the equilibrium constant for the over-all reaction

$$A_5CoOH_2{}^{3+} + X^- \underset{K}{\rightleftarrows} A_5CoX^{2+} + H_2O$$
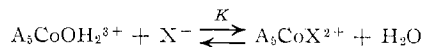
has the form $K = k_e k_x / k_w k_a$ assuming there is no significant ion pairing.[15]

The rate of oxygen exchange between $A_5CoOH_2{}^{3+}$ and water, k_e, is known and the rates of aquation of A_5-CoX^{2+} (X = Cl, Br, NO_3) and the equilibrium constant K are known also, whence k_x/k_w was calculated, Table VI. The equilibrium constants have now been remeasured at $\mu = 1$ by the ion-exchange method and they agree substantially with the values quoted by Haim and Taube.[2] The improved precision of the present work removes the apparent agreement between the values of k_x/k_w for the induced aquation reactions (Tables III–V) on the one hand and for the spontaneous (Table VI) on the other, which was indicated by the earlier work,[2] so there is no longer conflict between the competition experiments and the conclusions of Pearson and Moore.[3] This requires either a different intermediate for the anation reactions from that proposed here or a different mechanism.

In summary, the competition ratios for the nitrosation reactions are constant and may well agree with those for the anion-independent path for the Hg^{2+}-induced aquations[1] and are different from those for the normal aquation reactions.[2] The O^{18}/O^{16} fractionation factors for the azido reaction[5] and the Hg^{2+}-induced aquations of A_5CoX^{2+} (X = Cl, Br, I)[1,5] are constant, and both the competition ratios and fractionation fac-

TABLE VI

RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION

$$(NH_3)_5CoOH_2{}^{3+} + X^- \underset{k_w}{\overset{k_a}{\rightleftarrows}} (NH_3)_5CoX^{2+} + H_2O$$

$(25°, \mu = 0.5)^a$
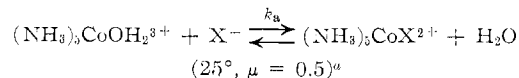
	k_R, sec^{-1}	K	k_x/k_w
Cl$^-$	1.7×10^{-6}	$1.25 (1.11)^b$	$0.35 (0.31)$
Br$^-$	6.5×10^{-6}	$0.39 (0.35)$	$0.43 (0.39)$
$NO_3{}^-$	2.9×10^{-5}	$0.077 (0.08)$	$0.38 (0.40)$

^{a} From Table IV of ref 2. ^{b} Measured using the ion-exchange technique at $\mu = 1.0$.

tors agree with the formation of a common $[(NH_3)_5$-$Co^{3+}]$ intermediate for the induced aquations. Finally the nature of the proposed intermediate involved in reactions 1–3 has been established by selectively deuterating the ammonia *trans* to the substituent.[22] The intermediate reacts with retention of the isotopic distribution imparted into the initial reactants for all three of reactions 1–3 in agreement with the conclusions derived from the anion competition and O^{18}/O^{16} fractionational values. The result suggests that the intermediate has the form substantially of a square pyramid and excludes the possibility of a symmetrical trigonal bipyramid.

(22) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967).

Stereochemistry and Rearrangement in Some Triethylenetetramine Disubstituted Cobalt(III) Ions

By D. A. BUCKINGHAM, P. A. MARZILLI, AND A. M. SARGESON

The preparation, stereochemistry, and aquation of the optically active *trans*-[Co(trien)Cl₂]⁺ ion is discussed. It is shown that $(+)_{589}$-*trans*-[Co(trien)Cl₂]⁺ aquates stereospecifically to the optically pure $(+)_{589}$-β-[Co(trien)ClOH₂]²⁺ ion which is identical with that obtained from $(+)_{589}$-β-[Co(trien)Cl₂]⁺. The preparation of the active *trans*-[Co(trien)Cl₂]⁺ ion allows some ring conformations to be assigned to this ion and the β-chloroaquo and some other β complexes. The two internal diastereoisomers of β-[Co(trien)(OH₂)₂]³⁺ are reported and the mutarotation of the less stable form is observed. The stereochemistry and rearrangements are discussed in the light of the properties of the optically active *sec*-NH centers of the coordinated quadridentate.

