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Metal Ammine Formation in Aqueous Solution

VI. Stability and Light Absorption of Copper Ethylenediamine Ions

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In continuation of earlier investigations in this field[1] the present paper reports a study of the complex formation between ethylenediamine and copper. The cupric complexes have recently been investigated by Carlson, McReynolds and Verhoek[2], and Table 1 furnishes a survey of their data and the results obtained in the present paper. Carlson *et al.* carry out their measurements by means of the glass electrode and make their calculations in exactly the same way as J. Bjerrum in his work on »Metal Ammine Formation»[3]. In the present investigation the two first consecutive formation constants are likewise determined by means of glass electrode, but, besides, together with the gross complexity constant $K_2 = k_1 k_2$ and its temperature coefficient, these constants are also determined by measurement with copper amalgam electrode. All determinations seem to be in satisfactory agreement, and only the results of Job[4] with respect to K_2 are, as previously pointed out (ref. 3, p. 75), completely misleading. The 3rd consecutive constant has previously, using Werner and Spruck's old freezing point measurements[5] (ref. 3, p. 110) been estimated with considerable uncertainty to have the value $k_3 \sim 3$. It is now, by accurate spectrophotometric measurements, found to be much smaller ($k_3 = 0.10$).

THE CONSTITUTION OF THE COPPER ETHYLENEDIAMINE COMPLEXES

As chelate ligand, ethylenediamine occupies two co-ordinate positions, and if N in general denotes the number of the first more firmly and uniformly bound ligands, J. Bjerrum's (ref. 3, p. 80) characteristic co-ordination number in systems with chelate-bound ethylenediamine is given by the expression $Z = 2N$. In the cupric-ethylenediamine system the two first consecutive constants k_1 and k_2 are both very large and of the same order of magnitude,

Table 1. Concentration complexity constants for the copper ethylenediamine complexes in salt solutions.

$$k_n = \frac{[\text{Me en}_n^{+\nu}]}{[\text{Me en}_{n-1}^{+\nu}]\,[\text{en}]}\,,\quad K_n = k_1 k_2 \ldots . k_n$$

$Me^{+\nu}$	Complexity constant	Temp. coef.	$t°$	Medium	Method	References
Cu^{++}	log k_1					
	10.72		25°	1.3 N (1 N KNO_3)	glass.electr.	This paper
	10.75		25°	1.3 N (1 N KNO_3)	Cu,Hg-electr.	» »
	10.55		30°	~ 1 N (KNO_3)	glass electr.	Carlson *et al.*[2]
Cu^{++}	log k_2					
	9.31		25°	1.3 N (1 N KNO_3)	glass electr.	This paper
	9.28		25°	1.3 N (1 N KNO_3)	Cu,Hg-electr.	» »
	9.05		30°	~ 1 N (KNO_3)	glass electr.	Carlson *et al.*[2]
		$\frac{d \log K_2}{d t°}$				
Cu^{++}	log K_2					
	20.03		25°	1.3 N (1 N KNO_3)	glass electr.	This paper
	20.07	— 0.064	25°	1.07 N (1 N KNO_3)	Cu,Hg-electr.	» »
	19.60		30°	~ 1 N (KNO_3)	glass electr.	Carlson *et al.*[2]
	5.8 ?*		16°		spectroph.	Job[4]
Cu^{++}	log k_3					
	— 1.0		25°	1.07 N (1 N KNO_3)	spectroph.	This paper
Cu^{+}	log K_2					
	~ 10.8		25°		estimation	» »

and the smallness of the 3rd consecutive constant therefore shows that the cupric ion quite distinctly has the characteristic co-ordination number 4.

For statistical reasons the ratio between k_1 and k_2 must be as $\frac{4}{1} : \frac{1}{2}$ when assuming that the cupric ion has planar square configuration (ref. 3, pp. 40, 101), and it will be seen that the corresponding statistical effect $S_{1,2} = 0{,}9$ explains the main part of the difference between the logarithms of the two constants.

The chelate-fortifying effect of ethylenediamine relative to the simple binding of ammonia molecules is relatively greater for the cupric- than for the zinc- and cadmium ion, and, as far as one can judge from the present experimental material, the other metal ions of the 1st transition-group fall

* The basis for the calculation of this value is not correct (*cf.* ref. 3, p. 75).

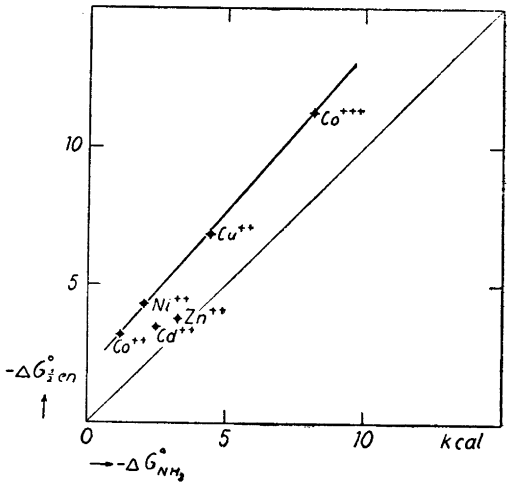

Fig. 1. The chelate-fortifying action of ethylenediamine relative to ammonia. The affinity of the metal ions to ethylenediamine is plotted as ordinate and their affinity to ammonia at the same temperatur (25° or 30°) is plotted as abscissa.

in the same class as the cupric ion. This is directly apparent in Fig. 1 where the affinity between metal ions and ethylenediamine per amino group

$$-G^0_{\frac{1}{2}\mathrm{en}} = \frac{1}{Z} RT \ln K_N$$

is plotted as ordinate against the affinity per ammonia molecule

$$-G^0_{NH_3} = \frac{1}{N} RT \ln K_N$$

as abscissa (*vide* ref. 3, p. 91 and ref. 1, p. 7).

In the ammine systems in question, the nickel- and cobolt ions have the characteristic co-ordination number 6 and octahedral configuration, while the zinc- and cadmium ions, like the cupric ion, though less pronounced, have the characteristic co-ordination number 4. In this connection it is notable, however, that the cupric ion in its compounds with 4 ligand groups has planar square configuration, while the zinc- and cadmium ions have tetrahedral configuration (ref. 3, p. 101). This difference in configuration is also of interest in connection with the possibilities arising relative to the binding of the 3rd ethylenediamine molecule. In the case of the zinc- and cadmium ions the uptake of this molecule is of necessity accompanied by a re-arrangement to octahedral configuration, but in case of the cupric ion it is also possible that the 3rd ethylenediamine molecule may be bound to the planar di-ethylenedia-

mine complex by only one of its amino groups. Such a configuration in the case of the tri-ethylenediamine complex seems a priori rather improbable, but finds strong support in a number of facts. Thus it is in excellent agreement with the circumstance that the cupric ion, according to J. Bjerrum's previous investigations [6, 7], even in liquid ammonia does not appear to bind more than 5 ammonia molecules. On the whole, the configuration is supported by the appearance of the absorption spectra (see Fig. 2).

