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The Stereochemistry of Complex Inorganic Compounds. XXIX.¹ The Base Hydrolysis of the Optically Active α -Dichlorotriethylenetetraminecobalt(III) Cation

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The base hydrolysis of the optically active α -dichlorotriethylenetetraminecobalt(III) ion and α -chloroaquo-triethylenetetraminecobalt(III) ion, under certain conditions, leads to a product of inverted configuration, while the same reaction, when carried out in the presence of a silver(I) or mercury(II) ion, proceeds with retention of configuration. The inversion is shown to take place during the second base hydrolysis in the formation of the dihydroxotriethylenetetraminecobalt(III) cation. Several possible mechanisms for the reactions are suggested. The method for assigning the relative configurations of cobalt complexes based on chirality about the C_2 axis is also discussed.

Introduction

The base hydrolysis of optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) ion, under certain conditions, leads to a product of inverted configuration.² This reaction represents the only thoroughly studied optical inversion in transition metal chemistry. In the hope of finding another example of this, and thereby extending our knowledge of the inversion, we have undertaken a study of the base hydrolyses of other cobalt(III) tetramine complexes. This paper gives some results of work done with the optically active α -dichlorotriethylenetetraminecobalt(III) cation.

In general, little synthetic or mechanistic information on cobalt trien³ complexes is available. Perhaps the best known complex of this series is $[\text{Co}(\text{trien})\text{Cl}_2]^+$. The cation can exist in five isomeric forms, two enantiomeric pairs of *cis* isomers, designated α and β , and a *trans* form (Figure 1). The preparation⁴ and partial resolution⁵ of the α form were reported several years ago. However, only recently have the β ⁶ and *trans*⁷ isomers been isolated and characterized. All previous attempts had resulted in the formation of the more

stable α form. The rate of acid hydrolysis of the α ,⁸ β , and *trans* isomers as well as the stereochemical pathway⁴ of their reactions have been determined.⁹ No similar study has been made of the base hydrolysis of these materials. However, it has been observed that the treatment of D^* - α - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ with hydroxide ion gives a product with a negative rotation, α_D .¹⁰

Results

In a previous publication,² the configuration of D^* -*cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ was designated as Λ on the basis of its relationship to Λ - $[\text{Co}(\text{en})_3]^{3+}$. The latter ion was assigned this configuration by examining the chirality about its C_3 axis; *i.e.*, the chelate rings form a left-handed system.¹¹ However, if the ion is viewed along one of the C_2 axes it is seen that the chelate rings form a right-handed system. Using a previous notation this is the D^* configuration.¹² There are a number of advantages inherent in choosing the C_2 (D^*) instead of the C_3 (Λ) as the axis of chirality: (1) historically, this isomer has been designated *d* or *D* and this notation is still used in much of the present literature; (2) D^* corresponds to the positive (dextro) specific rotation, $[\alpha]_D$, and a positive "Cotton effect" in the optical rotatory dispersion (O.R.D.) curve for the first cobalt(III) band; (3) this scheme can be used for ions that do not possess a C_3 axis but do have a C_2 axis. The latter point is important when considering *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, α - $[\text{Co}(\text{trien})\text{Cl}_2]^+$, and related ions.¹³

Recent rotatory dispersion and circular dichroism studies¹⁴ indicate that the D^* isomers of α - or β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ possess the same configuration as D^* -*cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. Spectroscopic and stereochemical considerations also show that the O.R.D. curve of the α isomer has a negative "Cotton effect" at long wave length, while the β isomer does not.¹⁴ The shapes of

(1) Paper XXVIII: E. Kyuno, L. J. Boucher, J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **86**, 3656 (1964).

(2) For a discussion see ref. 1 and the references cited therein.

(3) Trien represents triethylenetetramine.

(4) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

(5) B. Das Sarma and J. C. Bailar, Jr., *ibid.*, **77**, 5480 (1955).

(6) G. H. Searle, Ph.D. Thesis, Australian National University, 1963.

(7) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963).

(8) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(9) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 3561 (1963).

(10) F. P. Dwyer, private communication.

(11) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(12) R. D. Archer and J. C. Bailar, Jr., *ibid.*, **83**, 812 (1961).

(13) As a first approximation, differences in the unidentate ligands are ignored. Also, β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ has no C_2 axis and the above scheme cannot be strictly applied.

