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Metal Ammine Formation in Solution

IX. Heats and Entropies of Successive Steps in the Formation of Nickel(II) and Copper(II) Ethylenediamine and Trimethylenediamine Complexes

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Estimation of heats of reaction from temperature coefficients in systems with several consecutive constants demands a high precision of the measurements, and with many authors this fact has led to inconsistent results due to an overestimate of the data. In this paper we have, therefore, determined the heats by calorimetric titration of solutions in which the distribution of the complexes are known from affinity measurements. The nickel(II) and copper(II) systems with ethylenediamine (en) and trimethylenediamine (tn) were examined. The heats of successive steps were found to be rather constant. This means that the variation in free energy with the number of ligands taken up is mainly determined by the entropy change, and we suppose this to be a common rule for most complex systems with uncharged ligands.

J. Bjerrum [1,p. 289] has previously shown that the consecutive formation constants of various metal ammonia systems in aqueous solutions of ammonium nitrate (until 5 M), and in a small interval around a standard temperature T_0 (*e.g.* $T = 298° \pm 5°$ K) can be expressed by formulae of the type:

$$\log K_n = \log K_n^\circ + \alpha\,(T_0 - T) + \beta \cdot C_{salt} \qquad (1)$$

where α and β are constants for the system in question for all values of n until the characteristic coordination number is reached. Introducing the heats and entropies for the uptake of the n'th ligand, we may put *:

$$\log K_n = \frac{\Delta S_n}{2.3\ R} - \frac{\Delta H_n}{2.3\ RT}\ ,$$

* In this paper quantities for the n'th step is denoted by K_n, ΔH_n, ΔS_n *etc.*, and the corresponding gross qualities by $K_{1\text{-}n}$, $\Delta H_{1\text{-}n}$, $\Delta S_{1\text{-}n}$ *etc.*

where

$$\Delta H_n = 2.3\, RTT_0\alpha \sim 2.3\, RT_0^2\alpha.$$

The validity of formula (1) shows that the heats of the successive steps are the same within the uncertainty of the experiment, and further that the heats do not vary with the salt concentration of the medium. The variation of log K_n (i) with the salt medium and (ii) with the number of ligands taken up in sequence is mainly to be found in the entropy: a very reasonable result which agrees well with the fact that the ratios between the consecutive constants have been shown to be mainly statistically determined [1].

Estimation of heats from temperature coefficients in systems with several consecutive constants demands a high precision of the measurements, and with some exceptions [2] this fact has led many authors to inconsistent results due to an overestimate of their data. In this paper we have, therefore, preferred to determine the heats by calorimetric titration of solutions in which the distribution of the complexes are known from affinity measurements. Examined were the nickel(II) and copper(II) systems with ethylenediamine (en) and trimethylenediamine (tn) * in 1 M KNO_3 and partly also in solutions free from neutral salt. Calvin [6] and later Schwarzenbach [4] suggested that complex formation with chelates gives a higher entropy than with simple ligands, and it was a special purpose of this investigation to study this effect for non-charged ligands forming 5- and 6-membered rings.

In this paper we discuss first the calorimetric measurements, then potentiometric determinations of the complexity constants, and finally the thermodynamic data.

EXPERIMENTAL

The calorimeter was a 500 ml nickelplated brass calorimeter with a glass stirrer driven by air pressure. The Beckman thermometer was adjusted for each five degrees and could be read with an error of 0.001 degree. The heater used in the measurements of the heat capacity was made of two nickelplated brass rods connected with ten 0.1 mm coiled coil tungsten wires. The current was measured by means of a precision ammeter, which could be read within an error of 0.2 %, the potential over the wires was measured on a Vernier potentiometer from Cambridge Instrument Co., and the time, with an uncertainty of about one half of a second, on a stop watch connected to the heater switch. A few experiments in which was measured the heat capacity of 1.2 M potassium nitrate solution as well as that of mixed solutions of potassium nitrate and barium (or nickel) nitrate, showed that it was permissible to exchange up to 10 % of the potassium nitrate with the equivalent amount of bivalent nitrate and still get the same heat capacity of the solution within one half of a per cent. The heat capacities of the mixed solutions could therefore be identified with the heat capacities of pure potassium nitrate solutions of same total nitrate normality. The data for potassium nitrate was taken from Randall and Rossini [7], and a curve giving the specific heat capacity at 25° C as function of moles KNO_3 per 1 000 g H_2O was used in evaluating the heat capacities of the mixed solutions in question. The heat capacity of the calorimeter + part of the stirrer + part of the thermometer was considered constant throughout the experiments and calculated to

* 1,3-Diaminopropane or trimethylenediamine, abbreviated to *tn* by Werner [3], has recently been called propylenediamine (pn) by Schwarzenbach [4]. This is a very unfortunate choice since propylenediamine has hitherto always been identified with 1,2-diaminopropane. Irving *et al.*[5] use the abbreviation dmp for 1,3-diaminopropane. This is a better choice, but it does not allow to distinguish between the two isomers.

be 20.1 cal/degree using values of the specific heat capacities for brass and glass given in the Landolt-Börnstein tables.