Introduction

One of the recent developments in the chemistry of cobalt(III) complexes has been the resolution and racemization and proton-exchange reactions of coordinated asymmetric nitrogen atoms. The [Co-$(NH_3)_4(sar)]^{2+}$[1] (sar = N-methylglycinate), [Co-

$(NH_3)_4N$-Meen]$^{3+}$[2] (N-Meen = N-methylethylenediamine), *trans*-[Co(N-Meen)$_2$(NO$_2$)$_2$]$^+$,[3] and *trans*-[Co(N-EtOHen)$_2$(NO$_2$)$_2$]$^+$[3] (N-EtOHen = N-(2-hydroxyethyl)ethylenediamine) ions have been resolved, and the rates of racemization, k_R, and proton exchange, k_H,

(1) B. Halpern, A. M. Sargeson, and K. R. Trunbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).

(2) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).

(3) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, in press.

measured. Both processes have a rate law which is inverse in [H$^+$] and the ratio k_H/k_R for these ions varies between 3500 and 125,000 indicating that the lone pair of the conjugate base of the complex preserves its configuration most of the time. The extent to which the configuration about such asymmetric nitrogen centers can direct the stereochemisty and subsequent isomerization reactions has interested us for some time and this paper deals with this situation as applied to some cobalt(III) complexes of triethylenetetramine.

Triethylenetetramine may be arranged about the Co(III) ion in three topological ways, Figure 1. At first sight the two *cis* ions have a dissymmetric arrangement of the ligand about the metal ion whereas the *trans* isomer appears to have two planes of symmetry. However, the possiblility of a second source of asymmetry arises from the secondary >N–H groups. Dreiding stereo models demonstate that in the α structure the configuration adopted by the ligand requires that the two secondary H atoms be stereospecifically oriented in the L (and D) isomer(s), Figure 2, and only the L-*SS* and D-*RR*[4] isomers exist. The stable ring conformations are probably those shown in Figure 2.

In the β structure, however, two isomers may occur for one configuration of the ligand about the Co atom due to the orientation of the "planar" *sec*-NH proton. The D structures are shown in Figure 3. Figure 3a has the configurations about both *sec*-N atoms the same and may be related to the L-α-*SS* structure, Figure 2, by the movement of a terminal NH$_2$ group along an octahedral edge. The isomer in Figure 3b has the configurations about the two N atoms antimeric. It is not yet clear if there is any strain involved in the coordination of the "planar" *sec*-N atom, but if it does exist, it can be partly accommodated by the puckered nature of the cobalt–ethylenediamine rings. However, the configuration about the central N imposes certain requirements on the conformations of the linked chelate rings in this plane, namely, that they have antimeric configurations. Both the D-*SS* and D-*SR* structures should be inert in acidic solutions since configurational and conformational interchange cannot occur without loss of the proton on the "planar" *sec*-N atom. A related pair of isomers is possible for the L-β configuration.

In the *trans* structure the configurations about the *sec*-N atoms give rise to three possible isomers, Figure 4. The *RR* and *SS* forms are antimeric while the *RS* form is internally compensated. Dreiding stereo models imply that the central ring in the *meso* isomer has the eclipsed "envelope" form and possibly the two terminal rings also may have the same conformation. However the *RR* and *SS* forms have their *gauche* ring conformations precisely decided by the configurations about the *sec*-N atoms.

(4) Nomenclature for designating the configuration about the asymmetric N atom: The normal trigonal *sec*-N is named before the central *sec*-N of the three coplanar N atoms. The latter is referred to in the text as the "planar" *sec*-N atom. The asymmetric configuration is described as *R* or *S* according to the sequence rules of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).
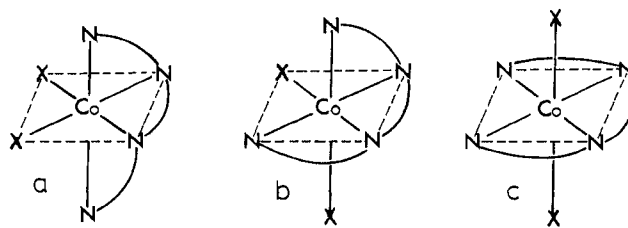
Figure 1.—Geometrical forms of the [Co(trien)X$_2$]$^{n+}$ ion: a, α structure; b, β structure; c, *trans* structure.
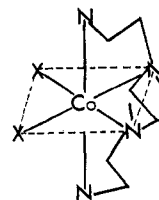
Figure 2.—Stereospecific orientation of the secondary amine protons in the L-α-*SS*-[Co(trien)X$_2$]$^{n+}$ ion.
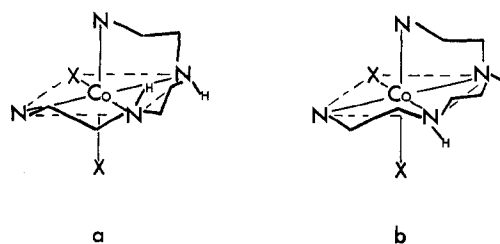
Figure 3 —Stereospecific orientations of the "planar" secondary amine proton in the D-β-[Co(trien)X$_2$]$^{n+}$ ion: a, D-β-*SS* configuration; b, D-β-*SR* configuration.
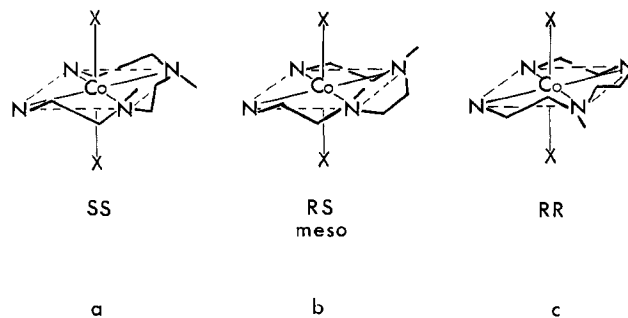
Figure 4.—Three isomers of the *trans*-[Co(trien)X$_2$]$^{n+}$ ion.