(14) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

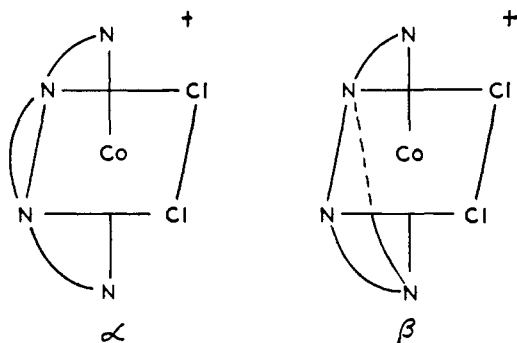


Figure 1. *cis* isomers of $[\text{Co}(\text{trien})\text{Cl}_2]^+$

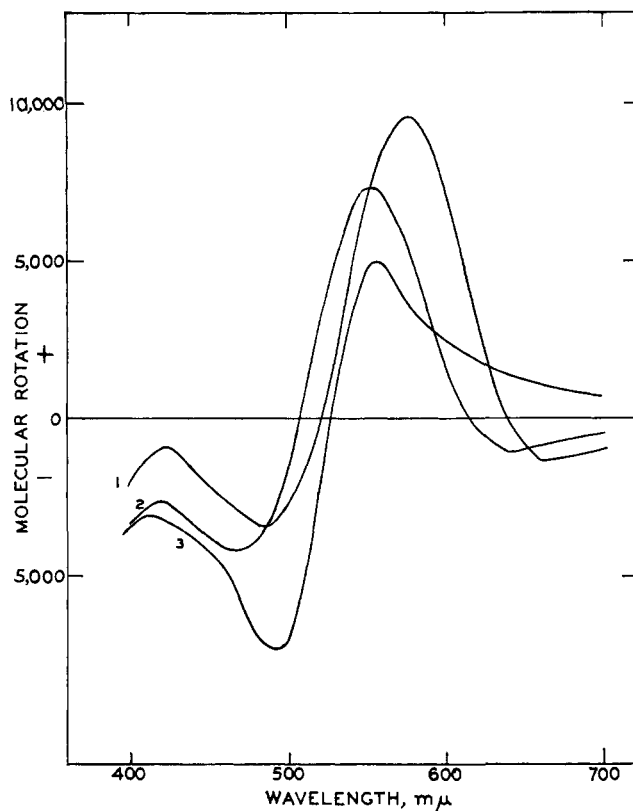


Figure 2. Optical rotatory dispersion of 1, (+)- D^* - $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$; 2, (+)- D^* - $[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}](\text{NO}_3)_2$; 3, (+)- D^* - $[\text{Co}(\text{trien})\text{CO}_3]\text{Cl}$.

the O.R.D. curves are indicative of a common configuration, D^* , and for $[\text{Co}(\text{trien})\text{Cl}_2]^+$ and $[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}]^{2+}$, of a common geometrical form, α (Figure 2).

Any stereochemical change during a reaction of $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ and related ions that involves the movement of two chelate rings, *i.e.*, $\text{D}^*-\alpha \rightarrow \text{D}^*-\beta$ or $\text{L}^*-\alpha$ or *trans*, is assumed to be less likely than a change that involves the movement of only one chelate ring, *i.e.*, $\text{D}^*-\alpha \rightarrow \text{L}^*-\beta$ (Figures 3 and 4). From this and the relationships deduced from O.R.D. measurements, it is easy to see that any reaction of the $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ or related ions, which gives a product with a positive Cotton effect in the 400–700- $\text{m}\mu$ region, proceeds with predominant retention of configuration $\text{D}^*-\alpha \rightarrow \text{D}^*-\alpha$. On the other hand, any reaction that results in a product with a negative "Cotton effect" must proceed with inversion of configuration (as well as isomerization), $\text{D}^*-\alpha \rightarrow \text{L}^*-\beta$.

