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The Reaction between the Copper(II)–Ethylenediamine Complexes and Erythritol Anhydride

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The reaction between erythritol anhydride (*cis*-3,4-dihydroxytetrahydrofuran) and the bis-ethylenediaminecopper(II) ion has been investigated using spectrophotometric and conductometric methods. In the presence of excess hydroxide ions one ethylenediamine molecule is displaced to give the erythritolanhydridoethylenediaminocopper(II) ion.

Introduction

Traube[2] observed that $[Cu(en)_2](OH)_2$ possessed the ability to dissolve cellulose and studied its effect on simpler polyhydric alcohols such as glycerol, mannitol and dulcitol. He concluded that with glycerol, for example, $[Cu(en)_2](O\text{-}CH_2\text{-}CHOHCH_2OH)_2$ is first formed, which then reacts with more $[Cu(en)_2](OH)_2$ to liberate ethylenediamine and form $[Cu(en)_2][Cu(OCH_2CHOHCH_2O)_2]$. Traube assumed that only the $[Cu(en)_2]^{2+}$ ion was present in this system.

No study seems to be reported in the literature for the reaction of the simpler polyhydric alcohols with the $[Cu(en)]^{2+}$ ion. The spatial requirements for complex formation between copper(II) ion and the hydroxyl groups of the polyhydroxy organic compounds as established in recent studies by Reeves[3] threw a new light on this problem.

The present paper presents one portion of a study undertaken to investigate the reactions of the bis-ethylenediaminecopper(II) ions with a simple glycol of fixed configuration—*cis*-3,4-dihydroxytetrahydrofuran (erythritol anhydride).

Experimental

A. **Reagents.**—A standard solution of 0.1031 *M* copper nitrate was prepared by dissolving reagent grade $Cu(NO_3)_2$ in distilled water. One drop of C.P. concd. nitric acid was added to 4 liters of the solution to prevent hydrolysis. The copper(II) ion concentration was determined by electrodeposition.

Commercial ethylenediamine was dried over C.P. sodium hydroxide, then over sodium metal. Fractional distillation from sodium metal gave the purified product (b.p. 119°, lit. b.p. ethylenediamine hydrate, 118°) which was used to prepare an aqueous 0.1128 *M* solution of ethylenediamine. The concentration of ethylenediamine was determined by titration with standard hydrochloric acid, using methyl orange indicator. All preparations of $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$ were made by dilution of pipetted volumes of the standard solutions calculated to give the required quantities of each compound.

Erythritol anhydride (*cis*-3,4-dihydroxytetrahydrofuran) was prepared from C.P. erythritol in the manner described by Henninger.[4] Direct titration of the product with lead tetraacetate[5] showed it to be 100% *cis*-glycol. The quantities of erythritol anhydride required for the complexes were obtained as needed by pipetting calculated volumes from the solutions of known concentrations.

B. **Spectrophotometric Studies.**—Absorption measurements in the visible spectral region were made with a Beckman Model B spectrophotometer using 1-cm. Corex cells. A constant ionic strength of 0.5 was maintained by the addition of calculated volumes of 1 *M* potassium nitrate solution.

All solutions, except that of $[Cu(en)]^{2+}$, examined spectrophotometrically contained sodium hydroxide in 0.1 *M* concentration. This concentration, necessary to bring about complex formation between the glycol and the ions, gives the solution a *p*H almost equal to that of the $[Cu(en)_2](OH)_2$ solution normally used to dissolve cellulose. Optical density measurements were made over the range 320 to 1000 mμ. Preliminary examinations in the ultraviolet region disclosed that the solutions were opaque; potassium nitrate had to be omitted here because of its strong characteristic absorption.

Continuous variation studies[6] were carried out at 350 and 550 mμ with 0.01 *M* bis-ethylenediaminecopper(II) and 0.01 *M* glycol solutions, and at 500, 575, 630 and 725 mμ with 0.02 *M* bis-glycolatocopper(II) and 0.02 *M* ethylenediamine solutions. All of these solutions were 0.1 *M* in sodium hydroxide.

The effect of sodium hydroxide concentration on the $[Cu(en)_2]^{2+}$ ion and on the ethylenediaminoglycolate copper(II) complexes was observed by obtaining the absorption spectra while varying the base concentration from 0.0 to 1 *M*.

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[1] Abstracted in part from a dissertation submitted by Leon Segal to the Tulane University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] W. Traube, *Ber.*, **54**, 3220 (1921).

[3] (a) R. E. Reeves, THIS JOURNAL, **71**, 212 (1949); (b) **71**, **215** (1949).