The isomeric possibilities in the [Co(trien)X$_2$]$^+$ system are therefore quite complex, two α, four β, and three *trans*. In an earlier publication[5] the dichloro complexes of two α, two β, and one *trans* isomer were reported, and the present paper is concerned with the detailed structures of some of these isomers, their reactions, and the description of some new isomers.

Experimental Section

Optical rotations ([M]$_\lambda$ in deg M^{-1} cm^{-1}) were measured in a 1-dm tube with a Bellingham and Stanley polarimeter or a Perkin-Elmer 141 polarimeter coupled with a Zeiss monochromator and fitted with a quartz–iodine lamp. Visible absorption spectra were recorded on a Shimadzu spectrophotometer RS-27 or a Cary 14 recording spectrophotometer fitted with

(5) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

thermostated cell holders and cell compartments. The pmr spectra were recorded on a Perkin-Elmer R10 spectrometer at 34.3° or a Varian A-60 nmr spectrometer at other temperatures. For pmr spectra of dilute solutions a CAT attachment for the Varian instrument was used.

Apart from the following preparations, all complexes were prepared according to methods published elsewhere.[5]

(±)-trans-[Co(trien)Cl₂]Cl.—Finely powdered racemic β-[Co(trien)Cl₂]Cl·0.5H₂O (10 g) was suspended in 250 ml of methanol (solvent grade, made slightly acid with dry HCl gas). The suspension was heated to reflux and stirred. At 20–30-min intervals the remaining undissolved β-[Co(trien)Cl₂]Cl was removed by filtration and extracted with a fresh portion of methanol. The brown-green filtrate was concentrated under reduced pressure until the green (±)-trans-[Co(trien)Cl₂]Cl began to crystallize. The product was collected on a filter and washed with acetone and ether; yield, after six extractions 1.84 g. The product was recrystallized from HCl (10^{-3} M) and collected in fractions, of which the first was the most pure (0.7 g). *Anal.* Calcd for [Co(trien)Cl₂]Cl·H₂O: C, 21.86; H, 6.12; N, 17.00. Found: C, 21.88; H, 6.33; N, 16.93.

(±)-trans-[Co(trien)Cl₂]ClO₄: This complex was prepared by the same extraction procedure as that used for the chloride salt except that the complex perchlorate crystallized when LiClO₄ was added to the warm methanol extracts. The bright green product was collected and washed with ethanol and ether. *Anal.* Calcd for [Co(trien)Cl₂]ClO₄: C, 19.19; H, 4.83; N, 14.92. Found: C, 19.45; H, 4.86; N, 14.87.

(+)-trans-SS-[Co(trien)Cl₂](ClO₄).—D-β-SS-[Co(trien)Cl₂]-(ClO₄), [M]D +880° (2 g), was dissolved in anhydrous methanol (500 ml acidified with dry HCl gas). The solution was heated at reflux for 20 min, cooled to room temperature, and filtered to remove the violet solid remaining. To the filtrate was added excess LiClO₄, and after scratching (at 0°) light green crystals formed; these were removed by filtration and washed with ethanol and ether. Further fractions from this filtrate were contaminated with the β isomer. The extraction procedure was repeated with the D-β-SS-[Co(trien)Cl₂]ClO₄ remaining; total yield, 1.75 g.