Thus it is very characteristic that the absorption maximum in visible light is displaced evenly towards blue at the taking up of the first four molecules monammine, respectively 2 molecules diamine, whereupon additional binding of one molecule ammonia or ethylenediamine displaces the absorption maximum in the opposite direction. Finally, it is a very important argument in favour of the configuration in question that the constant for the taking up of the 3rd ethylenediamine molecule ($k_3 = 0.10$)* here determined is substantially smaller than the corresponding constant in the ammonia system ($k_3 = 0.3$) and that the affinity constant determined by Rosenblatt [8] for the uptake by the di-ethylenediamine complex of one ammonia molecule

$$k_{2,1} = \frac{[\mathrm{Cu\ en_2(NH_3)^{++}}]}{[\mathrm{Cu\ en_2^{++}}]\ [\mathrm{NH_3}]}$$

likewise is about 1/3 (*cf.* ref. 3, p. 110). The main point of what has just been said is that the small value of k_3 relative to $k_{2,1}$ makes it rather improbable that there occurs a re-arrangement to octahedral configuration at the uptake to the 3rd ethylenediamine molecule, inasmuch as only a value of $k_3 > k_{2,1} \simeq k_5$ makes this re-arrangement energetically possible relative to the simple attachment of the ethylenediamine by only one end of its molecule.

There is nothing unique in the fact that ethylenediamine is bound by one of its amino groups only. Thus the silver ion, with the characteristic coordination number 2 and linear configuration, has only an extremely slight tendency to chelate-complex formation, as evident from the fact that the diethylenediamine complex has a stability similar to that of the diammonia complex (*cf.* ref. 3, p. 93). The mono-ethylenediamine complex, though, has a substantially greater complexity than the mono-ammonia complex and contains undoubtedly to a predominant degree chelate-bound diamine [9], and it is not until the binding of the 2nd ethylenediamine molecule that the ring is opened, resulting in an elongated complex where both ethylenediamine molecules are bound by one amino group only.

* Wrongly assuming that this constant was about 30 times larger, J. Bjerrum has previously believed it necessary to draw the opposite conclusion (ref. 3, p. 110).

It is reasonable to assume *a priori* that conditions are analogous in the cuprous-ethylenediamine system, a contention which is supported qualitatively by the fact that the equilibrium between cuprous-, cupric-complex and copper, which in ammoniacal solution is strongly in favour of the cuprous, in ethylenediamine containing solution is completely displaced in favour of the cupric step. Randles [10] has, by direct analysis, investigated this equilibrium in solutions containing an excess of ethylenediamine, and by combining his data with the present measurements K_2 in the cuprous system is roughly estimated (see Table 1). It is worthy of note that this constant is of the same order of magnitude as the corresponding constant in the cuprous ammonia system which previously, at the same temperature, has been found to be $10^{10.59}$, and this circumstance strongly supports the truth of the assumed configuration for the di-ethylenediamine-cuprous complex.

In the following, mention is first made of some hydrogen electrode determinations of the acid-base constant of ethylenediamine at high concentrations of ethylenediamine. Then follow the potentiometric determinations of the complexity constants of the cupric-ethylenediamine system, and, finally, the extinction measurements of the equilibrium between the di- and tri-ethylenediamine-cupric complexes.

SOME DETERMINATIONS OF THE ACID-BASE CONSTANT OF ETHYLENEDIAMINE

In order to follow the complex formation of metal ions with ethylenediamine by measurement of the hydrogen ion concentration of the solutions it is necessary to know the acid-base constants of the ethylenediamine under corresponding conditions. These constants have previously [1] been found to have the following values at 25°

$$k_{enH_2^{++}} = \frac{[H^+]\,[enH^+]}{[enH_2^{++}]} = 10^{-7.49}, \quad K_{enH^+} = \frac{[H^+]\,[en]}{[enH^+]} = 10^{-10.17}$$

in salt solutions with the following molar total concentrations:

$C_{KNO_3} = 1.00$, $C_{BaCl_2} = 0.100$, $C_{HNO_3} = 0.100$, and at not too high ethylenediamine concentration.

With increasing concentration of ethylenediamine k_{enH^+} showed a tendency to decrease. For the purpose of investigating this phenomenon, the hydrogen electrode measurements of Table 2 were carried out, the hydrogen ion concentration being determined by measurement relative to a standard acid solu-

tion having the composition: $C_{HNO_3} = 0.00499$, $C_{KNO_3} = 1.10$, $C_{BaCl_2} = 0.100$. The hydrogen electrode does not function in acid nitrate containing solutions and the glass electrode functions but poorly in alkaline solution with pH>10. For these reasons the standard nitric acid solution was measured with the glass electrode against a standard acetate solution ($E_{St-HNO_3} - E_{St-Ac}$), and the standard acetate solution in turn by means of a hydrogen electrode against the ethylenediamine solutions. With hydrogen electrode the following combinations was measured in a water thermostat at 25°:

— Pt, H_2	Ethylenediamine solution	KCl sat.	1 *N* KCl, Hg_2Cl_2	+ Hg
— Pt, H_2	0.1000 *N* HAc 0.1000 *N* NaAc	KCl sat.	1 *N* KCl, Hg_2Cl_2	+ Hg

and the respective potentials of the measured cells, converted to the hydrogen pressure 760 mm Hg (E (corr.) and E_{St-Ac} (corr.) respectively) and reckoned with sign in accordance with Luther, are recorded in Table 2. Both glass

Table 2. The acidic dissociation constant k_{enH^+} at high concentrations of the free base in 1.3 N salt solution at 25°.