Procedure. The measurements, *e.g.* the reaction between nickel ion and ethylenediamine, were carried out with the same amount of ethylenediamine in almost all cases and varying amounts of nickel nitrate, in order to obtain the mole ratios en : Ni^{++} of 1 : 1, 1 : ½ and 1 : ⅓. The proper amounts of the stock solutions of the various salts and distilled water were weighed into the calorimeter to give a total amount of solution of 430 ml (calculated as the sum of the volumes of the stock solutions and the volume of the water added). The temperature was followed until the rate of increase remained constant for about 10 minutes, and in the next minute about 5 ml of the diamine stock solution was added through a hole in the cover of the calorimeter after which the temperature was followed until the rate of increase (or decrease) again was constant for 10 minutes. The diamine was added by means of a calibrated syringe pipette and its temperature was known within 0.01° C. The heat of dilution of the diamine stock solution was determined in an analogous experiment in which the nickel (or copper) nitrate was replaced normally with an equivalent amount of barium nitrate. Measurements at different concentrations showed that the heat of dilution for the salt medium used decreased almost linearly with increasing total concentration of nitrate ions (*cf.* Table 1 A).

Solutions. The nickel nitrate stock solution (0.5 M) was made from ANALAR reagent and the concentration in moles per 1 000 g of solution was determined by precipitation with dimethylglyoxime. The copper nitrate stock solution was made from Merck's copper(II) nitrate *p.a.*, and the concentration (moles per 1 000 g of solution) determined by thiocyanate titration according to Hagen [8]. Ethylenediamine (en) from Sharplet Chemical Inc. Phil. was distilled through a column, and the fraction taken at 117° C. was diluted 1 : 1 with distilled water. Trimethylenediamine (tn) from Sharplet Chemical Inc. Phil. was distilled in the same way and the fraction 134—137° C diluted 1 : 1 with distilled water. The molar concentration of the amine stock solutions (about 7 M) was determined by titration with standard acid solution using methyl orange as indicator. The densities of the stock solutions were determined in all cases in order to make a correlation of the different concentration units possible.

CALORIMETRIC DATA

The data were calculated from the usual calorimeter equation, with a correction for the amount of heat added with the diamine solution:

$$Q = (C + cW)\,(t_2 - t_1) - c_a w\,(t_a - t_1)$$

In this equation $C = 20.1$ cal/degree is the total heat capacity of the calorimeter, and W the total gram weight of the solution including the weight of the added amine. $t_2 - t_1$, the temperature increase in ° C during the reaction, was obtained by graphical extrapolation. The specific heat capacity of the reacting solution, c, was estimated graphically as mentioned above from the total nitrate normality per 1 000 g H_2O in the final solution. c_a, the specific heat capacity of the diamine solutions, was chosen as 0.8 cal/degree from a consideration of the values of the heat capacities of various other organic bases in aqueous solution at a similar concentration. t_a is the temperature, and w, the gram weight of the added amount of amine solution. All the calorimetric measurements were performed at 20—22° C.

Table 1 A gives the experimental details about the heats of reaction (Q) determined for two nickel nitrate solutions and the corresponding measurements of the heats of dilution (Q_{dil}) of ethylenediamine in barium nitrate containing solutions. The difference $Q - Q_{dil}$ for solutions of the same total nitrate normality should be the heat of the ammine formation. Ethylene-

Table 1 A. Detailed calorimetric data for the reaction of two nickel and three barium solutions of similar nitrate normalities with a fixed amount of ethylenediamine.

No.	moles of KNO_3	moles of $Ni(NO_3)_2$	moles of en	moles NO_3^- per 1 000 g H_2O	W	c	t_2-t_1	w	t_a-t_1	Q
3	0.5156	0.01788	0.03856	1.36	468.5	0.882	0.901	5.3	−1.15	395.3
4	0.5162	0.01130	0.03856	1.31	467.8	0.885	0.828	5.3	+0.54	357.2
		moles of $Ba(NO_3)_2$								Q_{dil}
	0.5153	0.04292	0.03856	1.47	473.7	0.873	0.083	5.3	−0.66	38.8
3′	0.4752	0.04309	0.03856	1.37	472.6	0.881	0.088	5.3	−0.57	40.8
4′	0.5156	0.01295	0.03856	1.32	468.7	0.884	0.099	5.3	+0.40	41.3

diamine and trimethylenediamine are somewhat dissociated in unbuffered solutions of non-complex forming salts, but according to measurements in the literature [9] their heats of dissociation are very small, and it has been found unnecessary to introduce a correction for these heats in our calculations.

To obtain the heats of formation of the mono complexes Ni tn^{++} and Cu en^{++}, it was necessary to avoid precipitation of the hydroxides. Therefore we buffered the solutions by adding some nitric acid and a little more than the equivalent amount of diamine to the calorimeter solution before the reaction. Then using a suitable amount of the base for the reaction it was possible to keep the concentration of the diammonium ions constant during the reaction. The diammonium salt was replaced with an equivalent amount of potassium nitrate in the corresponding determination of Q_{dil}.