To remove residual β isomer, the product (0.95 g) was dissolved in ice cold 0.1 N HCl (15 ml) in which was suspended 1.06 g of tetraphenylarsonium chloride. The mixture was shaken for 5–7 min with glass beads at 0° and was then filtered through Super-Cell to remove tetraphenylarsonium perchlorate and washed with ice-cold 0.1 N HCl (2 ml). The filtrate was treated with excess NaClO₄ and cooled until the bright green crystals of trans-SS-[Co(trien)Cl₂](ClO₄) formed; these were collected in three fractions and washed with cold 0.1 N HCl containing NaClO₄, then ethanol, and ether; yield, 0.5 g. The product was dried under vacuum and kept in the dark. *Anal.* Calcd for [Co(trien)Cl₂](ClO₄): C, 19.19; H, 4.83; N, 14.92. Found: C, 19.07; H, 4.80; N, 14.70. A 0.05% solution in 0.1 M HClO₄ gave αD +0.400°, whence [α]D +800° and [M]D +3000° (±30°).
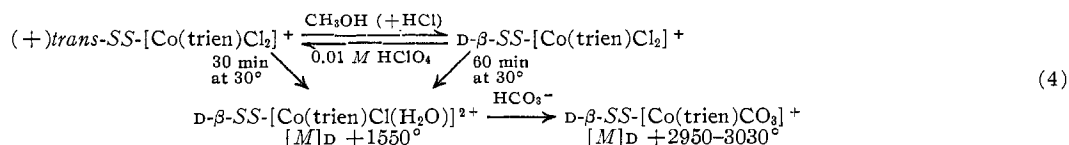
Kinetic Studies.—Hg(ClO₄)₂ solutions were prepared by dissolving weighed samples of HgO in standard HClO₄. The isomerization of (+)D-trans-SS-[Co(trien)(H₂O)₂]³⁺ was studied polarimetrically as follows: 0.01 g of optically pure trans-SS-[Co(trien)Cl₂](ClO₄) ([M]D +3000°) was dissolved at 0° in 20 ml of a known perchloric acid solution containing 0.1 M Hg-(ClO₄)₂ and then thermostated in a jacketed 1-dm polarimeter tube at the appropriate temperature. The change in rotation was followed at 640 and 440 mμ for the isomerization to D-β-SS- + D-β-SR-[Co(trien)(H₂O)₂]³⁺ and at 510 mμ for the mutarotation of D-β-SR- to D-β-SS-[Co(trien)(H₂O)₂]³⁺. Rotations were recorded for at least 4 half-lives and good straight lines were obtained from plots of log ($\alpha_t - \alpha_\infty$) vs. t. The isomerization reaction was followed over the temperature range 1–23° and the subsequent mutarotation reaction at 25–50°. The ionic strength was maintained constant by addition of NaClO₄.

The polarimetric rate for the aquation and isomerization of trans-SS-[Co(trien)Cl₂]ClO₄ to D-β-SS-[Co(trien)Cl(H₂O)]²⁺ was

Figure 5.—Visible absorption and RD curves for the trans-SS-[Co(trien)Cl₂]⁺ (– – – –) and the trans-SS-[Co(trien)(OH₂)₂]³⁺ ions (———) ([M] in deg M^{-1} cm^{-1}).

followed at 610 mμ in 0.1 M HClO₄ at 15° using a 0.05% solution of complex.

Spectrophotometric rates for the isomerization of trans- to β-[Co(trien)(H₂O)₂]³⁺ were followed at 415 mμ on a Shimadzu recording spectrophotometer using 0.02% solutions and a 5-cm thermostated cell.

Pmr Studies.—Pmr spectra were observed in DCl, D₂SO₄, and DClO₄ solutions. DClO₄ solutions were prepared from D₂SO₄ by the addition of anhydrous Ba(ClO₄)₂. Between 0.15 and 0.25 g of complex was dissolved in 0.5 ml of solvent in the nmr tube and the spectrum was recorded within 3 min. Sodium trimethyl-silylpropanesulfonate was used as a reference standard.

Results

trans-SS-[Co(trien)Cl₂]ClO₄ has been obtained from D-β-SS-[Co(trien)Cl₂]ClO₄ according to the reaction scheme

$$\text{D-}\beta\text{-SS-[Co(trien)Cl}_2]\text{ClO}_4 \xrightarrow[\text{reflux 30 min}]{\text{CH}_3\text{OH (trace HCl)}}$$
$$[M]_\text{D} +880°$$

$$trans\text{-SS-[Co(trien)Cl}_2]\text{ClO}_4 \quad (1)$$
$$[M]_\text{D} +3000°$$

and similar experiments using L-β-RR-[Co(trien)Cl₂]-ClO₄ and racemic β-[Co(trien)Cl₂]Cl,ClO₄ gave trans-RR-[Co(trien)Cl₂]ClO₄ and racemic trans-[Co(trien)-Cl₂]Cl·H₂O,ClO₄, respectively. The absorption spectrum and RD curve for the trans-SS isomer are given in Figure 5. The CD spectrum will be discussed elsewhere.

