]^{+2}$ does not appear to be applicable to the results obtained with the diamine complexes.

In conclusion it should be stated that in spite of having made numerous different determinations with the ethylenediamine systems, our values for ΔH and ΔS do not agree with those of other investigators.[11] However, the values of ΔF are in good agreement with those obtained by Irving.[11]

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(11) M. Calvin and R. Bailes, THIS JOURNAL, **68**, 953 (1946), report for the reaction $Ni^{+2} + 3\ en \rightleftarrows [Nien_3]^{+2}$ a value of −25 kcal. for ΔH and +2 cal./deg. for ΔS. H. Irving, unpublished results, taken from summary paper of a talk given in 1951 on "The Stability of Coordination Compounds in Aqueous Solution and the Varying Strengths of Metal–Ligand Bond." The results given by Irving are

	ΔF, kcal.	ΔH, kcal.	ΔS, cal./deg.
$Ni^{+2} + en \rightleftarrows [Nien]^{+2}$	− 9.9	−12.6	−11.9
$Ni^{+2} + 2\ en \rightleftarrows [Nien_2]^{+2}$	−18.0	−26.2	−26.6
$Cu^{+2} + en \rightleftarrows [Cuen]^{+2}$	−14.2	−18.9	−15.5
$Cu^{+2} + 2\ en \rightleftarrows [Cuen_2]^{+2}$	−26.3	−35.8	−31.4