A summary of all the calorimetric data is given in Table 1 B. In the experiments where nitric acid has been added, measurements of the hydrogen ion concentration ascertained that all the acid was neutralized by the base to form diammonium ions. Therefore, $\bar{n}^0$ and $\bar{n}$, the average number of diammine molecules bound per metal ion before and after reaction, respectively, could be directly deduced from the total amount of diamine after deduction of the amount bound as enH_2^{++} or tnH_2^{++}. In the unbuffered solutions $\bar{n}$ was taken normally as the ratio of moles of diamine to moles of nickel or copper ions in the solution. When $\bar{n}$ approaches 3 we have, especially in the nickel trimethylenediamine system, an appreciable amount of free base in the solution, and in these cases $\bar{n}$ was computed using our knowledge of the complexity constants. The last column in Table 1 B gives ΔH_a, the heat of formation per mole of diamine complexly bound to the metal ion, and it is seen that this quantity is nearly constant, independent of the composition of the solutions from which it is deduced. It is also seen that the heat of reaction is nearly independent of the salt medium, though it appears that ΔH_a is slightly higher in 1 M KNO_3-solutions than in solutions free from neutral salt.

The quantities we are especially interested in are the heats of the individual complexes. These were calculated from the measurements of solutions with *ca.* 1 M KNO_3. Denoting the heats of formation per mole of metal atom

Table 1 B. Summary of calorimetric data of the systems examined.

System No.	C_{KNO_3} (moles per liter)	moles of HNO_3	moles of $Me(NO_3)_2$	moles of amine before react.	moles of amine after react.	$\bar{n}^\circ$ before react.	$\bar{n}$ after react.	Q (cal.)	Q_{dil} (cal.)	$-\Delta H_a$ (kcal.)
Ni++, en										
1	1.0	0.0864	0.0432	0.0438	0.0823	0.014	0.905	388.3	39.2	9.07
2	1.0	0.0857	0.0429	0.0436	0.0821	0.016	0.914	387.2	39.2	9.04
3	1.2	0	0.0179	0	0.0386	0	2.16	395.3	40.8	9.18
4	1.2	0	0.0113	0	0.0386	0	3.00	357.2	41.3	9.32
5	1.2	0	0.0386	0	0.0386	0	1.00	391.2	39.6	9.11
5a*	1.2	0	0.0386	0.0386	0.0772	1.00	2.00	396.0	39.6	9.23
5b*	1.2	0	0.0386	0.0772	0.1157	2.00	2.98	398.2	39.6	9.48
6	0	0	0.0223	0	0.0449	0	2.01	449.0	54.9	8.78
7	0	0	0.0223	0	0.0449	0	2.01	454.0	54.9	8.89
8	0	0	0.0123	0	0.0449	0	3.00	393.8	56.4	9.14
9	0	0	0.0123	0	0.0449	0	3.00	389.4	56.4	9.02
Cu++, en										
1	1.0	0.0431	0.0434	0.0236	0.0621	0.046	0.933	542.9	40.8	13.04
2	1.0	0.0427	0.0433	0.0235	0.0620	0.048	0.938	538.5	40.8	12.93
3	1.1	0	0.0178	0	0.0392	0	2.00	494.7	42.3	12.71
4	1.1	0	0.0178	0	0.0392	0	2.00	494.6	42.3	12.71
5	0	0	0.0159	0	0.0449	0	2.00	451.8	55.0	12.48
6	0	0	0.0160	0	0.0449	0	2.00	447.8	55.0	12.28
Ni++, tn										
1	1.0	0.0428	0.0430	0.0222	0.0519	0.019	0.709	293.7	64.8	7.71
2	1.0	0.0428	0.0430	0.0222	0.0519	0.019	0.709	296.0	64.8	7.78
3	1.2	0	0.0221	0	0.0443	0	1.97	423.9	96.5	7.52
3a*	1.2	0	0.0221	0.0443	0.0886	1.97	2.56	183.6	96.5	6.68
4	1.1	0	0.0200	0	0.0443	0	2.09	409.2	97.7	7.45
5	1.1	0	0.0129	0	0.0443	0	2.35	318.5	97.7	7.28
Cu++, tn										
1	1.1	0	0.0180	0	0.0443	0	2.00	507.8	97.7	11.39
2	1.1	0	0.0180	0	0.0443	0	2.00	506.9	97.7	11.37

* The measurements are carried out with successive addition of the diamine solution.

by ΔH, and the gross heats for the complexes by ΔH_1, ΔH_{1-2}, *etc.*, we have for a system of three complexes:

$$\Delta H = (\alpha_1 - \alpha_1^\circ)\,\Delta H_1 + (\alpha_2 - \alpha_2^\circ)\,\Delta H_{1-2} + (\alpha_3 - \alpha_3^\circ)\,\Delta H_{1-3}$$

In this equation α_1, α_2 and α_3 denote the degrees of formation of the three complexes in the reaction mixture, and α_1°, α_2° and α_3° the same quantities in the starting solutions. Equations of this kind were combined in various ways in order to calculate the heats in question, which after all were only a little different from the total heats for all integral numbers of n. The α-quantities were calculated by means of the complexity constants to be discussed in the next section, and the computed heats are summarized in Table 1 C. The uncertainty in the heats is *ca.* $\pm$ 1 %, except for the values in the nickel trimethylenediamine system for which the uncertainty is about 2 %.

Table 1 C. Estimated heats of formation in kcal of the individual complexes in ca. 1 M KNO_3.