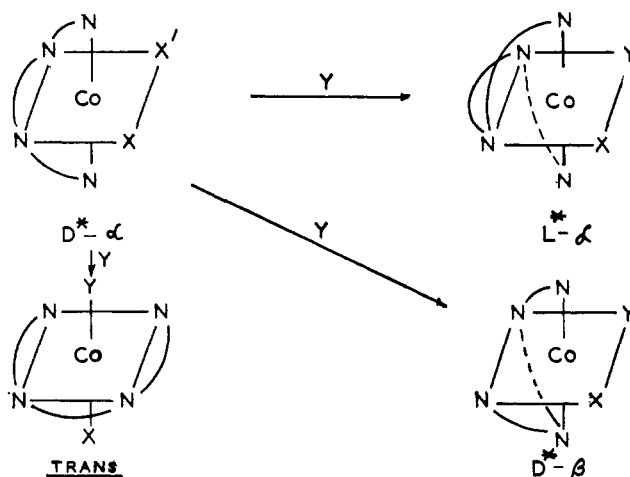


Figure 3. Displacement reaction of $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{X}_2]^+$ with movement of two chelate rings.

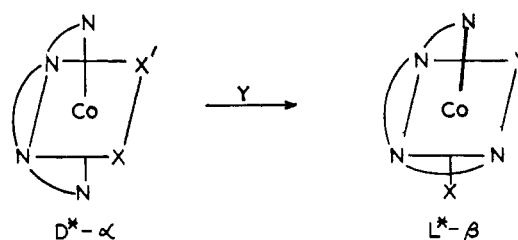
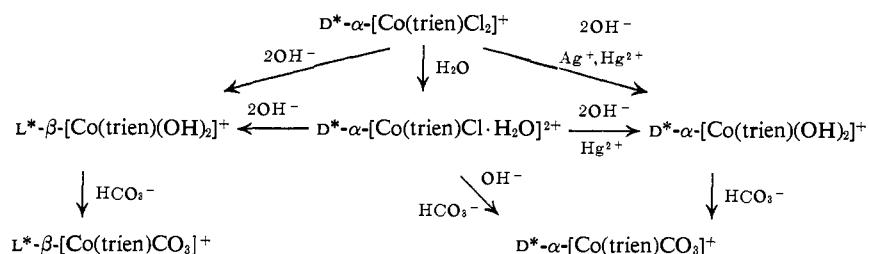


Figure 4. Displacement reaction of $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{X}_2]^+$ with movement of one chelate ring.

If $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ is dissolved in a solution containing hydroxide ion so that it is completely converted to the dihydroxo complex, the specific rotation of the product at the sodium D-line is negative. Experiments were carried out with solutions of various concentrations of base; the results of these are summarized in Table I. The table shows that there is no hydroxide ion concentration dependence for the hydrolysis; *i.e.*, the sign of $[\alpha]_D$ is the same, regardless of the concentration of OH^- . In addition, the base hydrolysis of $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}]^{2+}$ gives a product which shows a small positive specific rotation, independent of the OH^- concentration (Table I). However, after conversion of these dihydroxo species to $[\text{Co}(\text{trien})\text{ox}]^+$ by addition of a mixture of oxalic acid and potassium oxalate, a product was obtained which was shown to be about 20% $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{ox}]^+$ and 80% $\text{L}^*-\beta$ - $[\text{Co}(\text{trien})\text{ox}]^+$. In determining these percentages, the rotating power of the products of the reactions were compared with that of a mixture made from pure $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{ox}]^+$ and $\text{L}^*-\beta$ - $[\text{Co}(\text{trien})\text{ox}]^+$. When passed through a chromatographic column, a solution of the product of the reaction showed the same behavior as did a solution of the mixture of the two pure oxalato complexes. The preparation of the $\text{L}^*-\beta$ - $[\text{Co}(\text{trien})\text{ox}]^+$ will be described in the next paper.

If a solution of either $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ or $\text{D}^*-\alpha$ - $[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}]^{2+}$ which contains Ag^+ or Hg^{2+} is treated with hydroxide ion, the $[\alpha]_D$ of the product is strongly positive. The results of several experiments are summarized in Table II. The concentrations of

Scheme I



base and complex were such that in all cases the complex was converted to $[\text{Co}(\text{trien})(\text{OH})_2]^+$. Also, the ratio of added metal ion to complex was at least 2:1.

