phenol and 2-butanol, the change in frequency, $\Delta\nu$, for dimer formation is approximately half as big as $\Delta\nu$ for polymer formation. It is interesting that the characteristic pmr frequency of the 1:1 complex is approximately half as large as the frequency of the 1:2 complex. This is reasonable since the 1:1 species is associated through a hydrogen bond involving one of the OH bonds of the water molecule, the other bond remaining free, while the 1:2 species is associated through two hydrogen bonds.

It is unfortunate that in our experiments it is not possible to determine the equilibrium constant of the reaction

$$\mathrm{OH_2 + D = OH_2\cdots D} \qquad (9)$$

The presence of a large excess concentration of D is necessary, not only from solubility consideration, but also because various water–water association species would be formed in the absence of a large concentration of D. Since water is in such large abundance, however, it is useful to have information on values of the equilibrium constant and enthalpy change of reactions represented by eq 1 for various electron donors.

The values of $(\nu_{12} - \nu_{11})$ and $(\nu_{11} - \nu_{\mathrm{M}})$ may be regarded as the hydrogen-bond shifts for eq 1 and 9, respectively. If the equilibrium constants for the reactions represented by these two equations had taken on identical values, it might be supposed that $(\nu_{12} - \nu_{\mathrm{M}})$ would be equal to $2(\nu_{11} - \nu_{\mathrm{M}})$, since $(\nu_{12} - \nu_{\mathrm{M}})$ may be considered to be the hydrogen-bond shift for the reaction

$$\mathrm{OH_2 + 2D = OH_2{\cdot}2D} \qquad (10)$$

However, our data show that $(\nu_{12} - \nu_{\mathrm{M}})$ is different from $2(\nu_{11} - \nu_{\mathrm{M}})$ and reflect the unequal equilibrium constants of eq 1 and 9.

The Stereochemistry of Complex Inorganic Compounds. XXX.[1] The Base Hydrolysis of Some Optically Active β-Dihalotriethylenetetraminecobalt(III) Cations

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Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois. *Received August 5, 1965*

Abstract: The base hydrolysis of the optically active β-$[\mathrm{CoX_2(trien)}]^+$ ion in aqueous solution proceeds, under all the conditions studied, with retention of configuration. A similar result is given by the reaction with both liquid and gaseous ammonia. The presence of silver(I) or mercury(II) ions in the aqueous solution has no effect on the configuration of the product of the base hydrolysis. Racemization of β-$[\mathrm{Co(OH)_2(trien)}]^+$ in aqueous solution proceeds through the formation of the *trans* isomer as an intermediate.

In the previous paper,[1] it was pointed out that inversion takes place in the second step of base hydrolysis of the α-dihalotriethylenetetraminecobalt(III) ion.

$$\alpha\text{-}[\mathrm{CoX_2(trien)}]^+ \xrightarrow{\mathrm{OH^-}} \alpha\text{-}[\mathrm{CoXOH(trien)}]^+ \quad \text{retention} \qquad (1)$$

$$\alpha\text{-}[\mathrm{CoXOH(trien)}]^+ \xrightarrow{\mathrm{OH^-}} \beta\text{-}[\mathrm{Co(OH)_2(trien)}]^+ \quad \text{inversion} \qquad (2)$$

On the contrary, the first step of the base hydrolysis of *cis*-dichlorobis(ethylenediamine)cobalt(III) ion, at high $\mathrm{OH^-}$ concentrations, proceeds largely with inversion of configuration.[2]

$$cis\text{-}[\mathrm{CoCl_2(en)_2}]^+ \xrightarrow{\mathrm{OH^-}} cis\text{-}[\mathrm{CoClOH(en)_2}]^+ \quad \text{inversion} \qquad (3)$$

$$cis\text{-}[\mathrm{CoClOH(en)_2}]^+ \xrightarrow{\mathrm{OH^-}} cis\text{-}[\mathrm{Co(OH)_2(en)_2}]^+ \quad \text{retention} \qquad (4)$$

Recently, the β isomer of the dichlorotriethylenetetraminecobalt(III) complex has been prepared in optically active form, and its behavior on acid hydrolysis has been studied.[3,4] The absolute configurations of both D-α- and D-β-$[\mathrm{CoCl_2(trien)}]^+$ have been determined from optical rotatory dispersion (ORD), circular dichroism,[5] and kinetic studies[4,6] and are shown in Figure 1.