$C_{KNO_3} = 1.00$, $C_{BaCl_2} = 0.100$

$E_{St-HNO_3} - E_{St-Ac} = 0.1393$ V, E_{St-Ac} (corr.) $= -0.5589$ V, $-\log [HNO_3]_{St}$ (corr.) $= 2.307$

No.	C_{HNO_3}	C_{en}	$E_{corr.}$	$-\log [H^+]$	$-\log[OH^-]$	$[OH^-]$
1	0.0992	0.2485	— 0.8960	10.368	3.48	0.00033
2	0.1003	0.4970	— 0.9221	10.810*	3.04	0.00091
3	0.0995	0.9665	— 0.9444	11.187	2.66	0.0022
4	0.1006	1.949	— 0.9686	11.596	2.25	0.0056
5	0.0995	2.870	— 0.9859	11.889	1.96	0.0110

No.	$\bar{n}_{en}$	$\log \frac{\bar{n}_{en}}{1-\bar{n}_{en}}$	$-\log k_{enH^+}$	$-\Delta \log k_{enH^+}$	$f_{en} \cdot F$	[en]
1	0.4005	— 0.175**	10.191	0.021	1.05	0.149
2	0.2036	— 0.593	10.217	0.047	1.11	0.396
3	0.1052	— 0.929	10.258	0.088	1.23	0.865
4	0.0545	— 1.240	10.356	0.186	1.54	1.84
5	0.0385	— 1.398	10.491	0.321	2.09	2.76

* Glass electrode measurements in this solution gave $-\log[H^+] = 10.798$, a value which is but very little below that determined by means of the hydrogen electrode.

** If it is desired to correct for the presence of a small amount of enH_2^{++} there should here, in the calculation of $-\log k_{enH^+}$, be a further addition of -0.002 to $-\log[H^+]$.

electrode measurements and hydrogen electrode measurements as well as the preparation of the ethylenediamine solutions were carried out as previously described. From the data obtained, E_{St-HNO_3} is found to be $-0.5589 + 0.1393 = -0.4196$, and the true hydrogen ion concentration of the solutions measured is consequently given by the relation:

$$-\log [H^+] = \frac{-0.4196 - E \text{ (corr.)}}{0.0591} - \log [HNO_3]_{St} \text{ (corr.)}$$

The corr. added to $-\log [HNO_3]_{St}$ indicates that the concentration of free acid in the standard solution is corrected for a small basic impurity of the salts (*cf.* ref. 1, p. 12). The hydroxyl ion concentration of the particular solutions is calculated from the hydrogen ion concentration, the ionic concentration product of the water being put at $10^{-13.85}$, *i. e.* the value one calculates from N. Bjerrum and Unmack's interpolation formula for potassium chloride solutions at 25° and the ion normality 1.3.

The constant in question $-\log k_{enH+}$ is with sufficient approximation (*vide* footnote of the table) calculated from the relation:

$$-\log k_{enH+} = -\log [H^+] + \log \frac{\bar{n}_{en}}{1 - \bar{n}_{en}}$$

where

$$\bar{n}_{en} = \frac{C_{HNO_3} + [OH^-] - [H^+]}{C_{en}}$$

is the number of hydrogen ions bound per total ethylenediamine.

It seems quite obvious *a priori* to identify the change in the value $10^{-10.17}$ for k_{enH+} caused by the ethylenediamine with a change in the activity coefficient expression $f_{en} \cdot f_{H+}/f_{enH+}$, but in that case one ignores completely any effect in connection with the diffusion potential. If, on the other hand, it is assumed that the most predominating ions — the potassium and the nitrate ions — solely and separately to the same degree take care of the electricity transport, a simple calculation [12] shows that $-\triangle \log k_{enH+}$ is identical with the variation in $\log \frac{f_{en} \cdot f_{K+}^{\frac{1}{2}}}{f_{enH+} \cdot f_{NO_3^-}^{\frac{1}{2}}}$.

In the table the calculated activity coefficient expression is denoted by $f_{en} \cdot F$ and the most plausible conclusion that one can make from the figures is that f_{en} increases rather strongly with increasing ethylenediamine concentration when the concentration of the free base is greater than about

0.1 molar. In this connection it is also of some interest to draw a comparison with the conditions in strong ammonia-ammonium nitrate solutions where the corresponding function and f_{NH_3} both increase in a uniform manner with the ammonia concentration (*cf.* ref. 3, p. 141).

POTENTIOMETRIC DETERMINATION OF THE COMPLEXITY AND HEAT OF FORMATION OF THE DI-ETHYLENEDIAMINE CUPRIC ION

A copper amalgam electrode was employed in measuring a series of cupric-ethylenediamine solutions with more than two molecules ethylenediamine per cupric ion against a weak nitric acid cupric nitrate solution in the same salt medium at 18° and at 25°. As reference electrodes were employed two mutually well conforming 1 *N* calomel electrodes of which the older one had been used in the hydrogen electrode measurements just mentioned. Both calomel electrodes were prepared according to Gjaldbæk, in electrode vessels of the model introduced by Lewis, Brighton and Sebastian.

The experimental details were like those previously described.[7] It should be mentioned, though, that the measurements were more easily carried out since the copper amalgam already was so close to being in equilibrium with the copper solutions that it was unnecessary to shake the electrodes with contents in the thermostat before the measurement. Of course, it was necessary to work in a nitrogen atmosphere because metallic copper is rapidly dissolved in ethylenediamine solutions in the presence of free oxygen. The copper amalgam, which is a suspension of so-called γ-phase with about 25 % copper in almost pure mercury [13], was prepared as previously described [7] and was kept under a layer of weakly acidic cupric nitrate solution. The volume of the electrode vessels was about 50 ml and differed from those previously described by having the one-way tap on the side tube replaced by a three-way tap as used by Biilmann and Lund [14]; moreover, the ascending tube of the syphon was omitted. In the preparation of an electrode the amalgam was not added until the copper solution had been made free of oxygen by leading nitrogen through, the nitrogen being introduced through the syphon tube and the flow being continued for a while afterwards until all oxygen had been driven out of the apparatus. The nitrogen was obtained from a cylinder and purified like the hydrogen for the hydrogen electrodes, by being led over red-hot copper (*cf.* ref. 1, p. 11). Immediately before a measurement, the syphon tube was filled with copper solution by forcing a small amount of nitrogen in through the three-way tap, and after closing this tap, letting the excess pressure be equalized through the tap of the syphon tube. The intermediate liquid was a saturated potassium chloride solution. After immersion

of the electrode in this solution, the diffusion potential was established automatically at a certain height in the syphon tube when the tap of this tube was opened. In this way it was possible to reproduce the individual measurements with an accuracy of about 0.1 millivolt.