Table I. The Base Hydrolysis of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ and $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}]^{2+}$ to Form Optically Active $[\text{Co}(\text{trien})(\text{OH})_2]^+$ as a Function of OH^- Concentration

| Complex | OH^- concn., <i>M</i> | Product | |
|---|--------------------------------------|---------------------------------|-----------------------------------|
| | | $\alpha^{25}\text{D}$, deg. | $[\alpha]^{25}\text{D}$, deg. |
| $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ | 0.0064 | -0.032 ± 0.001 | -419 ± 13 |
| | 0.010 | -0.030 | -393 |
| | 0.020 | -0.032 | -419 |
| | 0.050 | -0.033 | -431 |
| | 0.250 | -0.028 | -367 |
| | 0.500 | -0.032 | -419 |
| | 1.25 | -0.030 | -393 |
| | 2.50 | -0.026 | -340 |
| $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}](\text{NO}_3)_2$ | 0.0064 | +0.005 | +52 |
| | 0.010 | +0.005 | +52 |
| | 0.050 | +0.003 | +31 |
| | 0.500 | +0.005 | +52 |

Table II. The Base Hydrolysis of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ and $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}]^{2+}$ to Form Optically Active $[\text{Co}(\text{trien})(\text{OH})_2]^+$ in the Presence of Ag^+ or Hg^{2+}

| Complex | Metal ion | Product | |
|---|------------------|------------------------------|-----------------------------------|
| | | $\alpha^{25}\text{D}$, deg. | $[\alpha]^{25}\text{D}$, deg. |
| $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ | None | -0.032 ± 0.001 | -419 ± 13 |
| | Ag^+ | +0.014 | +173 |
| | Hg^{2+} | +0.140 | +1959 |
| $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}\cdot\text{H}_2\text{O}](\text{NO}_3)_2$ | None | +0.004 | +41 |
| | Hg^{2+} | +0.038 | +496 |

The α and β isomers of $[\text{Co}(\text{trien})(\text{OH})_2]^+$ lose optical activity rapidly. The dihydroxo complex was therefore converted to $[\text{Co}(\text{trien})\text{CO}_3]^+$ by immediate reaction with bicarbonate ion. In addition to its optical stability, the carbonato complex possesses a large enough rotational strength to allow the detection of even a small preponderance of one enantiomeric form. Data from experiments on the direct reaction of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ and Li_2CO_3 or Ag_2CO_3 are listed in Table III. At low concentration of bicarbonate ion, in the presence or absence of silver ion, the predominant product is (+)- $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$. Because of the small concentration of hydroxide ion in these solutions, the product is produced primarily *via* an aquo intermediate rather than the hydroxo intermediate. However, as the concentrations of HCO_3^- and OH^- increase, $\text{L}^*-\beta\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$ is formed from

the hydroxo intermediate. If an excess of Ag_2CO_3 is used, two simultaneous reactions take place. One of these is the base hydrolysis, the necessary OH^- coming from the dissolved Ag_2CO_3 . This reaction leads to the formation of the L isomer. The other reaction involving Ag^+ , OH^- , and the complex leads to the formation of the D isomer. At sufficiently high concentration, Ag^+ (or Hg^{2+} , see Table II) plays a definite role in the reaction, with this process predominating. The shape of the O.R.D. curves and visible absorption spectra of the reaction products listed in Table III closely compare with those of the $\text{D}^*-\alpha$ or $\text{L}^*-\beta$ isomer of $[\text{Co}(\text{trien})\text{CO}_3]^+$.¹⁴ These and previous considerations¹⁵ indicate that the D^* isomer is $\text{D}^*-\alpha$ and the L isomer is $\text{L}^*-\beta$. Attempts to isolate crystalline α - or β - $[\text{Co}(\text{trien})\text{CO}_3]^+$ resulted in each case only in the formation of an intractable red oil.

Table III. The Base Hydrolysis of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ to Form Optically Active $[\text{Co}(\text{trien})\text{CO}_3]^+$ in the Presence of Li^+ or Ag^+

| Complex concn., <i>M</i> | Metal carbonate | | Product | |
|--------------------------------|--------------------|---------------------|------------------------------|-----------------------------------|
| | Metal ion | Concn., <i>M</i> | $\alpha^{25}\text{D}$, deg. | $[\alpha]^{25}\text{D}$, deg. |
| 0.01 | Li^+ | 0.01 | $+0.040 \pm 0.001$ | +152 |
| 0.01 | Li^+ | 0.02 | -0.134 | -411 |
| 0.01 | Li^+ | 0.03 | -0.134 | -411 |
| 0.06 | Ag^+ | 0.06 | +0.036 | +158 |
| 0.06 | Ag^+ | 0.09 | -0.026 | -130 |
| 0.06 | Ag^+ | 0.12 | -0.002 | -8 |
| 0.06 | Ag^+ | 0.18 | +0.043 | +216 |