It has been found that under none of the conditions which we studied does the conversion of optically active *cis*-$[\mathrm{CoF_2(en)_2}]^+$ to optically active $[\mathrm{CoCO_3(en)_2}]^+$ result in a change of configuration,[7] but under some conditions, both optically active *cis*-$[\mathrm{CoBrCl(en)_2}]^+$ and *cis*-$[\mathrm{CoBr_2(en)_2}]^+$ give $[\mathrm{CoCO_3(en)_2}]^+$ with optical inversion.[8] The differences in character between the Co–F, Co–Cl, and Co–Br bonds cause great differences in the mechanism of the base hydrolysis.

It has been shown that the D-*cis*-dichlorobis(L-propylenediamine)cobalt(III) ion, which is closely related to the ethylenediamine complex, can be converted to either D- or L-$[\mathrm{CoCO_3(\mathit{l}\text{-}pn)_2}]^+$.[9] Finally, an optical inversion has been found in the reaction of *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ with ammonia at low temperatures, but not at room temperature or above.[10,11]

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(1) Paper XXIX: E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

(2) L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 3656 (1964).

(3) G. H. Searle, Thesis, Australian National University, 1963.

(4) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).

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

(6) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

(7) W. R. Matoush and F. Basolo, *J. Am. Chem. Soc.*, **78**, 3972 (1956).

(8) J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940).

(9) J. C. Bailar, Jr., and J. P. McReynolds, *ibid.*, **61**, 3199 (1939).

(10) J. C. Bailar, Jr., J. H. Haslam, and E. M. Jones, *ibid.*, **58**, 2226 (1936).

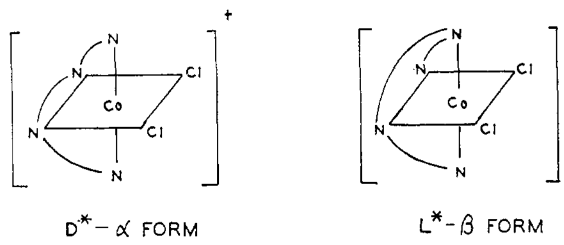

Figure 1. The absolute structures of *cis*-$[CoCl_2(trien)]^+$.

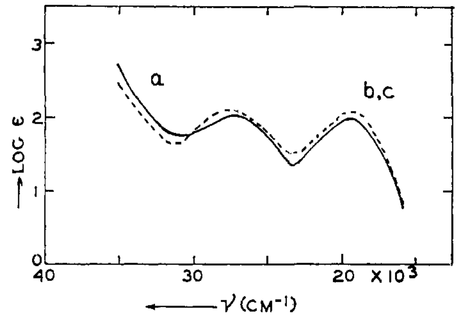

Figure 2. The absorption spectrum of *cis*-$[Co(OH)_2(trien)]^+$.

No details of structure of these complexes have yet been found to explain why the dihalobis(ethylenediamine) complexes react with inversion or retention of configuration under different conditions. The research described in this paper was undertaken in the hope of finding such information. Specifically, its purpose was to study the base hydrolysis and ammonation of closely related optically active geometrical isomers.

Results

The base hydrolysis of β-$[CoCl_2(trien)]^+$ to $[Co(OH)_2(trien)]^+$ gives the β isomer, as shown by the absorption spectrum (Figure 2). Solutions of L*-β-$[CoCl_2(trien)]Cl$ of fixed concentration were mixed with sodium hydroxide solutions of various concentrations, and the specific rotations of the solutions were determined at the sodium D-line. The results are summarized in Table I.

Table I. The Base Hydrolysis of L*-β-$[CoCl_2(trien)]^+$ (3.2×10^{-3} *M*) at Room Temperature

OH^- concn, *M*	Product $\alpha^{25}D^a$	Product $[\alpha]^{25}D^a$
2.5	−0.052 ± 0.002	−679 ± 26
5.0×10^{-1}	−0.052	−679
1.0×10^{-1}	−0.052	−679
5.0×10^{-2}	−0.053	−696
2.0×10^{-2}	−0.052	−679
6.4×10^{-3}	(2 equiv) −0.053	−696

[a] Throughout the paper, the values of α ^{25}D are expressed in degrees/centimeter, and those of $[\alpha]^{25}D$, in degrees × 100/decimeters × grams of solute.

The dihydroxo compound was converted to the optically active $[Co(ox)(trien)]NO_3$, and the configuration of this product was determined from its optical rotatory dispersion (Figure 3). A more detailed analysis of the product was carried out by column chromatography.[12] The results are shown in Figure 4, which records the rotations of samples of the eluent as elution proceeded.