[4] M. A. Henninger, *Ann. chim. phys.*, [6] **7**, 223 (1886).

[5] R. E. Reeves, *Anal. Chem.*, **21**, 751 (1949).

[6] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

Constant ionic strength could not be maintained in the solutions with hydroxide ion concentrations above 0.4 *M*.

C. **Conductometric Titrations.**—Conductometric titrations were made with an Industrial Instrument Co. 1000-cycle conductivity bridge using a dipping type cell with vertical electrodes. The temperature during titration was held at 25 ± 1° by immersing the glass container in a water-bath. The calculated conductances were corrected for dilution.

D. **Isolation of Complex.**—Equimolar quantities of erythritol anhydride and $[Cu(en)_2](OH)_2$ were mixed together and the resulting solution was allowed to dry over P_2O_5. The blue, dendritic crystals were washed with several portions of 95% ethanol and dried to constant weight over P_2O_5 *in vacuo*. $[Cu(en)_2](OH)_2$ treated in the same manner gave black cupric oxide. Micro-analysis of the blue compound indicated it to have the empirical formula $C_6H_{14}O_4N_2Cu$.

Results and Discussion

A. Spectrophotometric Studies.—The absorption spectra for the various complexes shown in Fig. 1 are given over the 320–800 mμ range where the characteristic absorptions are found.

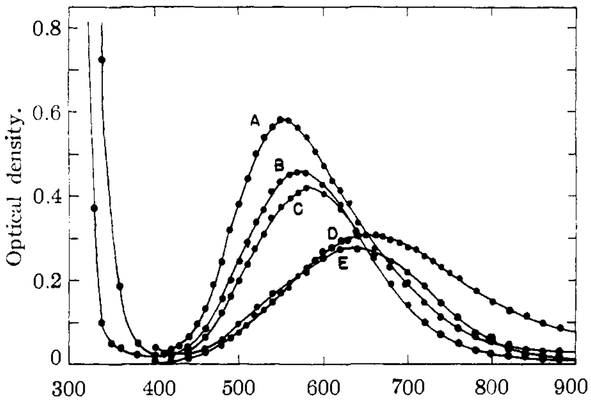


Fig. 1.—Absorption curves for the various complex ions in 0.1 *M* sodium hydroxide; Beckman Model B spectrophotometer, 1 cm. Corex cells; constant ionic strength of 0.5 maintained by addition of calculated volumes of 1 *M* potassium nitrate solution. A, $[Cu(en)_2]^{2+}$; B, $[Cu(en)_2]^{2+}$ + erythritol anhydride; C, $[Cu(en)]^{2+}$ + erythritol anhydride; D, $[Cu(en)]^{2+}$ (no NaOH); E, Cu^{2+} + erythritol anhydride; copper concentration 0.01 *M*, anhydride 0.02 *M*.

The addition of glycol to the $[Cu(en)_2]^{2+}$ and $[Cu(en)]^{2+}$ ions, or of ethylenediamine to the bis-glycolatocopper (II) complex, causes a shift in the position and optical density of the maxima of the respective solutions. The peak for $[Cu(en)_2]^{2+}$ upon addition of glycol, shifts toward a longer wave length while the optical density of the solutions decreases. With the $[Cu(en)_2]^{2+}$ solution, and with the bis-glycolatocopper(II) solution to which ethylenediamine is added, the peak shifts toward shorter wave length and greater optical density.

The curves for the products of the $[Cu(en)_2]^{2+}$–glycol and the $[Cu(en)]^{2+}$–glycol interactions seem to indicate that the same product is obtained from each of the complexes. Although the curves do not exactly coincide, the difference is small and is considered to be the result of incomplete reactions between the species in solution under these experimental conditions.

Continuous variation studies for the interaction between $[Cu(en)_2]^{2+}$ and the glycol at two different wave lengths, show a maximum at mole fraction 0.5 indicating that at a mole ratio of 1:1, one new colored complex is formed. No continuous variation study could be made with the $[Cu(en)]^{2+}$ ion since it is unstable in alkaline media.[7]

The continuous variation curves of bis-glycolatocopper(II) and ethylenediamine as the entering molecule at four different wave lengths show again only one maximum at the same mole fraction of 0.5, indicating a 1:1 interaction.

These evidences can be interpreted as a simple interaction between the complexes and the entering bidentate ligand if copper(II) ion is assumed to exist in the pentacovalent or hexacovalent configuration.

Since the hexacovalency of copper(II) is in serious doubt[8,9] this structure seems to be unlikely.

