tion of the active fractions obtained by the initial resolution and by the second-order asymmetric process yielded approximately 10 g. of active product: $[\alpha]_D$ +102°, −101°. The filtrates from this third active fraction were then concentrated to a small volume (20 to 30 ml.) and added to the solution in which the asymmetric process was occurring. After standing an additional 24 hours, this solution yielded a further fraction giving the same rotation as those previously isolated. After recrystallization from a small volume of hot water, this fraction amounted to about 10 g., $[\alpha]_D$ +102°, −101°.

In order to obtain an approximate material balance, the remaining solution was evaporated to dryness and weighed. This material was essentially racemic. Total recovery of material was approximately 95%. Total yield of active complex was 90 to 95 g. or 74 to 77%, based on total amount of complex (148 to 154%, based on the amount of the isomer originally present.) From 76 to 79% of the total material recovered was optically pure complex of one configuration.

The ultimate yield obtained by the method of resolution described here is determined by the volume of the solution in which the asymmetric process occurs. The quantities of the dextro and levo isomers remaining after as much active complex as possible has been removed are the same, this amount corresponding to a saturated solution of the least soluble diastereoisomer. The volume of the solution is determined by the first step in the resolution. Concentration of the original solution to facilitate crystallization of the least soluble form results in a very viscous solution which eventually begins to form a gelatinous mass. This limits the extent to which the volume may be reduced. It is, of course, theoretically possible to obtain a 100% yield in a process of this sort; however, the steps which would be necessary in order to obtain the final 20 to 25% of the complex in the desired active form are not sufficiently convenient to be justified.

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Inorganic Complex Compounds Containing Polydentate Groups. XI. Effect of Hydroxide Ion on the Bis-ethylenediaminecopper(II) Ion

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RECEIVED DECEMBER 13, 1954

The reaction of copper(II) ions with ethylenediamine has been studied in the past by Traube,[2a] Chattaway and Drew[2b] and Job[3] who concluded that only the $[Cu(en)_2]^{2+}$ ion existed in solution. Mandal[4] doubted the results of Chattaway and Drew, and in a later paper Carlson, McReynolds and Verhoek[5] accepted the existence of the $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$ ions. Bjerrum and Nielson[6] presented spectrophotometric evidence for these two ions, and their existence was conclusively demonstrated by Jonassen and Dexter[7] using spectrophotometric and conductometric titration studies.

Since it has been observed that upon addition of large excess of hydroxide ion, changes in absorption characteristics were produced, it was decided to investigate this phenomenon.[8]

Experimental

A. **Reagents.**—A standard solution of 0.103 *M* copper nitrate was prepared from reagent grade $Cu(NO_3)_2$. One drop of C.P. concd. nitric acid was added to 4 liters of the solution to prevent hydrolysis. The molarity of the solution was determined by electrodeposition. Commercial ethylenediamine after drying over C.P. sodium hydroxide and then over sodium metal, was fractionally distilled from sodium metal (b.p. 119°, lit. b.p. ethylenediamine hydrate, 118°). The purified product was used to prepare an aqueous 0.1128 *M* solution of ethylenediamine. The concentration of ethylenediamine was determined by titration with standard HCl, using methyl orange indicator.

All solutions of $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$ were prepared from pipetted volumes of the respective standard solutions.

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

The effect of sodium hydroxide concentration on the absorption spectra of the $[Cu(en)_2]^{2+}$ ion was observed while varying the base concentration from 0.05 to 1 *M*.

C. **Conductometric Titrations.**—An Industrial Instrument Co. 1000-cycle conductivity bridge with a dipping type cell with vertical electrodes was used. The temperature during titration was held at 25 ± 1° in a regulated waterbath. The calculated conductances were corrected for dilution.

Results and Discussion

A. **Spectrophotometric Studies.**—Jolley[9] reported that an increase in sodium hydroxide concentration from 0.1 to 0.9 *M* increased the solubility of the $Cu(OH)_2$ in ethylenediamine solution because it appeared to favor the formation of $[Cu(en)](OH)_2$ at the expense of $[Cu(en)_2](OH)_2$. Jonassen and Dexter,[7] however, showed that the addition of a slight excess of sodium hydroxide to $[Cu(en)]^{2+}$ results in the precipitation of $Cu(OH)_2$ and the formation of the $[Cu(en)_2]^{2+}$ ion.