System	Combination of Nos.	$-\Delta H_1$	$-\Delta H_{1-2}$	$-\Delta H_{1-3}$
Ni++, en	1, 3, 4	9.03	18.23	27.96
	1, 5a, 5b	9.06	18.17	27.79
	2, 3, 5b	8.89	18.28	27.88
	2, 4, 5a	8.94	18.04	27.96
	3, 4, 5	9.09	18.25	27.96
	5, 5a, 5b	9.12	18.19	27.82
	Average	9.01	18.19	27.90
Cu++, en	1, 3	13.13	25.42	
	2, 4	12.93	25.41	
	Average	13.03	25.42	
Ni++, tn	(1,2), 3, 3a	7.77	15.05	21.70
	(1,2), 3, 5	7.77	15.06	20.94
	(1,2), 3a, 5	7.77	14.78	21.46
	(1,2), 3a, 4	7.77	15.01	21.67
	(1,2), 4, 5	7.77	15.11	20.93
	Average	7.77	15.00	21.34
Cu++, tn	Average		22.76	

POTENTIOMETRIC DETERMINATION OF COMPLEXITY CONSTANTS

The formation constants of the nickel(II) ethylenediamine system have been determined by various authors [1,10–14] at various salt concentrations and temperatures, but the results do not agree very well. In this work they were, therefore, determined again at 25° from glass electrode measurements under conditions similar to those used by J. Bjerrum and co-workers [15,16] for the zinc(II), cadmium(II) and copper(II) ethylenediamine systems, *i.e.* the following total concentrations $C_{Me++} = 0.1$ M, $C_{HNO_3} = 0.1$ M, $C_{KNO_3} =$ 1 M and 0.05 M $< C_{en} <$ 0.5 M. The techniques were the same as used by J. Bjerrum and Nielsen [16], and we are indebted to Mr. C. J. Ballhausen for making these measurements. A selection of the data are given in Table 2, in which column 5 gives $\bar{n}_{en}$, the average number of hydrogen ions bound to not complexed ethylenediamine, and column 7 the average number of ethylenediamine bound to nickel ions. The data were computed in the usual way from the values of — log[en] for $\bar{n} = 0.5$, 1.5 and 2.5. The following values for the consecutive formation constants were obtained:

$$\log K_1 = 7.51, \qquad \log K_2 = 6.35, \qquad \log K_3 = 4.42.$$

The data of Carlson, McReynolds and Verhoek [10] and of Hares [13] seem to be in rather good agreement with these values.

The first two formation constants of the nickel(II) and copper(II) trimethylenediamine systems have been determined by Hares [13] in 1 M KNO_3 at 0° and 30°. Irving *et al.*[5] also recently determined the constants in the last mentioned system in 0.1 M KCl at 25°. In this work all three of the consecutive formation constants in the nickel and both of the formation constants in the copper system were determined at 25° C and at the same total concentrations as used in the ethylenediamine systems. There were no diffi-

Table 2. Glass electrode measurements of diamine containing metal salt solutions at 25° C.

Ni^{++}, en: Calc. with $-\log K_{enH_2^{++}} = 7.49$, $-\log K_{enH^+} = 10.17$.
$C_{HNO_3} = 0.1004$ M, $C_{KNO_3} = 1.00$ M.

No.	$C_{Ni(NO_3)_2}$	C_{en}	$-\log [H^+]$	$\bar{n}_{en}$	$-\log [en]$	$\bar{n}$
1	0.0947	0.0870	5.601	1.988	7.762	0.386
2	0.0947	0.1170	5.836	1.980	7.304	0.701
3	0.0947	0.1281	5.912	1.978	7.144	0.817
4	0.0947	0.1678	6.175	1.954	6.622	1.229
5	0.0947	0.1904	6.301	1.938	6.374	1.462
6	0.0947	0.2073	6.421	1.922	6.128	1.640
7	0.0947	0.2882	7.226	1.651	4.613	2.402
8	0.0947	0.3156	7.447	1.527	4.229	2.599

Ni^{++}, tn: Calc. with $-\log K_{tnH_2^{++}} = 9.12$, $-\log K_{tnH^+} = 10.62$.
$C_{HNO_3} = 0.0994$ and 0.0990 M (No. 11), $C_{KNO_3} = 1.00$ M.

No.	$C_{Ni(NO_3)_2}$	C_{tn}	$-\log [H^+]$	$\bar{n}_{tn}$	$-\log [tn]$	$\bar{n}$
1	0.1002	0.0810	7.143	1.990	6.760	0.310
2	0.1000	0.1122	7.427	1.980	6.194	0.620
3	0.1000	0.2042	8.359	1.852	4.363	1.508
4	0.0997	0.2338	8.647	1.745	3.817	1.778
5	0.1004	0.3010	9.671	1.139	2.091	2.129
6	0.1000	0.3527	10.163	0.820	1.531	2.315
7	0.1002	0.4116	10.463	0.626	1.197	2.523
	$C_{HNO_3} = 0.01992$ M, $C_{KNO_3} = 1.08$ M, $C_{BaCl_2} = 0.08$ M.					
8	0.02048	0.02203	7.734	1.961	6.283	0.579
9	0.02062	0.04296	8.736	1.707	4.351	1.521

Cu^{++}, tn: Calc. with $-\log K_{tnH_2^{++}} = 9.12$, $-\log K_{tnH^+} = 10.62$.
$C_{HNO_3} = 0.01992$ M, $C_{KNO_3} = 1.08$ M, $C_{BaCl_2} = 0.08$ M.