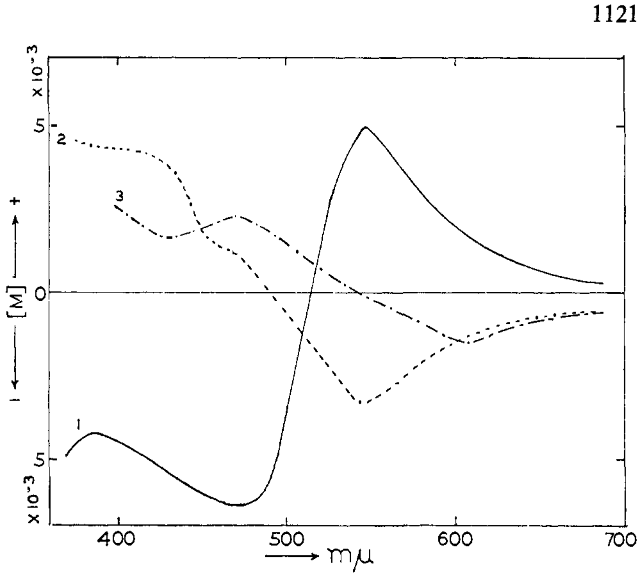

Figure 3. Optical rotatory dispersion of (1) (+)-D-α-$[Co(ox)(trien)]NO_3$; (2) (−)-D-β-$[Co(ox)(trien)]NO_3$; (3) (−)-D-β-$[CoCl_2(trien)]Cl$.

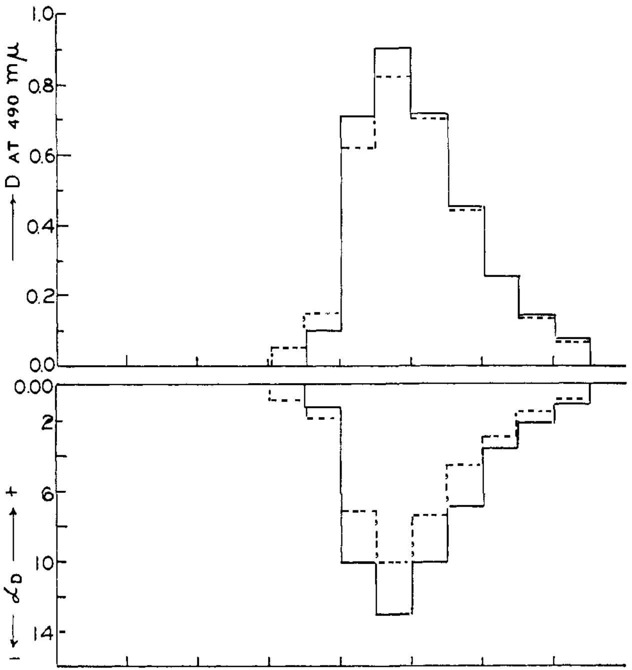

Figure 4. Optical densities and rotations of fractions obtained by the chromatographic analysis of the L*-β-oxalato complex: ———, pure L*-β-$[Co(ox)(trien)]NO_3$; – – – –, oxalato complex from L*-β-$[CoCl_2(trien)]Cl$.

Comparison of curves 2 and 3 in Figure 3 shows that the base hydrolysis to $[Co(OH)_2(trien)]^+$ and the conversion of this to the oxalato complex proceed without change in configuration. Even at high concentration of hydroxide ion, the base hydrolysis proceeds with re-

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(11) R. D. Archer and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **83**, 812 (1961).

(12) For the original technique and discussion of these complexes see, for example, E. L. King and R. R. Walters, *ibid.*, 74, 4471 (1952); M. Mori, M. Shibata, and M. Nanasawa, *Bull. Chem. Soc. Japan*, **29**, 947 (1950); G. B. Kauffman, R. Pinnell, and T. Takahashi, *Inorg. Chem.*, 1, 544 (1962).

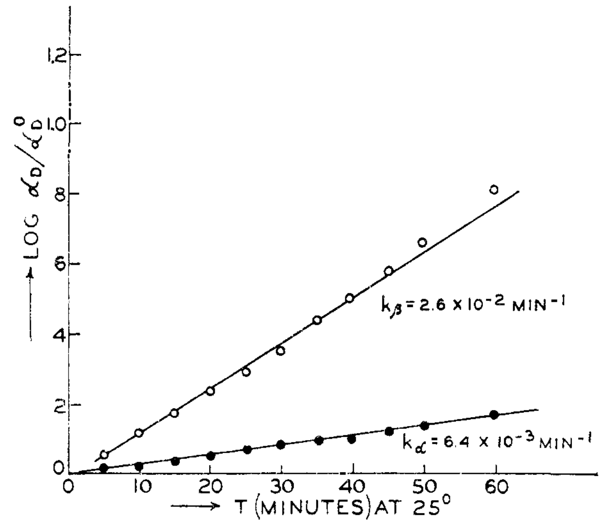

Figure 5. The rate of racemization of *cis*-$[Co(OH)_2(trien)]^+$: -●-●-, D*-α-$[Co(OH)_2(trien)]^+$; -○-○-, L*-β-$[Co(OH)_2(trien)]^+$.

tention of configuration (Table I). The same result was obtained under a variety of conditions (Table II). A slightly greater degree of retention was found in the case of β-$[CoBr_2(trien)]Br$ than in the case of the dichloro complex (Table III).