The effect of sodium hydroxide on the $[Cu(en)_2]^{2+}$ ion is shown in the change in absorption characteristics of the $[Cu(en)_2]^{2+}$ complex in increasing concentration of sodium hydroxide (Fig. 1). The presence of an isosbestic point at 590 mμ clearly indicates that a second complex ion is formed. Whereas Jolley claimed that $[Cu(en)]^{2+}$ was obtained, the curves of Fig. 1 show that even at an hydroxide ion concentration of 0.6 *M* the resulting absorption curve does not approach that of the $[Cu(en)]^{2+}$ ion (also given in Fig. 1). One possible explanation of these data is that under these extreme conditions of basicity one hydroxide ion adds to $[Cu(en)_2]^{2+}$ to give a pentacovalent copper (II) complex.

These conditions are as extreme as those under which Bjerrum and Nielson[6] obtained $[Cu(en)_3]^{2+}$. Other investigations also seem to favor such a pentacovalent structure for copper(II) complexes.[10] The results of continuous variation and saturation studies were meaningless since the complex is very unstable.

B. **Conductometric Studies.**—In Fig. 2 the first break in the conductance curve at a Cu/en ratio

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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] (a) W. Traube, *Ber.*, **54**, 3220 (1921); (b) F. W. Chattaway and H. D. K. Drew, *J. Chem. Soc.*, 947 (1937); (c) R. M. Levy and P. Muffat, *Paper Trade J.*, **118**, T40 (1944).

[3] P. Job, *Ann. Chim.*, [10] **2**, 113 (1928).

[4] K. L. Mandal, *Current Science*, **10**, 78 (1941).

[5] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

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

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

[8] H. B. Jonassen, R. E. Reeves and L. Segal, *ibid.*, **77**, 2667 (1955).

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

[10] H. B. Jonassen, M. M. Cook and J. S. Wilson, THIS JOURNAL, **73**, 4683 (1951).

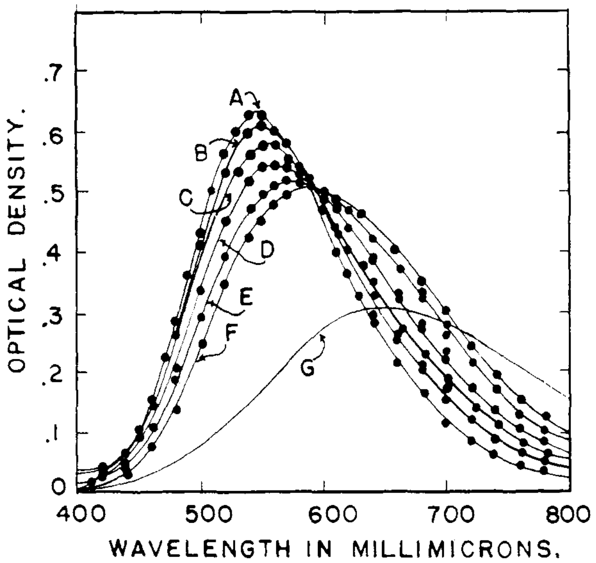
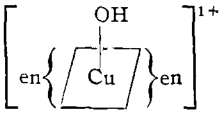


Fig. 1.—Absorption curves of $(Cu(en)_2)^{+2}$ in increasing concentrations of sodium hydroxide; copper concentration 0.01 *M:* A, no NaOH; B, 0.05 *M;* C, 0.1 *M;* D, 0.2 *M;* E, 0.4 *M;* F, 0.6 *M;* G, $(Cu\text{-}en)^{+2}$, no NaOH.

of 0.5 indicates that, as expected, two ethylenediamine molecules reacted with one copper(II) ion. The curve prior to the break, however, is nearly horizontal if only $[Cu(en)_2]^{2+}$ is formed. The negative slope obtained in the presence of excess hydroxide ions seems to indicate the withdrawal of highly conducting hydroxide ions.