A series of reactions was performed to determine the step in which the inversion process takes place. The results are summarized in Scheme I. The reactions shown represent the routes for the formation of the predominant product. The configurations of the various products were assigned by considering their O.R.D. curves. The aquation of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ has been previously shown to proceed with full retention of configuration.⁹

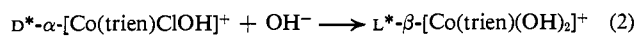
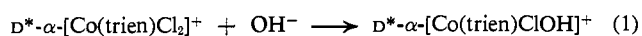
It must be understood that all such reactions yield a mixture of products, and no attempt has been made to separate these. The statement that a reaction leads to a given product is meant only to indicate that this product is the preponderant one.

Discussion

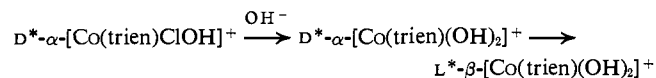
The base hydrolysis of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ leads to a product of inverted configuration which is identical with that formed by the hydrolysis of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$.

(15) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1368 (1964).

$\text{ClOH}]^+$. This implies that an inversion takes place in the second base hydrolysis of the dichloro complex.



The inversion process may occur in at least two ways: (1) nucleophilic attack by the hydroxide ion on the chlorohydroxo intermediate, as depicted by reaction 2; (2) *via* an intramolecular isomerization of the dihydroxo species



with the equilibrium favoring the $\text{L}^*-\beta$ form.

The latter pathway is reasonable in light of the reported isomerization of $\alpha\text{-}[\text{Co}(\text{trien})(\text{H}_2\text{O})_2]^{3+}$ to the β form *via* the intermediate $\alpha\text{-}[\text{Co}(\text{trien})\text{OH}\cdot\text{H}_2\text{O}]^{2+}$.⁷ The nucleophilic attack of the hydroxide ion on $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ and $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{ClOH}]^+$ probably involves a conjugate base intermediate (as do similar reactions of other cobalt(III) ammine complexes¹⁶). Following abstraction of an amine proton by the hydroxide ion, a "five-coordinate" intermediate is formed. This is rapidly attacked by a solvent molecule to give, in the case of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$, a product with the same configuration, and, in the case of $[\text{Co}(\text{trien})\text{ClOH}]^+$, a product with inverted configuration. Rapid rupture of the cobalt-chlorine bond by Ag^+ or Hg^{2+} leads to retention of configuration in both of the base hydrolyses. This suggests that, in the inversion process, the breaking of the Co-Cl bond occurs after the movement of the chelate ring, *i.e.*, a solvent assisted cobalt-amine bond breaking with a subsequent displacement of the chlorine atom by the free end of the chelate ring. There are some stereochemical rearrangements of cobalt(III) ethylenediamine complexes that have been rationalized by envisioning such a cobalt-amine bond breaking.¹⁷ This bond weakening is thought to be the consequence of the presence of the OH^- in the coordination sphere of the metal. It is hoped that further work will allow a more detailed picture of the inversion process.

Experimental Section

Preparation of Complexes. Some of the procedures below are generally the same as those given elsewhere.⁷ They are reported here in detail because of the relative unavailability of the other source.

***cis*- α -Dinitrotriethylenetetraminecobalt(III) Chloride.** A solution of 48 g. (0.20 mole) of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ in 50 ml. of water was added gradually to a cold mixture of 36 g. (0.25 mole) of triethylenetetramine, 40 ml. of 37% HCl (0.48 mole), 40 g. of NaNO_2 (0.58 mole), and 100 ml. of water. The resulting red-brown solution was oxidized by vigorous aeration until brown crystals precipitated. The crystals were washed with 50 ml. of a 1:1 mixture of ethanol and water and air-dried (yield 58 g., 83%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NO}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$: C, 20.58; N, 24.00; H, 5.76. Found: C, 20.68; N, 24.03; H, 5.98.

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 129-132.