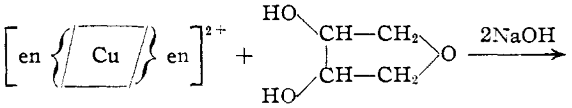
Bjerrum and Nielson[10] have shown that the tris-ethylenediamine copper(II) complex, in which the third ethylenediamine molecule is attached to the pentacovalent copper(II) ion by only one of its donor groups, is very unstable. The extreme conditions required for the formation of such a complex have not been used in the present study.

The close similarity of the absorption curves of the complexes resulting from addition of glycol to $[Cu(en)_2]^{2+}$ and $[Cu(en)]^{2+}$ solutions (Fig. 1) strongly suggests that the products are the same. This would be highly unlikely if the copper(II) ion in these copper complexes were pentacovalent, since in order to maintain the 1:1 molar ratio one product would have to be $[Cu(en)_2glycol]$ and the other $[Cu(en)glycol]$ which would be expected to have different absorption characteristics.

If tetracovalency is assumed for the copper(II) ion, the entering bidentate molecule adds to $[Cu(en)]^{2+}$ to give the Cu(en)glycol complex. Interaction of the $[Cu(en)_2]^{2+}$ and glycol will give the same product by elimination of one ethylenediamine molecule. This is in agreement with the findings of Traube[2] and of Jolley[11] and Strauss and Levy[12] with cellulose. It also satisfies the 1:1 molar ratio indicated in the continuous variation study.

The bis-glycolatocopper(II) complex would lose one glycolate group to take up one ethylenediamine molecule. This would satisfy the 1:1 molar ratio for the complex $[Cu(en)glycol]$.

From these considerations, the spectrophotometric data may be interpreted as indicating that the $[Cu(en)_2]^{2+}$ ion and erythritol anhydride interact in the following manner



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[7] H. B. Jonassen, R. E. Reeves and L. Segal, THIS JOURNAL, **77**, 2748 (1955).

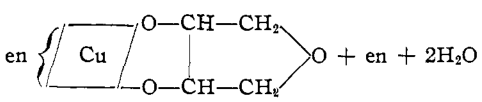
[8] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952, p. 286.

[9] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, THIS JOURNAL, **72**, 4968 (1950).

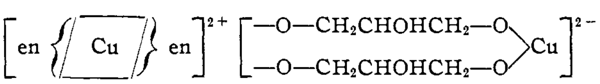
[10] J. Bjerrum and E. J. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

[11] L. J. Jolley, *J. Textile Inst.*, **30**, T22 (1939).

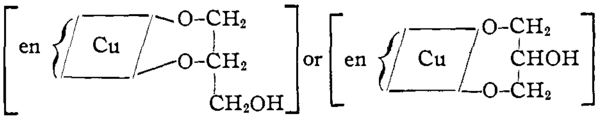
[12] F. L. Strauss and R. M. Levy, *Paper Trade*, **114**, T 23 (1942); **114**, T 211 (1942).



It should be observed that the copper–ethylenediamine–glycol ratio of 1:1:1 is exactly half of that given by Traube[2] for his copper–ethylenediamine–glycerol complex



It seems highly probable now that Traube actually obtained one of the two complexes given



This proposed structure of the product of the interaction of $[Cu(en)_2]^{2+}$ and glycol also is similar to that proposed by Jolley[11] and by Meyer.[13] The isosbestic point found[7] when the $[Cu(en)_2]^{2+}$ ion is treated with excess hydroxide ions was not found when glycol was included in this system.

The absorption curves given in Fig. 2 only show a decrease in optical density and a small shift in the wave length of the maximum. The addition of glycol thus seems to lead to the formation of a complex with $[Cu(en)_2]^{2+}$ and the glycol.

The curves of Fig. 2 show that a sufficiently high hydroxide ion concentration is necessary to drive the reaction between the $[Cu(en)_2]^{2+}$ ion and the glycol to completion. In the case of the reaction between $[Cu(en)]^{2+}$ and glycol, the effect of hydroxide concentration is somewhat different. When a solution 0.01 *M* in copper(II), 0.01 *M* in ethylenediamine, 0.02 *M* in the glycol and 0.01 *M* in sodium hydroxide was prepared, the solution was turbid.

Repeating this with 0.02 *M* sodium hydroxide gave a slightly hazy solution which later showed a precipitate. Only at base concentration of 0.05 *M* or above, was a clear stable solution obtained. The absorption curve for this solution showed only a slight difference from that obtained in the presence of 0.1 *M* sodium hydroxide.