Table II. The Base Hydrolysis of L*-β-$[CoCl_2(trien)]^+$ (3.2×10^{-3} *M*) in Various Media at Low Temperatures (NaOH, 1.0×10^{-1} *M*)

Media	Reaction temp, °C	Product α^{25}D	$[\alpha]^{25}$D
H_2O-C_2H_5OH (1:1)	0	−0.051 ± 0.002	−666 ± 26
H_2O-$(CH_3)_2CO$ (1:1)	0	−0.052	−682
H_2O-CH_3OH (1:1)	0	−0.051	−669
H_2O-CH_3OH (1:9)	−22	−0.050	−640

Table III. The Base Hydrolysis of L*-β-$[CoBr_2(trien)]^+$ (3.2×10^{-3} *M*)

OH^- concn, *M*	Product α^{25}D	$[\alpha]^{25}$D
2.5	−0.054 ± 0.002	−705 ± 20
1.0×10^{-1}	−0.055	−718
5.0×10^{-2}	−0.054	−705
6.4×10^{-3}	(2 equiv) −0.054	−705

It has been shown that in the base hydrolysis of D*-α-$[CoCl_2(trien)]^+$, the presence of Ag^+ or Hg^{2+} in the solution greatly facilitates the retention reaction.[1] In the case of *cis*-β-$[CoCl_2(trien)]^+$, however, it is without effect (Table IV).

Table IV. The Base Hydrolysis of L*-β-$[CoCl_2(trien)]Cl$ in the Presence of Ag^+ and Hg^{2+} Ions (NaOH, 1.0×10^{-1} *M*; Complex, 3.2×10^{-3} *M*)

Metal salts	Reaction time, min	Product α^{25}D	$[\alpha]^{25}$D
$AgNO_3$	2	−0.052 ± 0.002	−679 ± 26
$AgNO_2$	5	−0.051	−666
$Hg(OAc)_2$	5	−0.051	−666
$Hg(OAc)_2$	10	−0.050	−653

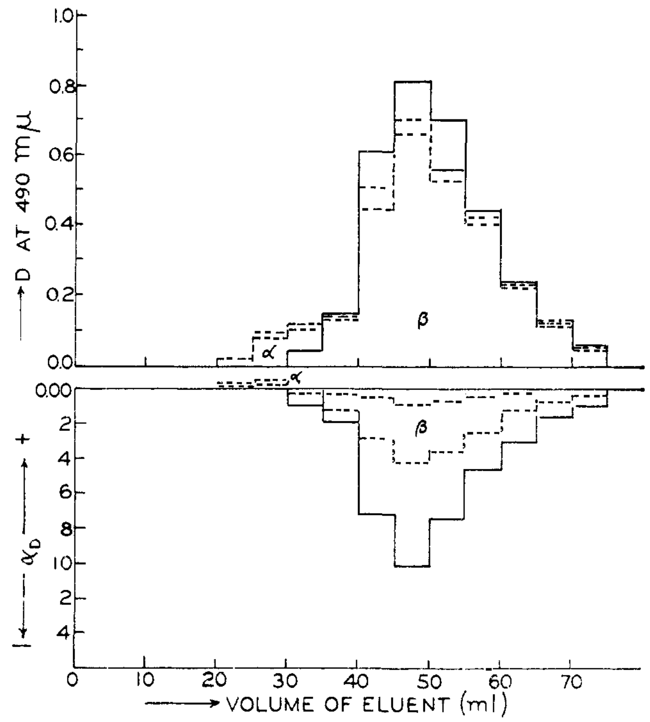

Figure 6. Optical densities and rotations of fractions obtained by the chromatographic analysis of $[Co(ox)(trien)]^+$ prepared from partially racemized L*-β-$[Co(OH)_2(trien)]^+$: ———, 0 hr; . . . . ., 2 hr; –·–·–, 12 hr.