(17) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 128 (1961); D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

***cis*- α -Dichlorotriethylenetetraminecobalt(III) Chloride.** A solution of 40 g. (0.13 mole) of *cis*- $\alpha\text{-}[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$ in 150 ml. of 37% HCl was kept for 24 hr. at room temperature. The violet solution was concentrated to half its volume by aeration, 50 ml. of ethanol was added, and the solution was kept in an ice bath for 1 hr. The violet crystals were filtered, washed with ethanol and ether, and air-dried (yield 31 g., 89%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl}$: C, 23.17; N, 17.85; H, 5.76; Cl, 33.77. Found: C, 23.00; N, 17.81; H, 5.89; Cl, 34.77.

α -Oxalatotriethylenetetraminecobalt(III) Chloride. A mixture of 31 g. (0.10 mole) of *cis*- $\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$, 18.4 g. (0.10 mole) of $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$, and 200 ml. of water was heated to about 65° for 1 hr. The purple solution was concentrated to half its volume by gentle aeration. The product was filtered and washed with ethanol and ether and air-dried (yield 23 g., 64%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{C}_2\text{O}_4]\text{Cl}$: C, 28.89; N, 16.85; H, 5.47. Found: C, 28.80; N, 16.82; H, 5.60.

$\text{D}^*-\alpha$ -Oxalatotriethylenetetraminecobalt(III) Nitrate. A solution of 20 g. (0.054 mole) of $\alpha\text{-}[\text{Co}(\text{trien})\text{ox}]\text{Cl}$ in 300 ml. of water was mixed slowly with a solution of 20 g. (0.051 mole) of ammonium *d*- α -bromocamphor- π -sulfonate in 150 ml. of water. After 12 hr. at room temperature, pink needles precipitated. These were washed with ethanol and ether and air-dried (yield 10 g., 60%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{C}_2\text{O}_4](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})$: C, 35.59; N, 9.02; H, 5.31. Found: C, 35.46; N, 9.10; H, 5.68. $[\alpha]^{25\text{D}} + 603 \pm 2^\circ$; $[\text{M}]^{25\text{D}} + 3650 \pm 12^\circ$ (0.1% aqueous solution).

The dried $[\text{Co}(\text{trien})\text{ox}](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})$ (10 g., 0.016 mole), was ground in an ice-cold mortar with a cold mixture (1:1:1) of 30 ml. of concentrated HNO_3 , ethanol, and ether for 5 min. The product was washed with ethanol and recrystallized from water (yield 5.0 g., 83%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{C}_2\text{O}_4]\text{NO}_3$: C, 26.75; N, 19.50; H, 5.05. Found: C, 26.72; N, 19.44; H, 5.06. $[\alpha]^{25\text{D}} + 791 \pm 2^\circ$; $[\text{M}]^{25\text{D}} + 2841 \pm 8^\circ$ (0.1% aqueous solution).

***cis*- $\text{D}^*-\alpha$ -Dichlorotriethylenetetraminecobalt(III) Chloride.** A finely powdered and dried sample of 5 g. (0.014 mole) of $\text{D}^*-\alpha\text{-}[\text{Co}(\text{trien})\text{ox}]\text{NO}_3$ was suspended in 100 ml. of absolute ethanol and dry HCl gas was introduced into it for 15 min. at ice temperature with occasional stirring. The mixture, saturated with dried HCl gas, was maintained for 48 hr. at room temperature. The violet precipitate was washed with a small amount of ethanol and ether and air-dried. It was recrystallized from concentrated HCl solution (yield 4.0 g., 90%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl}$: C, 23.12; N, 17.85; H, 5.76; Cl, 33.73. Found: C, 23.11; N, 18.17; H, 5.86; Cl, 33.75. $[\alpha]^{25\text{D}} 2770 \pm 2^\circ$; $[\text{M}]^{25\text{D}} + 8630 \pm 6^\circ$ (0.1% aqueous solution).

$\text{D}^*-\alpha$ -Chloroaquatetriethylenetetraminecobalt(III) Nitrate. A solution of 40 g. (0.128 mole) of *cis*- $\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ in 180 ml. of water was shaken with glass beads in a stoppered flask for 3 days at room temperature. The beads and a small amount of residue were removed by filtration. To the filtrate was added

35 g. (0.107 mole) of ammonium *d*- α -bromocamphor- π -sulfonate, and the solution was allowed to stand in an ice bath for 2 hr. The crystals which formed were washed with small amounts of water and ether and air-dried (yield 8 g., 14%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{16}\text{N}_4)\text{ClH}_2\text{O}](\text{C}_{10}\text{H}_{14}\text{O}_4\text{-SBr})_2 \cdot 2\text{H}_2\text{O}$: C, 34.13; N, 6.12; H, 5.76. Found: C, 34.08; N, 6.05; H, 5.83. $[\alpha]^{25\text{D}} + 360 \pm 2^\circ$; $[\text{M}]^{25\text{D}} + 3179 \pm 18^\circ$.