Table 3. The normal oxidation potentials $Cu,Hg \rightarrow Cu(H_2O)_4^{++}$ and $Cu,Hg \rightarrow Cu(en)_2^{++}$ (relative to the normal calomel electrode) in 1 N KNO_3 at 18° and 25° C from measurements of the cells:

No. 1:

—						+
Cu,Hg	$C_{Cu(NO_3)_2}$, C_{HNO_3}, 1.05 N KNO_3	KCl sat.	1 N KCl, Hg_2Cl_2	Hg

No. 2—6:

—						+
Cu,Hg	$C_{Cu(NO_3)_2}$, C_{en}, C_{HNO_3} 1.00 N KNO_3	KCl sat.	1 N KCl, Hg_2Cl_2	Hg

No.	$C_{Cu(NO_3)_2}$	C_{HNO_3}	E (18°)	0.02887 logC_{Cu++}	$E°$ (18°)
1	0.00983	0.0025	— 0.0103	— 0.0579	+ 0.0476
			E (25°)	0.02957logC_{Cu++}	$E°$ (25°)
1	0.00983	0.0025	— 0.0113	— 0.0593	+ 0.0480

	$C_{Cu(NO_3)_2}$	C_{HNO_3}	C_{en}	[en]	E (18°)	0.02887 log$\frac{C_{Cu++}}{[en]^2}$	$E°$ (18°)
2	0.00972	0.0499	0.1698	0.1004	— 0.5457	— 0.0005	— 0.5452
3	0.00972	0.0499	0.2319	0.1625	— 0.5591	— 0.0125	— 0.5466
4	0.00972	0.0499	0.3239	0.2545	— 0.5711	— 0.0238	— 0.5473
5	0.00972	0.0499	0.4724	0.4030	— 0.5834	— 0.0353	— 0.5481
6	0.00972	0.0499	0.7094	0.6400	— 0.5978	— 0.0469	— 0.5509
					E (25°)	0.02957 log$\frac{C_{Cu++}}{[en]^2}$	$E°$ (25°)
2	0.00972	0.0499	0.1698	0.1004	— 0.5460	— 0.0005	— 0.5455
3	0.00972	0.0499	0.2319	0.1625	— 0.5597	— 0.0128	— 0.5469
4	0.00972	0.0499	0.3239	0.2545	— 0.5721	— 0.0244	— 0.5477
5	0.00972	0.0499	0.4724	0.4030	— 0.5847	— 0.0362	— 0.5485
6	0.00972	0.0499	0.7094	0.6400	— 0.5993	— 0.0480	— 0.5513

Table 3 summarizes the measurements. Of the directly measured potentials E the normal potential copper amalgam-cupric ion (relative to the calomel electrode) is calculated by means of the expression

$$E = E° + \frac{RT}{2F \cdot \log e} \log [Cu^{++}]$$

and the normal potential copper amalgam di-ethylenediamine-cupric ion by means of the expression

$$E = E^\circ + \frac{RT}{2F \cdot \log e} \log \frac{[\mathrm{Cu\ en_2^{++}}]}{[\mathrm{en}]^2}$$

In the acid solution the cupric ion concentration is identified by the total copper concentration, and in case of the ethylenediamine solutions the calculation is carried out with the assumption that the copper solely is present as di-ethylenediamine-cupric complex and that the concentration of $\mathrm{enH^+}$ is identical with the added nitric acid concentration. It is evident from the other measurements in the present paper that these assumptions are sufficiently satisfied. When the amalgam-cupric-ethylenediamine normal potential is not entirely constant but shows a slight fall with increasing ethylenediamine concentration it is presumably to a large extent because the activity of the free ethylenediamine shows an increase which is more pronounced than that of the concentration (comp. ref. 7, p. 18).

If the normal potentials from solutions 1 and 2 are combined, log K_2 for the reaction

$$\mathrm{Cu^{++} + 2\ en \rightleftharpoons Cu\ en_2^{++}}$$

in 1 N $\mathrm{KNO_3}$ is calculated to be

$$\frac{0.0476 + 0.5452}{0.02887} = \underline{20.53 \text{ at } 18^\circ}, \text{ and } \frac{0.0480 + 0.5455}{0.02957} = \underline{20.07 \text{ at } 25^\circ}$$

From the change in log K_2 with the temperature one calculates $-\Delta H$ or the decrease in the heat content for the same reaction to be 26.1 kcal. The heat evolution at the formation of the corresponding tetrammine complex is 19.7 kcal (*cf.* ref. 3, p. 79).

THE MAGNITUDE OF THE STABILITY OF THE CUPROUS-ETHYLENEDIAMINE COMPLEX

Randles[10] has, at 25°, investigated the equilibrium between cuprous-cupric complex and metallic copper in the presence of an excess of ethylenediamine, *i. e.* under conditions where both the cupric and cuprous copper must be assumed to be present as di-ethylenediamine complex. Randles' measurements are rather inaccurate, and one must take into account that the copper activity of copper amalgam is somewhat smaller than that of pure copper, but, regarded simply as an estimate, one finds:

$$K_{Cu,Hg} = \frac{[Cu\ en_2^{++}]\ [en]^2}{[Cu\ en_2^{+}]^2} = 0.4 \cdot 10^5$$

For the corresponding constant for the equilibrium between the copper-aquo ions one may put at 25° (ref. 7, p. 23)

$$K_{Cu,Hg} = 1.63 \cdot 10^6$$

If these equilibrium constants are combined with the values for the normal potentials determined by means of the solutions 1 and 2 the corresponding cuprous normal potentials

$$E^\circ\ (Cu,Hg \rightarrow Cu^+) = + 0.0480 + 0.02957\ \log\ (1.63 \cdot 10^6) = + 0.232$$
$$E^\circ\ (Cu,Hg \rightarrow Cu\ en_2^+) = - 0.5455 + 0.02957\ \log\ (\ 0.4 \cdot 10^5) = - 0.409$$

are calculated, and with the aid of these constants one calculates in turn the cuprous-complexity constant log K_2 to be

$$\frac{0.232 + 0.409}{0.05914} \sim 10.8 \text{ at } 25^\circ$$

CONVERSION OF THE NORMAL POTENTIALS TO THE NORMAL HYDROGEN ELECTRODE

The potential of the 1 N calomel electrode against the normal hydrogen electrode is known from the literature and calculated on the basis of the data given by N. Bjerrum and Unmack (ref. 11, pp. 34, 81) this potential is calculated to be 0.2844 at 18° and 0.2831 at 25°. If, at the respective temperatures these values are added to the normal potentials found (E°) relative to the calomel electrode one gets the normal potentials relative to the normal hydrogen electrode (E°_H). In this calculation it is tacitly assumed that the saturated potassium chloride solution eliminates the diffusion potential between the copper solution in 1 N KNO_3 and the 1 N calomel electrode. Finally it is an assumption applying to the whole calculation that the calomel electrodes have the correct potential. This assumption is supported by the circumstance that the potential between the hydrogen electrode in standard-acetate and the 1 N calomel electrode (with potassium chloride as intermediate liquid), which in the present paper is found to be — 0.5589 at 25° (see Table 2), is calculated to be — 0.5579 on the basis of the data given by Clark [15] and Bjerrum and Unmack [11]. Moreover, the potential of the following two cells:

+ Cu, Hg	$C_{Cu(NO_3)_2} = 0.1165$, $C_{HNO_3} = 0.01$	2 N NH_4NO_3	NH_4NO_3 2.1 N	1 N KCl, Hg_2Cl_2	— Hg

$E = 0.0214$

+ Cu, Hg	$C_{Cu(NO_3)_2} = 0.1165$, $C_{HNO_3} = 0.01$	2 N NH_4NO_3	KCl sat.	1 N KCl, Hg_2Cl_2	— Hg

$E = 0.0254$

was measured at 18°. The potential 0.0214 found for the upper one of these cells is in fairly good agreement with J. Bjerrum's [7] previously determined mean value 0.0209 for this combination. The potential of the second cell shows the importance of inserting a saturated potassium chloride solution. The diffusion potential must be assumed to be the smallest in the combination with potassium chloride inserted, and the previously determined normal potentials in 2 N NH_4NO_3 (ref. 7, p. 64) should probably be corrected accordingly.

DETERMINATION OF THE CONSECUTIVE COMPLEXITY CONSTANTS IN THE CUPRIC-ETHYLENEDIAMINE SYSTEM

Here measurements were made at 25° of a series of cupric nitrate-ethylenediamine solutions, employing both glass and copper amalgam electrodes. The investigations involved solutions having the composition: $C_{Cu(NO_3)_2} = 0.1$ $C_{HNO_3} = 0.1$, $C_{KNO_3} = 1.00$ and varying ethylenediamine concentration, *inter alia* in order to be able to apply the previously determined values for the acid-base constants of ethylenediamine $k_{enH_2}{}^{++} = 10^{-7.49}$ and $k_{enH^+} = 10^{-10.17}$ to the calculation of $\bar{n}_{en}$ and the concentration of free ethylenediamine from the experimentally determined hydrogen ion concentration. In the determination of this concentration, use was made of the already (p. 302) mentioned standard nitric acid solution while the cupric ion concentration of the particular solutions were determined by measuring relative to a copper standard solution having the following concentrations: $C_{Cu(NO_3)_2} = 0.09742$, $C_{HNO_3} = 0.0025$, $C_{KNO_3} = 1.10$. Measured against the calomel electrode a copper amalgam electrode in this solution

+ Cu, Hg	$C_{Cu(NO_3)_2} = 0.09742$, $C_{HNO_3} = 0.0025$	1.1 N KNO_3	KCl sat.	1 N KCl, Hg_2Cl_2	— Hg

had the potential 0.0198 at 25°, and relative to a weaker copper solution in an analogous salt medium

Table 4. Calculation of the consecutive complexity constants on the basis of measurements with glass electrode and copper amalgam electrode at 25° C.

Calc. with $-\log k_{enH_2}{}^{++} = 7.49$ and $-\log k_{enH}{}^{+} = 10.17$.
Solutions of the following composition were measured:

$$C_{Cu(NO_3)_2} = 0.09716\,,\ C_{HNO_3} = 0.1001\,,\ C_{KNO_3} = 1.00$$

No.	C_{en}	$-\log[H^+]$	$\bar{n}_{en}$	$\bar{n}$	$-\log[en]$	$\log k_1$	$-E_{Cu,Hg}$	$-\log a_{Cu}{}^{++}$	$\log k_1$
1	0.0683	3.791	2.000	0.190	11.379	10.741	0.0027	0.090	10.737
2	0.0866	3.996	2.000	0.379	10.969	10.731	0.0063	0.212	10.759
3	0.1020	4.128	1.999	0.520	10.705	10.685	0.0097	0.327	10.739
4	0.1229	4.282	1.999	0.754	10.396	10.736	0.0158	0.533	10.746
						$\log K_2$			
5	0.1423	4.436	1.998	0.954	10.088	20.03	0.0236	0.797	10.746
6	0.1579	4.569	1.998	1.135	9.822		0.0313	1.058	10.725
						$\log k_1$			
7	0.1761	4.696	1.997	1.303	9.569	10.704	0.0411	1.389	10.765
8	0.2037	4.916	1.996	1.589	9.129	10.716	0.0594	2.008	10.750
9	0.2132	5.010	1.996	1.679	8.941	10.747	0.0687	2.322	10.775
					Mean	10.720		Mean	10.749
									$\log K_2$
10	0.2535	7.063	1.728	2.014	4.909		0.3011	10.182	20.00
11	0.3002	9.023	0.962	2.019	2.171		0.4648	15.718	20.06
								Mean	20.03
						$\log k_2$			$\log k_2$
					Mean	9.310		Mean	9.281

$$+\ \text{Cu,Hg}\ \Big|\ C_{Cu(NO_3)_2} = 0.0974,\ C_{HNO_3} = 0.0025\ \Big|\ 1.1\ N\ KNO_3\ \Big|\ \begin{matrix}\text{KCl}\\ \text{sat.}\end{matrix}\ \Big|\ 1.1\ N\ KNO_3,\ C_{Cu(NO_3)_2} = 0.0197,\ C_{Ba(NO_3)_2} = 0.0800,\ C_{HNO_3} = 0.0025\ \Big|\ -\ \text{Cu,Hg}$$

the potential 0.0210, in good agreement with the theoretical value 0.0205 for this concentration cell. Table 4 records $E_{Cu,Hg}$, the copper amalgam potential in the complex solution measured relative to the standard copper solution, and $a_{Cu}{}^{++}$, *i. e.* the fraction of the total copper that is present as cupric ion is consequently given by the relation

$$E_{Cu,Hg} = 0.02957\ \log \frac{a_{Cu}{}^{++} \cdot 0.09716}{0.09742}$$

where 0.09716 refers to the total copper concentration of the measured complex solutions.