No.	$C_{Cu(NO_3)_2}$	C_{tn}	$-\log [H^+]$	$\bar{n}_{tn}$	$-\log [tn]$	$\bar{n}$
1	0.02111	0.04326	7.328	1.984	7.089	1.574
2	0.02119	0.04570	7.464	1.978	6.818	1.681

culties in preparing nickel trimethylenediamine solutions of this composition, but the corresponding copper solutions separated basic precipitates unless $\bar{n} \gtrsim 1.5$. For this reason the gross complexity constant K_{1-2} was determined with copper amalgam electrode in solutions with excess of diamine.

Table 3 gives some glass electrode measurements of the acid-base constants of trimethylenediamine in solutions with 0.1 M HNO_3, 0.1 M $BaCl_2$ and 1 M KNO_3. We are indebted to Mrs. S. Refn for making these measurements. The true hydrogen ion concentration was determined by measuring against a standard acid solution of the composition: $C_{HNO_3} = 0.005$ M, $C_{BaCl_2} = 0.1$ M, $C_{KNO_3} = 1.1$ M. For low values of $\bar{n}_{tn} = C_{HNO_3}/C_{tn}$ the solutions were so alkaline that the glass electrode might show deviations from the reversible hydrogen electrode. Therefore the product of the acid dissociation constants of the diammonium ion was determined from the interpolated hydrogen ion concentration ($= 10^{-9.87}$) for $\bar{n}_{tn} = 1$:

$$K_{tnH_2^{++}} K_{tnH^+} = [H^+]^2_{\bar{n}=1} = 10^{-19.74}.$$

Table 3. Acid-base constants of trimethylenediamine at 25° C.
C_{KNO_3} = 1.00 M, $BaCl_2$ = 0.100 M.

No.	C_{HNO_3}	C_{tn}	$-\log [H^+]$	$\bar{n}_{tn}$	$-\log K_{tnH^+}$
1	0.0994	0.1051	9.965	0.946	
2	0.0994	0.1012	9.897	0.982	
3	0.0994	0.09282	9.759	1.071	
			9.87 (int.)	1.00	
4	0.0994	0.06765	9.134	1.475	9.134
5	0.0994	0.06712	9.114	1.481	9.121
6	0.0994	0.06398	8.997	1.554	9.119

$K_{tnH_2^{++}}$ was determined from the formula

$$K_{tnH_2^{++}} = \frac{(2-\bar{n})\,[H^+]^2 - \bar{n} K_{tnH_2^{++}} K_{tnH^+}}{(\bar{n}-1)\,[H^+]}$$

in the buffer range for this constant. In average was found $-\log K_{tnH_2^{++}} = 9.12$, $-\log K_{tnH^+} = 10.62$. From Hares' [13] data at 20° and 30° C one computes the values 9.10 and 10.70, respectively, in 1 M KNO_3 at 25° C.

A selection of the measurements made on nickel and copper trimethylenediamine solutions is given in Table 2. In order to vary the concentration of the complex-forming metal ion without changing the salt medium the 0.1 molar concentration of nickel (or copper) nitrate was in some cases (see Table 2) partly exchanged with an equivalent concentration of barium chloride, and the 0.1 molar nitric acid correspondingly with potassium nitrate. The consecutive constants in the nickel system were obtained from the values of $-\log [tn]$ for $\bar{n} = 0.5$, 1.5, and 2.5, which were determined graphically to be 6.40, 4.38, and 1.23, respectively. Because of the very slight overlap of the three steps, these values differ only a little from the computed formation constants:

$$\log K_1 = 6.39, \qquad \log K_2 = 4.39, \qquad \log K_3 = 1.23.$$

They do not agree very well with Hares' [13] values for the first two formation constants. From his data we get: $\log K_1 = 5.58$, $\log K_2 = 3.52$ in 1 M KNO_3 at 25° C.

The gross complexity constant in the copper trimethylenediamine system was determined by measuring with the copper amalgam electrode a series of copper(II) trimethylenediamine solutions with excess of diamine. A 1 N calomel electrode was used as reference electrode. The cells examined and a selection of the measurements made are summarized in Table 4. The measurements were made in an atmosphere of nitrogen applying the same technique as previously used by Bjerrum and Nielsen [16] in the determination of the gross complexity constant in the copper(II) ethylenediamine system. From the directly measured potentials E the normal potential copper amalgam-copper(II) ion (relative to the calomel electrode) is calculated by means of the expression

$$E = E^\circ_{Cu,Cu^{++}} + \frac{RT}{2F} \ln [Cu^{++}]$$

Table 4. The normal oxidation potentials Cu,Hg → Cu^{++} and Cu,Hg→ $Cu\,tn_2^{++}$ (relative to the normal calomel electrode) in 1 M KNO_3 at 25° C from measurements of the cells:

No. 1: Cu,Hg | $C_{Cu(NO_3)_2}$, C_{HNO_3}, 1.10 M KNO_3 | KCl sat. | 1 M KCl, Hg_2Cl_2 | Hg