The retention of configuration in the ammonation of the complex is shown in Table V. The ammonation of the complex, both at −33 and at 100°, gave chiefly L*-β-$[Co(NH_3)_2(trien)]Cl_3$, with retention of configuration, though at the higher temperature there was much racemization. The retention of configuration is significant in view of the fact that ammonation of the D*-α complex in liquid ammonia at −33° gives L*-β-$[Co(NH_3)_2(trien)]Cl_3$ with optical inversion, but with the gas at 100° gives the D*-α isomer with retention of configuration (with a good deal of racemization). Details of this reaction will be published later.

Table V. The Ammonation of L*-β-$[CoCl_2(trien)]Cl$

State of NH_3	Reaction temp, °C	Reaction time, days	Product α^{25}D[a]	$[\alpha]^{25}$D
Liquid	−33	1	−0.024 ± 0.002	−120 ± 13
Gas	+100	10	−0.010 ± 0.001	−50 ± 5

[a] 0.2% aqueous solution.

The L*-β-$[Co(OH)_2(trien)]^+$ ion in aqueous solution racemizes more rapidly than the corresponding α isomer (Figure 5). The racemization is not accompanied by extensive isomerization to the D*-α isomer, as is shown by the results of chromatographic analysis (Figure 6). A small amount of D*-α-$[Co(ox)(trien)]^+$ is detected chromatographically in the first fractions of solutions which had stood in the dihydroxo form for several hours before conversion to the stable oxalato complex. This is shown both by the lower optical activity and the lower optical density of the final solution.

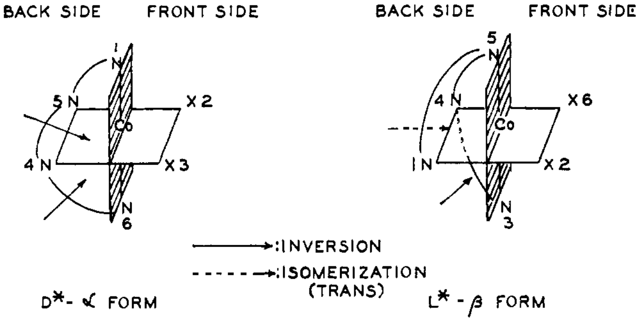

Figure 7. The isomerization scheme of *cis*-$[CoX_2(trien)]^+$.

Discussion

It has been shown that the base hydrolysis of L*-β-$[CoX_2(trien)]^+$, unlike that of D*-α-$[CoX_2(trien)]^+$, proceeds with almost complete retention of configuration. A similar difference was observed in the case of ammonation with liquid ammonia at −33°. On the basis of geometrical considerations alone, and excluding the possibility that the secondary nitrogen atoms can change their positions in the coordination sphere, an optical inversion of the α isomer without isomerization to the β form would be very difficult, for it would require a "back-side attack" on both edge 1,4 and edge 5,6, with both primary nitrogen atoms moving the full diameter on the octahedron (Figure 7). However, the β isomer would be formed easily from the α isomer by attack at only one edge—either edge 1,4 or edge 5,6 with one primary nitrogen atom moving to an adjacent corner of the octahedron. Also, an optical inversion in a reaction starting with the β isomer is much more difficult than one in a reaction of the α isomer because "back-side attack" on the β form will give equal amounts of inactive *trans* isomer and the α isomer of the opposite optical rotation.

Although there are not enough data to allow a final conclusion, it seems that the rate of hydrolysis is not the only factor which is important in determining whether inversion will take place. Thus, the acid hydrolysis of β-$[CoCl_2(trien)]^+$,[4] which leads to a noninverted product, proceeds one-tenth as fast as that of the α isomer, which gives an inverted product. On the other hand, the base hydrolysis of the α isomer is $^1/_{200}$th as fast as that of *cis*-$[CoCl_2(en)_2]^+$,[13] but both proceed with inversion.

The crystal field splitting energy (CFSE) in complexes of this sort is sometimes thought to be a factor in substitution reactions, and it may play a part in determining whether inversion takes place. For example, *cis*-$[CoF_2(en)_2]^+$ has a higher CFSE (and it absorbs at higher frequencies) than the corresponding chloro and bromo complexes.[14] Its reaction with silver carbonate proceeds with retention of configuration,[7] whereas the corresponding reaction of *cis*-$(CoCl_2(en)_2]^+$,[15] *cis*-$[CoBrCl(en)_2]^+$, and *cis*-$[CoBr_2(en)_2]^{+8}$ are characterized by inversion of configuration. Measurements of the absorption spectra in solution have shown that the β isomer absorbs at slightly higher frequencies than the α isomer does (Table VI). On this basis alone, we might therefore expect a lower tendency to enter into reactions involving inversion. Perhaps the difference in activation energy between "back-side attack," which leads to inversion, and "front-side attack," which leads to retention, may be only a few kilocalories per mole in the cobalt(III) complexes.