The consecutive constants were determined in two different ways: (1) from our knowledge of the formation curve, calculated as previously described (ref. 1, p. 8), and (2) by means of the values, determined for a_{Cu++} in connection with our knowledge of —log [en].

As for (1): The first consecutive constant was calculated in this case with the aid of the previously (ref. 3, p. 133) derived formula

$$k_1 = \frac{(2 - \bar{n})\ [\text{en}]^2\, K_2 - \bar{n}}{(\bar{n} - 1)\ [\text{en}]}$$

For the gross constant K_2 there was inserted the value that was calculated from —log [en] in the midpoint of the formation curve for $\bar{n} = 1$. For this $\bar{n}$-value —log [en] was determined by graphical interpolation to be = 10.015, whence follows log $K_2 = 20.03$.

As for (2): Here the first consecutive constant was calculated with the aid of the relation

$$\frac{1}{a_{Cu^{++}}} = 1 + k_1\ [\text{en}] + K_2\ [\text{en}]^2$$

For solutions 10 and 11 in Table 4, the di-ethylenediamine complex is the only complex present so that K_2 can be directly calculated by means of the expression

$$K_2 = \frac{1}{a_{Cu^{++}} \cdot [\text{en}]^2}$$

On this basis one calculates log K_2 to be 20.00 and 20.06 respectively, *i. e.* in average the same value as that calculated from —log [en] in the midpoint of the formation curve, and this value of log K_2 is therefore used in the calculation of values of log k_1 recorded in the last column of Table 4.

Table 4 summarises all of the worked-up material. If one compares the values for log k_1 calculated in the two different ways and the mean values for log k_1 and log k_2 it is seen that all of the measurements made are in good agreement.

EXTINCTION MEASUREMENTS AND DETERMINATION OF THE THIRD CONSECUTIVE CONSTANT

Table 5 shows some determinations of the molar extinction coefficient in various cupric-ethylenediamine solutions. The molar extinction coefficient is calculated in accordance with the expression:

$$\varepsilon = \frac{\log \frac{I_0}{I}}{C_{Cu} \cdot d}$$

where I_0 and I denote the intensity of the incident and the transmitted light respectively, C_{Cu} the total copper concentration, and d the thickness of the absorbing layer in cm. The measurements were carried out by means of a König-Martens Spetrophotometer equipped with the »grosse Beleuchtungseinrichtung». The smallest possible slit opening was used, and as a rule the measurement gave the mean extinction coefficient for a range of wavelengths of the order of magnitude of $\pm$ 4 mμ (*vide* ref. 6, p. 6).

According to the magnitude of the 2nd consecutive complexity constant the formation of the di-ethylenediamine complex is completed at a concentration of free ethylenediamine as low as about 10^{-7}, and the extinction coeffi-

Table 5. Molar extinction coefficients of some cupric ethylenediamine solutions at 25°.

With potassium nitrate (1 *N*)

No.	$C_{Cu(NO_3)_2}$	C_{en}	C_{HNO_3}	[en]	ε_{670}	ε_{650}	ε_{630}	ε_{590}
10 (Table 4)	0.09716	0.2535	0.1001	$10^{-4.91}$	17.49	23.78	31.35	50.50
1	0.09716	0.3181	0.1001	$10^{-1.62}$	17.38	23.30	31.28	50.47
2	0.00972	0.05347	0.0499	$10^{-4.36}$	16.91	22.91	30.58	49.58
4 (Table 3)	0.00972	0.3239	0.0499	0.2545	18.24	24.48	32.15	—
6 (Table 3)	0.00972	0.7094	0.0499	0.6400	21.78	28.21	36.09	54.39
3	0.05034	1.736	0.0505	1.585	29.11	35.79	43.76	59.62
5	0.00983	1.635	0.0505	1.565	29.20	35.85	43.97	59.84
7	0.00476	1.649	0.0503	1.589	30.00	36.57	44.54	58.46
8	0.00983	3.256	0.0505	3.186	44.31	51.94	60.25	72.41
Without potassium nitrate								
9	0.00983	3.272	0.0505	3.202	40.52	47.66	56.72	69.54
11	0.00570	7.101	0		75.03	83.10	90.74	96.98
12	0.00729	9.208	0		84.86	95.02	103.5	106.4
13	0.00977	12.18	0		87.38	98.31	107.0	108.6

cients of Table 5 clearly show that this complex thereafter is predominant over a wide range of concentration. Not until the concentration of free ethylenediamine exceeds 0.1 molar does the extinction coefficient in the red part of the spectrum begin to show noticeable growth which thereafter becomes increasingly stronger with the base concentration. Comparison of solutions 3, 5 and 7 show, however, that Beer's law applies rather accurately to solutions with the same concentration of ethylenediamine. This excludes the formation of polynuclear complexes like for example

$$\mathrm{en_2^{++}CuNH_2CH_2CH_2NH_2Cu^{++}en_2}$$

A graphical presentation of how the extinction coefficient changes with both ethylenediamine concentration and wavelength is shown in the upper left of Fig. 2. It will be seen that the absorption maximum shows both an increase and a displacement towards red at the same time as the curves converge towards a limiting curve at very high concentrations of ethylenediamine. It is seen, moreover, that the absorption curves all pass through one and the same point of intersection, which shows that one has to do with a system of only two absorbing complexes (*cf.* ref. 6, p. 7). It therefore seems logical to assume that the limiting curve at high ethylenediamine concentrations represents the absorption curve for the tri-ethylenediamine complex, and with this assumption a calculation has been made of the 3rd consecutive constant at each of the 4 wavelengths in Table 5. The result of this calculation is summarized in Table 6. The individual values of k_3 are calculated by means of the expression

$$k_3 = \frac{\varepsilon_{\mathrm{NoX}} - \varepsilon_{\mathrm{No2}}}{(\varepsilon_{\mathrm{No13}} - \varepsilon_{\mathrm{NoX}})\ [\mathrm{en}]}$$

where $\varepsilon_{\mathrm{NoX}}$ denotes the extinction coefficient of the solution in question at the particular wavelength. The very small extinction differences $\varepsilon_{\mathrm{No4}} - \varepsilon_{\mathrm{No2}}$ and $\varepsilon_{\mathrm{No6}} - \varepsilon_{\mathrm{No2}}$ are, in order to obtain values for k_3 at all usable, determined by direct measurement of the particular solutions relative to solution 2. The concentration of free ethylenediamine is in all cases with sufficient accuracy calculated by means of the expression

$$[\mathrm{en}] = C_{\mathrm{en}} - C_{\mathrm{HNO_3}} - 2C_{\mathrm{Cu(NO_3)_2}}$$

The basis for the calculation of k_3 is essentially less favourable at wavelength 590 mμ than at the three other wavelengths, and for this reason the values calculated at this wavelength are not included in the general mean value

Table 6. Values for the third consecutive complexity constant calculated from the extinction coefficients given in Table 5.

