NOTES

High Yield Resolution of Tris-(ethylenediamine)-cobalt(III) by a Second-order Asymmetric Process

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The resolution of tris-(ethylenediamine)-cobalt(III) ion was first accomplished by Werner[1] in 1912, and, following his procedure, numerous other investigators and students have been able to obtain this compound in optically pure form. The results reported here show that it is possible to obtain yields in excess of 150% of the amount of the dextro or levo isomer originally present, as a result of a second-order asymmetric process. This involves coupling the conditions for racemization with the conditions for selective crystallization of one of the diastereoisomeric salts.

Racemization of Tris-(ethylenediamine)-cobalt(III) Ion.—The ethylenediamine complex of cobalt(III) is of great configurational stability, its solutions showing no loss in optical activity after several weeks. Prior to the work reported here, a single method for the catalytic racemization of tris-(ethylenediamine)-cobalt(III) ion had been reported. This involved the use of active carbon as a heterogeneous catalyst.[2]

The method employed here is based on the electron exchange of tris-(ethylenediamine)-cobalt(III) ion with tris-(ethylenediamine)-cobalt(II) ion. The kinetics of this electron exchange have been investigated.[3] The reaction is bimolecular and essentially first order in the concentration of both complex ions. Since the cobalt(II) complex is configuratively unstable, the path of racemization is considered to involve conversion of the *d*-$[Co^{III}en_3]$ ions into *d*-$[Co^{II}en_3]$ ions, which racemize instantly. The simultaneously formed $[Co^{III}en^{3}]$ ions supposedly have an equal probability of being either dextro or levo.[4] The net effect is racemization of the active cobalt(III) complex by a process of homogeneous catalysis. The racemization process may be terminated at any point by acidifying the solution since this destroys the cobalt(II) complex and thereby prevents further electron exchange.

Second-order Asymmetric Induction.—Werner[5] and Dwyer and Gyarfas[6] have shown that when one of the diastereoisomers of a salt of an optically labile complex ion is much less soluble than the other, virtually all of the complex may be obtained as the less soluble form. This occurs because the more soluble isomer racemizes, as the less soluble isomer crystallizes, thus producing more of the less soluble form, which then crystallizes. The process is termed a second-order asymmetric induction because a second substance, the precipitating ion, is necessary for its promotion.

In the instances previously reported, the complexes involved were by nature optically labile, and therefore naturally underwent this asymmetric process. It has now become possible to obtain such an asymmetric induction with a substance ($[Co^{III}en_3]$ ion) which normally does not tend to racemize or otherwise undergo changes in configuration. As the *d*-$[Co^{III}en_3]Cl$(*d*-tartrate) is crystallized from solution, the remaining *l*-$[Co^{III}en_3]$ ion is catalytically racemized, providing more of the dextro form, which then crystallizes. The process has also been employed utilizing *levo*-tartrate with a resulting high yield of *l*-$[Co^{III}en_3]Cl$(*l*-tartrate).

Experimental

Materials.—Tris-(ethylenediamine)-cobalt(III) chloride was prepared and purified by the method of Work.[7] *d*-Tartaric acid was J. T. Baker reagent grade while the *l*-tartaric acid was obtained from Aldrich Chemical Company. Silver tartrate was prepared in the necessary amount for each run. The specific rotations reported were calculated from observed rotations made on 1% solutions in a 1.01 dm. all glass polarimeter tube, using a Schmidt and Haensch Polarimeter, Number 11698 (precision, ±0.02°).

Preparation of $[Co^{III}en_3]Cl$(*d*- or *l*-tartrate).—One hundred and six grams of silver tartrate was prepared by adding 99 g. of silver nitrate, dissolved in 120 ml. of water, to 43.5 g. of *d*-(or *l*)-tartaric acid dissolved in 117 ml. of 5 *N* sodium hydroxide, which had been diluted to 200 ml. The precipitated silver tartrate was filtered onto a 4-inch buchner funnel and the water was removed by thorough washing with acetone. The acetone was then removed under suction and the product was used immediately.

The silver tartrate was triturated for 15 minutes in a 6-inch mortar with a hot (90°) solution of 100 g. of tris-(ethylenediamine)-cobalt (III) chloride in 400 ml. of water. The precipitated silver chloride was removed by filtration and washed with 100- to 150-ml. portions of hot water (90°) until the filtrate emerging from the funnel was colorless. The volume of the combined filtrate and washings was approximately 800 ml. This solution then contained 123 g. of tris-(ethylenediamine)-cobalt(III) chloride *d* (or *l*-)-tartrate.

Resolution.—The solution obtained by the method described above was placed in an evaporating dish and concentrated in a stream of air for approximately 24 hours. The crystals of active complex which formed were separated by filtration. The mother liquor was again concentrated for approximately 3 hours and cooled. Any additional solid was then removed by filtration. Yield of crude active complex was 60 to 70 g. (This represents more than the theoretical yield; however, the excess is due to the presence of a considerable amount of racemic material.) Recrystallization from approximately 200 ml. of hot water (90°) yielded 45 to 50 g. of optically pure complex; reported $[\alpha]_D$ 101°, found $[\alpha]_D$ +102°, −103°.

The viscous mother liquor (volume 75 to 100 ml.) from the separation of the active form was placed in a flask and oxygen-free nitrogen was passed through it for 15 minutes. Three and one-half milliliters of 95% ethylenediamine and one gram of cobalt(II) chloride 6-hydrate were then added and the solution was maintained under a stream of nitrogen for 12 hours. During this time a considerable amount of the active complex crystallized. Yields of recrystallized complex by second-order process were 25 to 30 g., $[\alpha]$ +101°, −101°. The mother liquor from this process was placed under nitrogen as rapidly as possible to limit the oxidation of the cobalt(II) complex.

Concentrating and cooling the filtrates from recrystalliza-

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[1] A. Werner, *Ber.*, **45**, 121 (1912).

[2] B. Douglas, This Journal, **76**, 1020 (1954).

[3] W. B. Lewis, C. D. Coryell and J. W. Irvine, Jr., *J. Chem. Soc.*, S386 (1949).

[4] The kinetics of racemization of active $[Co^{III}en_3]$ ion, by this catalytic process, are now under investigation. The results may clarify this point.

[5] A. Werner, *Ber.*, **45**, 3061 (1912).

[6] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950).

[7] J. B. Work, *Inorganic Syntheses*, **2**, 221 (1946).

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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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.

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

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