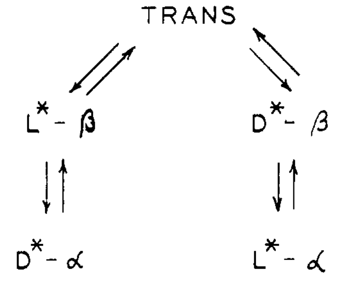

Figure 8. A possible pathway for racemization of L*-β-$[Co(OH)_2(trien)]^+$.

Table VI. The Absorption Maxima of Some Triethylenetetramine Complexes in Aqueous Solution

Complexes	Absorption maxima, 10^3 cm^{-1} (log ϵ) γ_1	γ_2	ν_3
α-$[CoCl_2(trien)]Cl$	18.52 (2.02)	26.32 (1.94)	42.37 (4.24)
β-$[CoCl_2(trien)]Cl$	19.27 (2.10)		44.05 (3.81)
α-$[CoCl(H_2O)(trien)](NO_3)_2$[1]	19.08 (2.06)	27.03 (1.97)	. . .

Relative rates of reactions and differences in CFSE may play a role in this inversion reaction, but they seem to be very much less important than the stereochemical factors.

It is interesting that ammonation with liquid ammonia and base hydrolysis in aqueous solution follow the same path; both lead to inversion in the reactions of *cis*-$[CoCl_2(en)_2]^+$ and D*-α-$[CoCl_2(trien)]^+$, but to retention of configuration in reactions of L*-β-$[CoCl_2(trien)]^+$.

The results shown in Figures 5 and 6 suggest that L*-β-$[Co(OH)_2(trien)]^+$ racemizes to a mixture of inactive α and β isomers through the unstable *trans* isomer (Figure 8).

Experimental Section

Preparation of Complexes. The complexes were prepared by methods described in earlier papers in this series. Unless otherwise specified, all reactions described in this study were carried out at room temperature. The values of α^{25}D are in deg/cm. and those of $[\alpha]^{25}$D are in deg × 100/dm × g of solute.

A. L*-β-Oxalatotriethylenetetraminecobalt(III) Nitrate (L*-β-$[Co(ox)(trien)]NO_3$). A finely powdered sample of D*-α-$[CoCl_2(trien)]Cl$ (6.2 g, 0.02 mole) was ground in a cold mortar with 20 ml of water containing 2.8 g of potassium hydroxide (0.048 mole) for 1 min, and then $C_2H_2O_4 \cdot 2H_2O$ (3.0 g, 0.024 mole) was ground with it. The mixture was evaporated to dryness under vacuum at 45°. A cold mixture of 5 ml of concentrated HNO_3 and 10 ml of ethanol was added, and the lumpy mixture was broken up by grinding. After 5 min, the mixture was filtered and the crystals were washed successively with a mixture of water and ethanol (2:3), ethanol, and ether, and air-dried. The yield of impure product was 6.5 g (91%), $[\alpha]^{25}$D −331°. The material was purified by recrystallization from water. After purification, the yield was 2.2 g (34%), $[\alpha]^{25}$D −644°, $[M]^{25}$D −2313° (0.1% aqueous solution).

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(13) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956).

(14) In general, in the cobalt(III) complexes, the substitution of the heavier halogens for the lighter ones shifts the d–d absorption bands to lower frequencies. The CFSE energy decreases in the same order: see Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **28**, 572 (1955); **29**, 311 (1956).

(15) J. C. Bailar, Jr., and R. W. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934).

Table VII. The Spectra of α- and β-[Co(ox)(trien)]NO$_3$ in Aqueous Solution

Complexes	— Absorption maxima, 10^3 cm^{-1} (log ϵ) —		
	ν_1	ν_2	ν_3
α-[Co(ox)(trien)]NO$_3$[1]	20.28 (2.03)	27.93 (2.14)	43.29 (4.40)
β-[Co(ox)(trien)]NO$_3$	20.12 (2.25)	28.01 (2.27)	42.02 (4.20)

Anal. Calcd for [CoC$_8$H$_{18}$N$_4$O$_4$]NO$_3$: C, 26.75; N, 19.50; H, 5.05. Found: C, 26.70; N, 19.43; H, 5.25.

The chief features of the spectrum are shown in Table VII.