B. Conductometric Titrations.—When solutions of ethylenediamine and of the glycol were each titrated with sodium hydroxide, the plotted conductometric data produced straight lines. The same result was obtained when a solution of $[Cu(en)_2]^{2+}$ ion was titrated with sodium hydroxide. These data indicate that these compounds were either not affected by sodium hydroxide in the concentration used, or new ions were not produced until the hydroxide ion concentration was so high that they did not affect the over-all conductance of the solution.

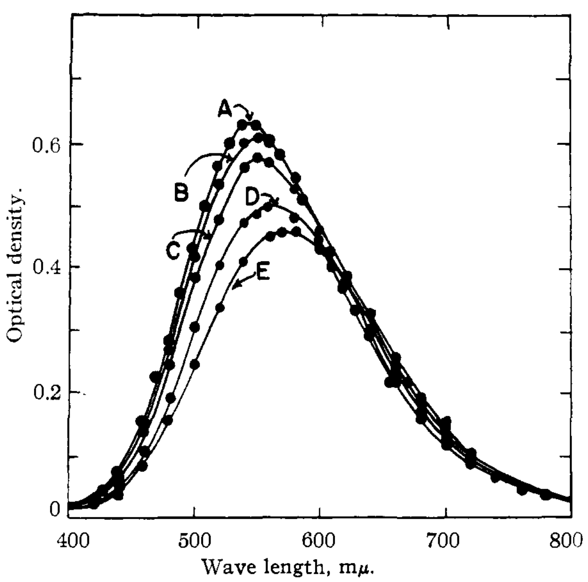
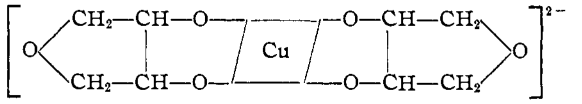


Fig. 2.—Effect of sodium hydroxide concentration on the complex from anhydride and $[Cu(en)_2]^{2+}$; Beckman model B spectrophotometer; 1-cm. Corex cells. A, $[Cu(en)_2]^{2+}$ alone; B, 0.01 *M* NaOH; C, 0.02 *M* NaOH; D, 0.05 *M* NaOH; E, 0.1 *M* NaOH.

In the case of the glycol, the latter conclusion seems to be correct because polyhydric alcohols display a weakly acidic character. An illustration of the fact that such ions may be produced at "swamping" concentrations of base where they do not affect the over-all conductance was obtained by titrating a solution of copper(II) and erythritol anhydride with 0.5 *M* sodium hydroxide. Copper hydroxide precipitated when the $(OH)^-/Cu(II)$ ratio reached 2, at which point the curve broke sharply. No further breaks in the curve were found upon continued titration even though the precipitate dissolved and a clear blue solution resulted when the OH/Cu ratio reached seventeen.



Production of the blue color by the formation of the complex ion was not accompanied by a change in conductance at the high base concentration present. On the other hand, when the concentration of sodium hydroxide was held constant at 0.05 *M* and the system was titrated with copper nitrate, a sharp break in the conductance is observed at a Cu/glycol ratio of 0.5. This indicates that two glycolate ions react with one copper(II) ion. The slope of the line upon further addition of copper nitrate after the break point is $^1/_2$ that of the line before that point, indicating that the change in conductance on addition of copper(II) ion is one-half of what it was before the break point. This effect is consistent with the number of highly conducting hydroxide ions being withdrawn from solution before and after the break point, since these are the principal highly conducting ions involved in the reaction. Thus, four $(OH)^-$ ions are being withdrawn in forming the bis-glycolatocopper(II) ion, while only two are being withdrawn in forming $Cu(OH)_2$. The curve resulting from titration of $[Cu(en)]^{2+}$ ion with NaOH displayed a sharp break at the OH/Cu ratio of 1, shown as the lowest curve in Fig. 3. This is in agreement with the finding reported by

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[13] K. H. Meyer, "Natural and Synthetic Polymers," Interscience Publishers, Inc., New York, N. Y., 1950, pp. 352–353.