Eight grams (0.009 mole) of $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl} \cdot \text{H}_2\text{O}](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})_2 \cdot 2\text{H}_2\text{O}$ was ground in a cold mortar with a mixture of 5 ml. of concentrated HNO_3 , 10 ml. of ethanol, and 3 ml. of ether for 5 min. The product was filtered and washed with ethanol and ether and air-dried (yield 3.5 g., 100%).

Anal. Calcd. for $[\text{Co}(\text{C}_6\text{H}_{16}\text{N}_4)\text{Cl} \cdot \text{H}_2\text{O}](\text{NO}_3)_2$: C, 18.83; N, 21.96; H, 5.27; Cl, 9.26. Found: C, 19.20; N, 22.06; H, 5.28; Cl, 9.89. $[\alpha]^{25\text{D}} + 660 \pm 2^\circ$; $[\text{M}]^{25\text{D}} 2420 \pm 8^\circ$.

Inversion and Retention Reactions. The data reported in Table I were gathered in the following way: $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ or $\text{D}^*\text{-}\alpha\text{-}(\text{trien})\text{Cl} \cdot \text{H}_2\text{O}(\text{NO}_3)_2$ (3.2×10^{-5} mole) was dissolved rapidly in 5 ml. of water at 25° . To this solution 5 ml. of a sodium hydroxide solution of the appropriate concentration was added. After 30 sec. the optical activity of the solution was measured.

The data reported in Table II were gathered as follows. A mixture of $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ or $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl} \cdot \text{H}_2\text{O}](\text{NO}_3)_2$ (3.2×10^{-5} mole) and AgNO_3 or $\text{Hg}(\text{OAc})_2$ (1.0×10^{-4} mole) was dissolved rapidly in 5 ml. of water at 25° . After a few minutes, 5 ml. of 0.4 *N* sodium hydroxide solution was added. The solution was filtered rapidly (approximately 2 min.) and the optical activity measured.

The data reported in Table III were obtained in the following way. $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ (1×10^{-4} or

6×10^{-4} mole) was intimately ground with the appropriate amount of lithium or silver carbonate and 10 ml. of water was added. After standing 30 min. at 25° , the mixture was filtered. The filtrate was diluted to 100 ml. and the optical activity of the solution was measured.

The transformation of $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ into $\text{L}^*\text{-}\beta\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$ was accomplished by dissolving the starting material (0.005 mole) in 25 ml. of 0.4 *N* sodium hydroxide solution at 25° . After 1 min., an equimolar amount of sodium bicarbonate was added and the solution was allowed to stand for 30 min. The rotatory dispersion curve of the solution was then measured; $[\alpha]^{25\text{D}} - 445^\circ$.

The change of $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl} \cdot \text{H}_2\text{O}](\text{NO}_3)_2$ into $\text{L}^*\text{-}\beta\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$ and $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{CO}_3]^+$ was effected by dissolving the complex (0.005 mole) in 25 ml. of either 0.4 or 0.2 *N* sodium hydroxide solution at 25° . After 1 min., an equimolar amount of sodium bicarbonate was added and the solution was allowed to stand for 30 min. The absorption bands are λ_{max} 507, 358 (ϵ_{max} 153, 136) and λ_{max} 505, 357 (ϵ_{max} 138, 117), respectively. The rotatory dispersion curves of the solutions were measured: $[\alpha]^{25\text{D}} - 220^\circ$; $[\alpha]^{25\text{D}} + 1242^\circ$ (for a typical curve see Figure 3).

Apparatus. The optical activity of the solutions was measured with a ETL-NPL Bendix Type 143A automatic polarimeter in 1-cm. quartz cells. Rotatory dispersion curves were drawn by a Rudolph Model 260/655Y850 recording spectropolarimeter. Spectrophotometric measurements were made with a Cary Model 14M recording spectrophotometer using aqueous solutions on 1-cm. quartz cells.

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