1 *N* potassium nitrate

No.	$C_{Cu(NO_3)_2}$	[en]	670	650	630	590	k_3 (mean)
4	0.00972	0.2545	0.076	0.084	0.083	—	0.081
6	0.00972	0.6400	0.116	0.118	0.121	(0.139)	0.118
3	0.05034	1.585	0.132	0.130	0.131	(0.130)	0.131
5	0.00983	1.565	0.135	0.133	0.136	(0.135)	0.135
7	0.00476	1.589	0.144	0.139	0.141	(0.112)	0.141
8	0.00983	3.186	0.200	0.197	0.199	(0.198)	0.199
			Without potassium nitrate				
9	0.00983	3.202	0.157	0.153	0.162	(0.159)	0.157

determination in Table 6. It will be seen that the mean values thus calculated for k_3 increase rather strongly with the ethylenediamine concentration, and that the calculated constant in dilute solution is smaller than in 1 *N* potassium nitrate at the same ethylenediamine concentration. The trend of the calculated values for k_3 agrees qualitatively with the fact that f_{en} increases with the ethylenediamine concentration (compare with $f_{en} \cdot F$ in Table 2) as well as with increasing salt concentration (*cf.* ref. 3, p. 129). The value of k_3 determined by means of solution 4 is, for reasons of calculation, rather uncertain, but if log k_3 is plotted against the concentration of free ethylenediamine a determination can be made, graphically utilizing the whole material, of k_3 in 1 *N* KNO_3 at small ethylenediamine concentrations. In this way k_3 is found to be, on the average, about 0.10.

COMPARISON OF THE EXTINCTION CURVES OF THE CUPRIC-ETHYLENEDIAMINE COMPLEXES WITH THE CORRESPONDING CURVES FOR THE AMMONIA- AND PYRIDINE COMPLEXES

In order to establish the absorption curve for the mono-ethylenediamine complex, determinations were made, at a series of wavelengths, of the molar extinction coefficient of solutions 3, 4 and 5 in Table 4 as well as that of a pure copper nitrate solution in 1 *N* KNO_3. The relative distribution of the copper in the solutions is calculated with the aid of the values determined for k_1 and K_2 and is, along with the calculated complex distribution at a number of other ethylenediamine concentrations, recorded in Table 7. The experimentally determined extinction curves, and the values of the light absorption

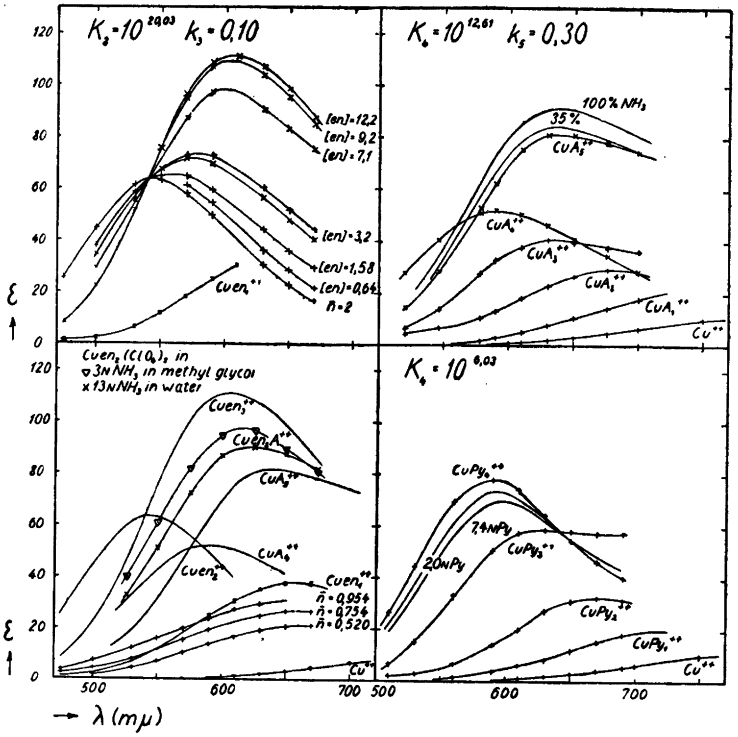

Fig. 2. Extinction curves for cupric complexes with ethylenediamine, ammonia and pyridine.

Upper left: Curves for cupric nitrate in 1 *N* KNO_3 (+ points) and without salt added (× points) at various concentrations of free ethylenediamine. The highest of the concentrations [en] = 12.2 corresponds very closely to ethylenediamine hydrate.

Lower left: Curves for 3 mixed solutions having $\bar{n} = 0.520$, 0.754 and 0.954 (+ points) as well as a curve for the mono-ethylenediamine complex determined with the aid of these curves. The last mentioned curve is partly drawn at the upper left, and the scattering of the calculated points is indicated by a special signature. The graph moreover contains curves for Cu en_2^{++} ($\bar{n} = 2$), Cu en_3^{++} ([en] = 12.2) as well as for $Cu(NH_3)_4^{++}$ and $Cu(NH_3)_5^{++}$ and the mixed complex Cu $en_2(NH_3)^{++}$. The curves for the latter ion are determined by graphical interpretation of Rosenblatt's measurements [8].

Upper right: J. Bjerrum's [6,7] curves for the cupric ammonia ions in 2 *N* NH_4NO_3 (+ points) and in ammonia solutions without added salt (× points) as well as for the cupric complex in 35 % and 100 % NH_3.