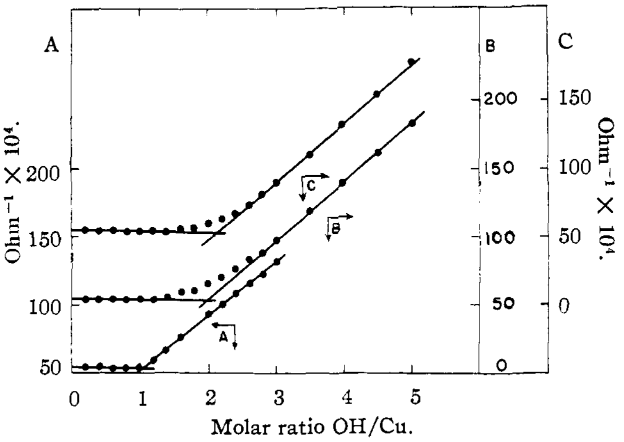
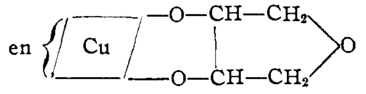


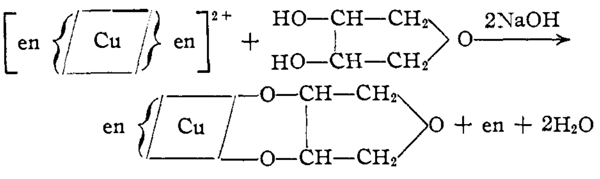
Fig. 3.—Conductometric titration of $[Cu(en)]^{2+}$ and $[Cu(en)]^{2+}$-anhydride with 0.25 M NaOH; Industrial Instrument Company 1000-cycle conductivity bridge, dipping type cell with vertical electrodes, temperature 25 ± 1°, $[Cu(en)]^{2+}$ concentration 0.0025 M: A, $[Cu(en)]^{2+}$ alone; B, complex with 0.005 M anhydride; C, complex with 0.0125 M anhydride.

Jonassen and Dexter,[14] that half of the total copper(II) precipitates as $Cu(OH)_2$ with liberation of ethylenediamine which reacts with the remaining half of the copper(II) ions to form $[Cu(en)_2]^{2+}$. The upper two curves of Fig. 3 were obtained after inclusion of the glycol in the $[Cu(en)]^{2+}$ solution. The breaks in both of the titration curves occur at the OH/Cu ratio of 2, not withstanding the 2- and 5-fold excess concentrations of glycol over that of the copper(II) ion. Thus, two $(OH)^-$ ions seem to react, indicating the formation of the complex



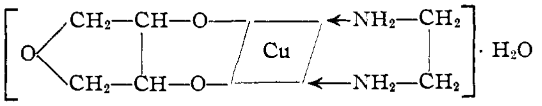
When the $[Cu(en)_2]^{2+}$ ion was titrated with sodium hydroxide, only a straight line resulted.

Inclusion of the glycol with the $[Cu(en)_2]^{2+}$ ion resulted in a break at the OH/Cu ratio of 2. Since this is the same ratio as that obtained when the $[Cu(en)]^{2+}$ ion reacted with the glycol, it seems reasonable to assume that a similar complex has been formed in this case



In this reaction, the molar ratio between the glycol and the $[Cu(en)_2]^{2+}$ ion is 1:1, and ethylenediamine is liberated. This is identical with the reaction postulated by interpretation of the spectrophotometric data above.

C. Isolation of Complex.—The empirical formula $C_6H_{10}O_4N_2Cu$ found by analysis of the solid can be fitted to the structural formula



Overnight drying in an Abderhalden at 100° resulted in a weight loss equivalent to one molecule of water and a color change from blue to violet.

Spectrophotometric examination of an aqueous solution of the blue solid gave curve B of Fig. 4. This curve displayed close similarity to that obtained from $[Cu(en)_2]^{2+}$ glycol in 0.1 M NaOH (curve A), indicating that the dissolved materials were similar.

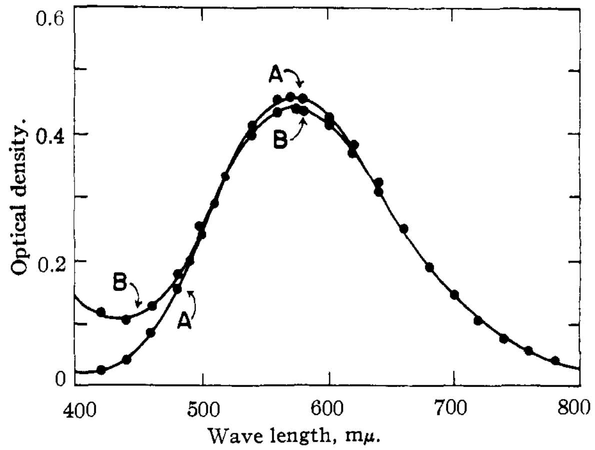


Fig. 4.—Absorption curves; Beckman model B spectrophotometer, 1-cm. Corex cells: A, $[Cu(en)_2]^{2+}$-glycol in 0.1 M NaOH; B, isolated complex.

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[14] H. B. Jonassen and T. H. Dexter, THIS JOURNAL, **71**, 1553 (1949).