B. **L*-Dichlorotriethylenetetraminecobalt(III) Chloride** (**L*-β-[CoCl$_2$(trien)]Cl**).[16] A finely powdered sample of L*-β-[Co(ox)-(trien)]NO$_3$ (3.6 g, 0.01 mole) was suspended in 60 ml of absolute ethanol, and dry HCl gas was bubbled into the mixture for 15 min while the solution was cooled in an ice bath. The mixture was kept for 2 days at room temperature. It was then filtered and the product was washed with small amounts of ethanol and ether and air dried. The yield was 2.4 g (77%), $[\alpha]^{25}$D $-267°$, $[M]^{25}$D $-831°$ (0.1% aqueous solution).

Anal. Calcd for [CoCl$_2$C$_6$H$_{18}$N$_4$]Cl: C, 23.12; N, 17.85; H, 5.76; Cl, 33.73. Found: C, 23.24; N, 18.03; H, 5.90; Cl, 32.50.

The infrared spectra (in Nujol mull) show the following peaks: D*-α-[CoCl$_2$(trien)]Cl: 3050 (sh), 1630 (m), 1570 (m), 1300 (w), 1196 (w), 1163 (m), 1105 (w), 1057 (s), 1030 (s), 1007 (w), 792 (m), 771 (m), 676 (m), 639 (m), 602 (w), 576 (m), 485 (m), 452 (w), 427 (w), and 368 (w); L*-β-[CoCl$_2$(trien)]Cl: 3050 (sh), 1580 (m), 1540 (m), 1300 (w), 1172 (w), 1150 (m), 1100 (w), 1070 (s), 1050 (w), 1020 (w), 986 (w), 830 (w), 606 (m), 570 (m), 522 (w), 505 (m), 492 (m), 404 (m), 337 (m), and 290 (m).

C. **L*-Dibromotriethylenetetraminecobalt(III) Bromide.** L*-β-[CoBr$_2$(trien)]Br was prepared by the same method, using HBr gas in place of HCl: yield 3.6 g (80%), $[\alpha]^{25}$D $-200°$, $[M]^{25}$D $-890°$.

Anal. Calcd for [CoBr$_2$C$_6$H$_{18}$N$_4$]Br: C, 16.19; N, 12.59; H, 4.08. Found: C, 16.22; N, 12.50; H, 3.92.

The chief bands in the infrared spectrum for L*-β-[CoBr$_2$(trien)]Br are 3200 (sh), 1650 (s), 1310 (w), 1192 (w), 1155 (m), 1091 (w), 1087 (m), 1076 (w), 998 (w), 831 (w), 606 (m), 570 (m), 516 (w), 502 (m), 489 (m), 418 (w), 396 (m), and 750 (w).

D. **L*-β-Diamminetriethylenetetraminecobalt(III) Chloride** (L*-β-**[Co(NH$_3$)$_2$(trien)]Cl$_3$**). A finely powdered sample of L*-β-[CoCl$_2$-(trien)]Cl (1.6 g, 0.005 mole) was added to 20 ml of liquid ammonia in a Dry Ice–acetone bath. Moisture was excluded by the use of soda lime traps. When the temperature rose to the boiling point of ammonia, the solution changed from violet to orange.

At the end of the reaction period, the excess ammonia was allowed to evaporate. About 30 ml of ethanol was added to the yellow residue and the mixture was filtered. The product was washed with ethanol and then ether, and air dried: yield 1.4 g (81%), $[\alpha]^{25}$D $-170°$, $[M]^{25}$D $-587°$ (0.2% aqueous solution). Further purification was effected by reprecipitation from a small amount of concentrated aqueous solution by addition of a large amount of absolute ethanol.

Anal. Calcd for [CoC$_6$H$_{24}$N$_6$]Cl$_3$: C, 21.14; N, 24.02; H, 7.00. Found: C, 21.02; N, 24.20; H, 6.89.

The ultraviolet spectrum in aqueous solution for L*-β-[Co-(NH$_3$)$_2$(trien)]Cl$_3$ showed the following absorption maxima (10^3 cm^{-1} (log ϵ)): ν_1, 21.14 (1.95); ν_2, 29.23 (1.93); ν_3, 46.08 (4.01).

The sample solutions reported in Figure 2 were prepared as follows.

D*-α-[Co(OH)$_2$(trien)]$^+$ (Curve a, Figure 2). A solution of D*-α-[CoCl$_2$(trien)]Cl (0.031 g, 1.0 × 10^{-4} mole) and mercury(II) acetate (0.032 g, 1.0 × 10^{-4} mole) in 5 ml of water was kept for 5 min at room temperature to convert the complex to D*-α-[Co(H$_2$O)$_2$(trien)]$^{3+}$.[1] Then 5 ml of 0.2 *M* NaOH solution was added to give D*-α-[Co(OH)$_2$(trien)]$^+$. After dilution with 10 ml of 0.1 *M* NaOH, the solution was filtered and the absorption spectrum was measured.