Nos. 2–4: Cu,Hg | $C_{Cu(NO_3)_2}$, C_{tn}, C_{HNO_3}, 1.0 M KNO_3 | KCl sat. | 1 M KCl, Hg_2Cl_2 | Hg

No.	$C_{\overline{Cu(NO_3)_2}}$	C_{HNO_3}	C_{tn}	[tn]	E	$\frac{RT}{2F}\ln C_{Cu^{++}}$	$E°_{Cu,Cu^{++}}$
1	0.0998	0.0024	0	0	+ 0.0190	− 0.0296	+ 0.0486
						$\frac{RT}{2F}\ln\frac{C_{Cutn_2^{++}}}{[tn]^2}$	$E°_{Cu,Cutn_2^{++}}$
2	0.0997	0.0500	0.3703	0.1208	− 0.4345	+ 0.0247	− 0.4592
3	0.0996	0.0500	0.3906	0.1414	− 0.4384	+ 0.0206	− 0.4591
4	0.0999	0.0501	0.4113	0.1614	− 0.4439	+ 0.0173	− 0.4612

and the normal potential copper amalgam-bis(trimethylenediamine) copper (II) ion by means of the expression

$$E = E°_{Cu,Cutn_2^{++}} + \frac{RT}{2F}\ln\frac{[Cu\,tn_2^{++}]}{[tn]^2}$$

From the results of Randles' [17] investigation of the equilibrium between copper(I) and copper(II) ions in the presence of trimethylenediamine we estimate that for a copper concentration of about 0.1 M and a concentration of free diamine less than 0.2 M, it seems reasonable to neglect any disturbing influence of copper(I) ions. The copper(II) ion concentration to be used in the calculation was assumed to be the same as the total copper(II) concentration in the acid solution. In the solutions with trimethylenediamine it was assumed that the copper was present solely as the bis(trimethylenediamine) complex and that the concentration of the monoammonium ion tnH^+ was equal to the nitric acid concentration added.

The computed value for the normal potential of the copper-trimethylenediamine system shows a slight tendency to fall with increasing concentration of free diamine. This can perhaps be explained in the same manner as the observed fall in the normal potential of the corresponding copper-ethylenediamine system [16]. If the values of the normal potentials of $E°_{Cu,Cu^{++}}$ and $E°_{Cu,Cutn_2^{++}}$ from solutions 1 and 2 are combined, we get for the gross constant in question

$$\log K_{1-2} = \frac{0.0486 + 0.4592}{0.02957} = 17.17.$$

Since $K_1 \gg K_2$, values for the second consecutive constant can be directly obtained from the measurements in Table 2. From solutions 1 and 2 are estimated $\log K_2 = 7.22$ and 7.15, respectively. As an average we therefore get for the consecutive constants $\log K_1 = 9.98$, $\log K_2 = 7.19$. These values agree fairly well with Hares' [13] values: $\log K_1 = 9.79$, $\log K_2 = 7.16$ in 1 M KNO_3 at 25° C. Irving *et al.*[5] estimate similar values in 0.1 M KCl, but find

Table 5. Thermodynamic data for some nickel and copper (II) amine systems at 25° C.

System	log K ($\mu\sim1$)	$-\Delta G$ kcal.	$-\Delta G'$ kcal.	$-\Delta H$ kcal.	ΔS e.u.	$\Delta S'$ e.u.	Difference between consecutive ΔS values	Statistical effect
Ni^{++} + 3en	18.28	24.90	31.98	27.90	−10.1	13.6		
n = 1	7.51	10.23	12.59	9.01	4.1	12.0		
n = 2	6.35	8.65	11.01	9.18	− 1.8	6.1	5.9	3.12
n = 3	4.42	6.02	8.38	9.71	−12.4	− 4.5	10.6	4.44
Ni^{++} + 3tn	12.01	16.36	23.44	21.3	−16.6	7.1		
n = 1	6.39	8.69	11.05	7.8	3.0	10.9		
n = 2	4.39	5.98	8.34	7.2	− 4.1	3.8	7.1	3.12
n = 3	1.23	1.68	4.04	6.3	−15.5	− 7.6	11.4	4.44
Ni^{++} + $6NH_3$	8.61	11.73	25.89	21.0	−31.1	16.3		
n = 1	2.77	3.77	6.13	3.5	0.9	8.8		
n = 2	2.22	3.02	5.38	3.5	− 1.6	6.3	2.5	1.74
n = 3	1.71	2.33	4.69	3.5	− 3.9	4.0	2.3	1.25
n = 4	1.17	1.59	3.95	3.5	− 6.4	1.5	2.5	1.14
n = 5	0.73	0.99	3.35	3.5	− 8.4	− 0.5	2.0	1.25
n = 6	0.01	0.01	2.37	3.5	−11.7	− 3.8	3.3	1.74
Cu^{++} + 2en	20.03	27.28	32.00	25.4	6.3	22.1		
n = 1	10.72	14.60	16.96	13.0	5.4	13.3		
n = 2	9.31	12.68	15.04	12.4	0.9	8.8	4.5	4.13
Cu^{++} + 2tn	17.17	23.39	28.11	22.8	2.0	17.8		
n = 1	9.98	13.59	15.95					
n = 2	7.19	9.79	12.15					
Cu^{++} + $4NH_3$	12.63	17.20	26.64	20.0	− 9.4	22.2		
n = 1	4.14	5.64	8.00	5.0	2.1	10.0		
n = 2	3.49	4.75	7.11	5.0	− 0.8	7.1	2.9	1.95
n = 3	2.88	3.92	6.28	5.0	− 3.6	4.3	2.8	1.61
n = 4	2.12	2.89	5.25	5.0	− 7.1	0.8	3.5	1.95
n = 5	− 0.55	− 0.75	1.61	3.2	−13.3	− 5.4		