Lower right: Estimated values for the pyridino cupric complexes in 0.5 *N* $PyHNO_3$-pyridine solutions as well as the values for cupric nitrate in the same salt medium for [Py] = 2.0 and 7.4. The latter concentration corresponds to 590 g of pyridine per liter.

of the mono-ethylenediamine complex calculated therefrom by means of the relation

$$\varepsilon = \alpha_0 \varepsilon_{Cu^{++}} + \alpha_1 \varepsilon_{Cu\ en_1^{++}} + \alpha_2 \varepsilon_{Cu\ en_2^{++}}$$

and from our knowledge regarding $\varepsilon_{Cu^{++}}$, $_{Cu\ en_2^{++}}$ and the α-coefficients, are shown graphically in the lower left of Fig. 2. The calculation is carried out for each one of the mixed solutions measured, and the scattering of the points computed is marked by a special signature. The curve for the mono-ethylenediamine complex intersects the curves for the experimental mixtures, and the points computed for the pure complex are for this reason partly plotted in the upper left of the figure. Table 8 records the mean values found, together

Table 7. Distribution of the different complexes in 1 N KNO_3 at 25°.

$$\alpha_n = \frac{[Cu\ en_n^{++}]}{C_{Cu^{++}}}, \quad \bar{n} = \Sigma n \alpha_n$$

Calculated with $k_1 = 10^{10.72}$, $K_2 = 10^{20.03}$

No.	—log [en]	α_0	α_1	α_2	α_3	$\bar{n}$
3 (Table 4)	10.705	0.482	0.498	0.020	0	0.520
4 »	10.396	0.305	0.643	0.053	0	0.754
5 »	10.088	0.167	0.714	0.119	0	0.954
	9.00	0.006	0.327	0.667	0	1.661
	8.00	0	0.047	0.952	0	1.952
	2.00	0	0	0.999	0.001	2.001
	1.00	0	0	0.990	0.010	2.010

Table 8. Estimated molar extinction coefficients for the cupric ethylenediamine ions at 25° C.

Cu^{++} Extinction coefficients of the solution: $C_{Cu(NO_3)_2} = 0.09742$, $C_{HNO_3} = 0.00025$, $C_{KNO_3} = 1.10$.
$Cu\ en^{++}$ Calculation from the extinction coefficients of sols. no. 3, 4 and 5 in Table 4.
$Cu\ en_2^{++}$ Extinction coefficients of solution no. 2 in Table 5.
$Cu\ en_3^{++}$ Extinction coefficients of solution no. 13 in Table 5.

Wavelengths in mμ

	670	650	630	610	590	570	550	530	500	475
Cu^{++}	4.51	3.14	2.01	1.21	0.75	0.40	0.21	0.10	0.03	—
$Cu\ en^{++}$	37.5	37.5	35.0	30.6	24.7	18.0	11.7	6.4	2.3	1.4
$Cu\ en_2^{++}$	16.91	22.91	30.58	(39.0)	49.58	57.94	63.05	61.23	44.34	25.19
$Cu\ en_3^{++}$	87.38	98.31	107.0	(110.8)	108.6	96.09	75.37	51.77	22.32	8.65

with the directly determined extinction coefficients for the aquo-cupric ion and the di- and tri-ethylenediamine complex.

The absorption curves for the cupric-ammonia complexes have previously been determined (ref. 6, p. 52, *cf.* also ref. 7, p. 55), and the absorption curves for the cupric-pyridine complexes have recently been determined by J. Bjerrum in an investigation not yet published. The pyridine investigation was carried out in an aqueous 0.5 *N* $PyHNO_3$, and the consecutive formation constants for the tetra-pyridino complex were found, at 25°, to be:

$$k_1 = 10^{2.41},\ k_2 = 10^{1.88},\ k_3 = 10^{1.14},\ k_4 = 10^{0.60}$$

The absorption curves for the pure ammonia- and pyridine complexes are shown at the right in Fig. 2. It will be seen how the absorption maximum is displaced evenly towards blue from the aquo-cupric ion to the tetrammine complexes, at the same time as the magnitude of the absorption increases in the same sequence (*cf.* ref. 3, p. 196). The displacement towards blue per amino group is very nearly the same for the ammonia- and the pyridine complexes, but somewhat smaller than in the case of the mono- and di-ethylenediamine complexes, a circumstance which presumably is associated with the chelate binding of the diamine (*cf.* ref. 16). The special character of the pentammine- and tri-ethylenediamine complexes is reflected in the circumstance that the absorption maximum of these complexes, relatively to the respective tetrammine complexes, is shifted towards red. But it is seen that the tetrapyridine spectrum does not at all suffer a corresponding change even at very high pyridine concentrations. This is hardly due to the relatively small complexity of the tetrapyridino-cupric ion, but rather to steric reasons. In this connection it is worthy of note that hexapyridino complexes of the luteo type apparently cannot be prepared*, and one cannot therefore be sure that the existing molecular compounds with 6 molecules pyridine [17] have all their pyridine co-ordinated to the metal ion.

In a strongly ammoniacal solution of Cu $en_2(ClO_4)_2$ the copper is predominantly present as the mixed complex Cu $en_2(NH_3)^{++}$ [8]. In the lower left part of Fig. 2 the absorption curves for 2 such solutions are compared with the absorption curves for the pentammine- and tri-ethylenediamine complex. It will be noticed that the curves for the 3 complexes are located relative to one another in such a way that one must assume that the three complexes all have the same constitution. Hence the optical data are in every respect in support

* One of the authors (J. Bjerrum) has tried in vain to do so.

of the idea that the tri-ethylenediamine complex actually is a pentammine complex with the amino molecule last taken up bound only by one of its amino groups.

SUMMARY

The consecutive formation constants of the di-ethylenediamine cupric ion are determined with the aid of glass- as well as copper amalgam-electrode, and the 3rd consecutive complexity constant from extinction measurements made by means of a König-Martens spectrophotometer (*vide* Table 1).

The following is a survey of the normal-oxidation potentials established in connection with the electrometric measurements in 1 *N* KNO_3 and converted to the normal hydrogen electrode.

Electrode reaction	E_H° (18°)	E_H° (25°)
$Cu(amalg.) + 2\ en = Cu\ en_2^{++} + 2\ e^-$	— 0.2608	— 0.2624
$Cu(amalg.) + 2\ en = Cu\ en_2^{+} + e^-$		c. — 0.126
$Cu(amalg.) + 4\ H_2O = Cu(H_2O)_4^{++} + 2\ e^-$	+ 0.3320	+ 0.3311
$Cu(amalg.) + 2\ H_2O = Cu(H_2O)_2^{+} + e^-$		c. + 0.515

In connection with the optical measurements a determination was made of the extinction curves for the mono-, di- and tri-ethylenediamine cupric ion, and a comparison with the corresponding spectra of the cupric-ammonia- and the cupric-pyridine complexes. The material as a whole is in strong support of the idea that the tri-ethylenediamine complex is a pentammine complex with the ethylenediamine molecule last taken up bound by only one of its amino groups.

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