L*-β-[Co(OH)$_2$(trien)]$^+$ from D*-α-[CoCl$_2$(trien)]$^+$ (Curve b, Figure 2) and from L*-β-[CoCl$_2$(trien)]$^+$ (Curve c). To a solution of the complex (0.031 g, 1.0 × 10^{-4} mole) in 5 ml of water was added 5 ml of 0.2 *M* NaOH. After dilution with 10 ml of 0.1 *M* NaOH, this solution was 5.0 × 10^{-3} *M* with respect to L*-β-[Co(OH)$_2$-(trien)]$^+$ and was used directly for the measurement of the spectrum.

Base Hydrolysis. The data reported in Table I were gathered in the following way. L*-β-[CoCl$_2$(trien)]Cl (0.010 g, 3.2 × 10^{-5} mole) was dissolved in 10 ml of sodium hydroxide solution at room temperature. After 30 sec, the rotation of the solution was measured. The data reported in Table II were obtained by using several media at 0 and $-22°$. The data reported in Table III were obtained in a similar way, using L*-β-[CoBr$_2$(trien)]Br as the starting material. The data reported in Table IV were collected in the following way. Mixtures of L*-β-[CoCl$_2$(trien)]Cl (0.010 g, 3.2 × 10^{-5} mole) and AgNO$_3$ (0.034 g, 2.0 × 10^{-4} mole) or Hg(OAc)$_2$ (0.032 g, 1.0 × 10^{-4} mole) were dissolved in 5 ml of water at room temperature. Each solution was allowed to stand for a given length of time at room temperature, after which 5 ml of 0.2 *M* NaOH was added. After filtration, the optical activity was measured.

Optical rotatory dispersion curves were measured on solutions which were 5.0 × 10^{-3} *M*.

Chromatographic Analysis. The data for the chromatographic analysis (Figure 4) were obtained as follows. To a solution of L*-β-[CoCl$_2$(trien)]Cl (0.031 g, 1.0 × 10^{-4} mole) in 5 ml of 0.1 *M* NaOH solution was added 5 ml of a solution of oxalate (0.63 g of H$_2$C$_2$O$_4$·2H$_2$O and 1.84 g of K$_2$C$_2$O$_4$·H$_2$O per 100 ml of water). The mixture was heated at 50° for 30 min. When cold, it was absorbed on the cation exchanger (Dowex 50WX4, sodium form, 200–400 mesh; *d*, 1.0 cm; *l*, 5.0 cm) as it was washed with 5 ml of water. It was eluted with 0.5 *M* NaCl solution (about 0.5 ml/min) and 5-ml samples were collected. The optical activity (sodium D-line) and optical density (at 490 mμ) of each were measured. A solution of pure L*-β-[Co(ox)(trien)]NO$_3$ (0.036 g, 1.0 × 10^{-4} mole) was used as the standard.

Racemization Studies. The racemization studies (Figure 5) were carried out in the following way. Samples of D*-α-[Co-(OH)$_2$(trien)]$^+$ and L*-β-[Co(OH)$_2$(trien)]$^+$ were obtained in the same way as those used for the solutions shown in Figure 2 except that 1.0 *M* NaOH was used instead of 0.1 *M* NaOH.

The optical activity of the solutions was measured at 25° and the rate constant of the racemization was calculated. The data reported in Figure 6 were gathered in the following way. A solution of L*-β-[CoCl$_2$(trien)]Cl (0.031 g, 1.0 × 10^{-4} mole) in 5 ml of 0.1 *M* NaOH solution was kept in a thermostat at 25°. After specified lengths of time (0 hr, 2 hr, 12 hr), 5-ml portions of a solution containing 0.634 g of H$_2$C$_2$O$_4$·2H$_2$O and 1.84 g of K$_2$C$_2$O$_4$·H$_2$O per 100 ml of water were added and the solution was treated in the same way as those shown in Figure 4. Five-milliliter fractions were collected, and the optical density at 490 mμ and optical activity at the sodium D-line of each was measured.

Apparatus. Colorimetric determinations of the solutions were made on a Bausch and Lomb Type 340 instrument using 1.0-cm cells. Infrared determinations of both sodium chloride and cesium bromide regions were made with Beckman IR5A instruments using Nujol mulls. The other apparatus used was the same as described in an earlier paper.[1]

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[16] G. H. Searle has prepared the isomeric perchlorates by another method.[3]