for concentrations of free diamine higher than $10^{-4.5}$ that $\bar{n}$ rises slightly above two. Irving *et al.* mention that a corresponding effect is not found in the spectra. This seems to show that not more than 4 nitrogen atoms are coordinated to the copper.

DISCUSSION OF THERMODYNAMIC DATA

The complexity constants and heats determined for the nickel and copper diamine systems are collected in Table 5. Davies, Singer and Staveley [9] recently measured the heat of formation of the ethylenediamine complexes of

nickel, copper, zinc, and cadmium by a more accurate calorimeter setup than used in our investigation, but as they did not measure below $\bar{n}$ equals 1.9, their heats for the first complex cannot be very accurate as they state themselves. For the other complexes they find the following figures in fair agreement with our determinations

	Ni	Cu	Zn	Cd
$-\Delta H_{1-2}$	17.25	25.16	11.45	13.33
$-\Delta H_{1-3}$	28.01		18.46	19.70

It will be seen that Davies *et al.* also find roughly the value 3 : 2 for the ratio of the heats of the 1-3 and 1-2 complexes in the zinc and cadmium systems. In the copper ethylenediamine system Spike and Parry [2] using the temperature coefficient method found the values $-\Delta H_1 = 14.6$, and $-\Delta H_{1-2} = 28.4$ to be compared with the value $-\Delta H_{1-2} = 26.1$ of Bjerrum and Nielsen [16]. Also for other amine systems Spike and Parry [2] obtained similar results in fair agreement with the assumption that the heats of successive steps are the same within the uncertainty of the experiment. There is, therefore, some justification for Bjerrum's use of equation (1), and we consider this to be a common rule for all normal complex systems with dipole ligands: if by normal is understood systems free from steric strain in which no change in configuration and total spin quantum number occurs [18,19]. In the nickel trimethylenediamine system ΔH_3 seems to be somewhat smaller than ΔH_1 and ΔH_2. This might be due to the greater error in the determination of the heat for the third complex in this case, but paying due regard to the great spreading of the complexity constants it may also be caused by the steric strain in the system (*cf.* Ref. 1, p. 91). However, it is noteworthy that the relatively small affinity to the 3rd ethylenediamine in the zinc and cadmium systems does not show itself in the heats determined by Davies *et al.*[9]

In Table 5 are the values found for the diamine complexes compared with corresponding data for the ammonia complexes. The complexity constants are J. Bjerrum's values in 1 M NH_4NO_3 at 25°, and the heats are taken from the literature. The value for $-\Delta H_{1-6} = 21$ in the nickel system is estimated from Fyfe's calorimetric measurements [20] considering that the complex formation is not completed for $[NH_3] \sim 0.5$ M. The values for ΔH_{1-4} and ΔH_5 in the copper ammonia system are computed from the thermochemical measurements of Bouzat [21] (*cf.* Ref. 22, p. 18). To obtain the heats of the single steps we have divided the total heat by the number of uniformly bound ligands N using the approximation contained in the equation (1) about the equality of the ΔH_n values.

The large chelate effect of ethylenediamine relative to ammonia defined by Bjerrum and Nielsen [16] as

$$-\Delta G\,(\tfrac{1}{2}\,\mathrm{en}) + \Delta G\,(NH_3) = \frac{RT}{N}\left(\frac{1}{2}\ln K_{1-N}\,(\mathrm{en}) - \ln K_{1-N}\,(NH_3)\right) \quad (2)$$

and by Schwarzenbach [4] as

$$\mathrm{Chel} = \log K_1\,(\mathrm{en}) - \log K_{1-2}\,(NH_3) \quad (3)$$

has been discussed by several authors. Schwarzenbach [4] has discussed the mechanism of chelation and presented an explanation of the effect. As Calvin and Bailes [6] he considers it to be an entropy effect. Spike and Parry [3] has shown that this is very nearly the case in the zinc and cadmium systems as different from the copper and nickel systems, for which the chelate effect is partly an enthalpy effect. The data in Table 5 show directly that, *e.g.*, $-\Delta H_1$ (en) is considerably higher than $-\Delta H_{1-2}$ (NH_3) in these systems. In this connection it is interesting that the chelate effect is relatively the highest for the transition group elements as first pointed out by Bjerrum and Nielsen (*cf.* Fig. 1 in Ref. 16). The loss in enthalpy by chelation of transition elements is therefore perhaps related to the fact that the crystal field stabilization [23] is higher for the ethylenediamine than for the ammonia complexes. A simple calculation shows that this stabilization amounts to about 1 kcal in the nickel systems or about half of the loss in enthalpy by exchange of two ammonia molecules with one ethylenediamine.