The change in conductance indicated by the slope after the second break in the curve corresponds to the withdrawal of two hydroxide ions and the formation of $Cu(OH)_2$. Since this slope is twice that of the line prior to the first break, this seems to indicate that the change in the conductance of the region prior to the first break arises from the withdrawal of only one hydroxide ion from the solution.

The withdrawal of one hydroxide ion and the simultaneous reaction of two molecules of ethylenediamine with the copper(II) ion can be explained by the formation of a complex of the type



$$\left[\text{en}\left\{\overset{\text{OH}}{\text{Cu}}\right\}\text{en}\right]^{1+}$$

where the copper(II) ion is pentacovalent. For the average equilibrium constant for this reaction

$$[Cu(en)_2]^{2+} + OH^- \rightleftharpoons [Cu(en)_2(OH)]^{1+}$$

calculated from the absorption curves of Fig. 1, $\log K = 0.7301$. It is postulated that this complex of pentacovalent copper(II) is responsible for Jolley's observation of the increased solubility of cupric hydroxide in ethylenediamine solution when sodium hydroxide is added to the system. It can be explained by the equations

$$Cu(OH)_2 + 2en \rightleftharpoons [Cu(en)_2]^{2+}$$

$$[Cu(en)_2]^{2+} + OH^- \rightleftharpoons [Cu(en)_2(OH)]^{1+}$$

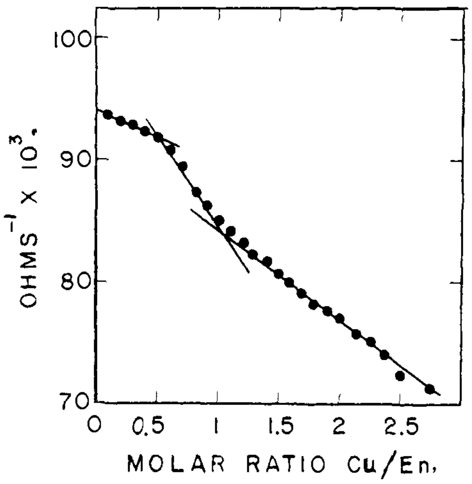


Fig. 2.—Conductometric titration of 0.004 *M* ethylenediamine in 0.05 *M* NaOH with 0.1 *M* copper nitrate.

$$[Cu(en)_2(OH)]^{1+} + Cu(OH)_2 \rightleftharpoons [Cu(en)_2]^{2+} + [Cu(OH)_3]^{1-}$$

$$[Cu(OH)_3]^{1-} + OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$$

The over-all reaction would be

$$2Cu(OH)_2 + 2en \xrightarrow{\text{excess }(OH^-)} [Cu(en)_2]^{2+} + [Cu(OH)_4]^{2-}$$

Without sodium hydroxide the reaction would be

$$Cu(OH)_2 + 2en \rightleftharpoons [Cu(en)_2]^{2+}(OH)_2$$

It might be pointed out that the cuprate ion[11] $[Cu(OH)_4]^{2-}$ gives a blue solution which would not have been noticed by Jolley in the intense blue of the $[Cu(en)_2]^{2+}$ ion.

[11] R. Scholder, R. Felsenstein and A. Apel, *Z. anorg. Chem.*, **216**, 138 (1933).

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The Stability of the Silver Complex of Tris-(hydroxymethyl)-aminomethane[1]

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RECEIVED DECEMBER 22, 1954

In connection with a recently developed method for the determination of sulfhydryl groups in proteins,[2] in which the silver–tris complex is used as the titrant, it became of interest to determine the stability of this complex.

The association constants were determined by the method of Bjerrum.[3] The tris used was a recrystallized sample of "Sigma 121" (Sigma Chemical Co., St. Louis, Mo.) and the silver nitrate was Merck "Primary Standard." The $\bar{n}$ for the complex approached a limiting value of 2, which is analogous to other silver–amine complexes and which excludes interaction between the silver and the oxygen atoms of the tris. The association con-

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[1] This compound will hereafter be referred to as tris.

[2] Benesch, *J. Biol. Chem.*, in press.

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