For a complex reaction of the type:

$$MA_{n-1} + A = MA_n + \text{water}$$

the formation constant: $K_n = \dfrac{[MA_n]}{[MA_{n-1}]\,[A]}$

as well as the free energy: $\Delta G_n = -RT \ln K_n$,

and the entropy: $$\Delta S_n = \frac{1}{T}(\Delta H_n - \Delta G_n)$$

is dependent on the standard states of the reactants. To escape this dependence on the standard states, Bjerrum [24] introduced the water concentration in the equilibrium constant and used the quantity $\frac{1}{Z} \log K_{1-n} + \log 55$, where Z is the characteristic coordination number, as a more correct measure for the affinity than $\frac{1}{Z} \log K_{1-n}$. Adamson [25] who takes another starting point introduces the mole fraction instead of molar concentrations in K_n. In the simple case for $Z = N$ the two treatments lead to the same result, but in case of chelation, *e.g.* for $Z = 2\ N$, the two treatments give different results as Bjerrum introduces no correction for the asymmetry of *e.g.* the reaction

$$MA_N + \frac{N}{2}\,\text{en} = M\,\text{en}_{\frac{N}{2}} + NA.$$

Following Adamson, we have corrected the usual values for ΔG (in kcal) and ΔS (in e.u.) by means of the formulae:

$$\Delta G' = \Delta G + \Delta\nu\, RT \ln 55.5 = \Delta G + 2.36\Delta\nu$$
$$\Delta S' = \Delta S - \Delta\nu\, R \ln 55.5 = \Delta S - 7.9\Delta\nu$$

where $\Delta\nu$ denotes the moles of products minus those of reactants, exclusive of solvent.

The data given in Table 5 show that the chelate effect according to (2) and (3) in the main is an arbitrary dilution effect which nearly vanishes when the corrected free energies are considered. This result, of course, does not interfere with the statements of Schwarzenbach, but has something to do with the fact that the entropy changes for reactions between reactants in pure states usually are small. The corrected entropy $\Delta S'_{1-6} = 16$ e.u. in the nickel ammonia system is seen to be only little different from the corresponding entropy $\Delta S'_{1-3} = 14$ e.u. in the nickel ethylenediamine system, and is distinctly higher than $\Delta S'_{1-3} = 7$ e.u. in the nickel trimethylenediamine system. In the corresponding copper systems $\Delta S'_{1-4}(NH_3) = 22$ e.u. is equal to $\Delta S'_{1-2}$ (en), and $\Delta S'_{1-2}$ (tn) = 18 e.u. is also here somewhat smaller.

Latimer and Jolly [26,27] have estimated the heat of reaction for the successive steps in the formation of the aluminium fluoride complexes. They found that the ΔS values decrease with the stepwise formation of the complexes and assume this to be due to a charge effect, which can be calculated by deducting the constant value of the replacement entropy 15.6 e.u. from the ΔS values. This replacement entropy should be due to the reaction:

$$H_2O \text{ (bound)} + F^- \text{ (aq.)} = H_2O \text{ (liq.)} + F^- \text{ (bound)}.$$

In the same paper they suggest the value 5.5 e.u. for the replacement

$$H_2O \text{ (bound)} + NH_3 \text{ (aq.)} = H_2O \text{ (liq.)} + NH_3 \text{ (bound)}$$

and argue that this is the principal effect on ΔS in complex formation with this ligand, as it is uncharged. Contrary to this suggestion the data in Table 5 show that also the ΔS values for the stepwise formation of the complexes with uncharged ligands decrease and in much the same way as for the charged ligand F^-.

Different empirical equations for calculation of the partial molar entropy $\overline{S}^\circ$ for complex ions have been put forward recently by Cobble [28], and George, Hanania and Irvine [29]. Cobble calculated the $\overline{S}^\circ$ value for the ion $Ni(en)_3^{++}$ in two different ways: (i) an entirely empirical value 163 e.u. and (ii) a partly empirical value 154 e.u. from the sum $\overline{S}^\circ_{Ni++} + 3\,\overline{S}^\circ_{en} + \Delta S_{1-3}$ for the reaction

$$Ni^{++} + 3\,en = Ni\,(en)_3^{++}$$

For ΔS_{1-3} they used the value + 41 e.u. determined by Basolo and Murmann [12]. If our value —10 e.u. is used for the same calculation, we get $\overline{S}^\circ$ equal to 103 e.u., which is much lower than the empirical value 163 e.u.

The value of the equation proposed by George *et al.*[29]

$$\overline{S}^\circ = A - Bz + CN$$

where A, B and C are numerical constants for the ligand in question, while N is the total number of ligands in the complex ion and z is the charge, is that the ΔS values of the successive steps in the formation of the complexes are zero when corrected by the statistical factors. This is in agreement with our results within the 3.4 e.u. mentioned by the authors except for the last step in the nickel diamine systems, but more experimental work is necessary before

much can be said about the values of the constants A and B for the ethylenediamine and trimethylenediamine complexes.

We have calculated the difference in ΔS between two successive steps in the complex formation and comparing these differences with the statistical effects [1,27] in Table 5 it will be noticed that they are very much alike in behavior although the differences seem to be twice as high as the statistical effects.

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