trans-SS-[Co(trien)Cl₂]ClO₄ was shown to be optically pure by the sequence of reactions shown in eq 2.

$$\textit{trans-SS-}[\text{Co(trien)Cl}_2]^+ \xrightarrow[\text{30 min, 30}^\circ]{0.01\ M\ \text{HClO}_4} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)Cl(H}_2\text{O})]^{2+} + \text{Cl}^-$$
$$[M]_\text{D} +3000^\circ \qquad\qquad\qquad\qquad\qquad [M]_\text{D} +1560^\circ$$

$$\left.\begin{array}{c}0.1\ M\ \text{Hg}^{2+}\\1\ M\ \text{HClO}_4\end{array}\right\}4\ \text{days, }25^\circ \qquad \xrightarrow{0.1\ M\ \text{Hg}^{2+}} \qquad\qquad \Big\downarrow \text{HCO}_3^-$$

$$\xleftarrow[\text{1}\ M\ \text{HClO}_4]{} \qquad (2)$$

$$\text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)(H}_2\text{O})_2]^{3+} \xleftarrow[]{\text{HClO}_4} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)CO}_3]^+ + \text{H}^+ + \text{Cl}^-$$
$$[M]_\text{D} +840^\circ \qquad\qquad\qquad [M]_\text{D} +2980^\circ$$

These products compare with those from the similar reactions using optically pure starting materials (eq 3)

$$\text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)CO}_3]^+ \xrightarrow{0.1\ M\ \text{HClO}_4} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)(H}_2\text{O})_2]^{3+} + \text{CO}_2$$
$$[M]_\text{D} +2970^\circ \qquad\qquad\qquad\qquad [M]_\text{D} +850^\circ$$

$$[M]_{510} +1400^\circ \Big\uparrow 0.1\ M\ \text{Hg}^{2+} \qquad\qquad (3)$$

$$\text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)Cl}_2]^+ \xrightarrow[\text{60 min, 30}^\circ]{0.01\ M\ \text{HClO}_4} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)Cl(H}_2\text{O})]^{2+} + \text{Cl}^-$$
$$[M]_\text{D} +880^\circ \qquad\qquad\qquad\qquad [M]_\text{D} +1500^\circ$$

and have been shown previously to involve essentially full retention of configuration.[6] This result shows that little or no *meso-trans* isomer is included in the *trans-SS*-[Co(trien)Cl₂]ClO₄ isolated from reaction 1. The possibility that some *trans-SR* isomer was formed in reaction 1 but was not isolated owing to an equilibrium strongly in favor of racemic β-[Co(trien)Cl₂]⁺ was checked by isolating a sample of the reaction mixture containing ∼50% β and ∼50% *trans* formed from optically pure *trans-SS*-[Co(trien)Cl₂]ClO₄ and by aquating the mixture to the β-chloraquo complex

rium. Also, it was possible to establish separately the optical purity of D-β-*SS*-[Co(trien)Cl₂]ClO₄ formed in reaction 4 by removing it from the equilibrium mixture as the [Co(en)(C₂O₄)₂]⁻ salt.

The relation between *trans-SS*-[Co(trien)Cl₂]ClO₄ and the racemic material previously used by Sargeson and Searle[7] was established by comparing the rates of aquation and isomerization to D-β-*SS*-[Co(trien)Cl-(H₂O)]²⁺ in 0.1 M HClO₄ at 15°. The polarimetric rate constant obtained from the linear plot of log $(\alpha^0 - \alpha^0_\infty)$ vs. t, $k = 0.72 \times 10^{-3}$ sec⁻¹, agrees well with the spectrophotometric and conductometric value of 0.75×10^{-3} sec⁻¹ obtained previously.[7]

$$(+)\textit{trans-SS-}[\text{Co(trien)Cl}_2]^+ \underset[\text{0.01}\ M\ \text{HClO}_4]{\overset{\text{CH}_3\text{OH (+HCl)}}{\rightleftharpoons}} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)Cl}_2]^+$$
$$\underset[\text{at 30}^\circ]{\text{30 min}}\searrow \qquad\qquad \swarrow\underset[\text{at 30}^\circ]{\text{60 min}} \qquad (4)$$
$$\text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)Cl(H}_2\text{O})]^{2+} \xrightarrow{\text{HCO}_3^-} \text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)CO}_3]^+$$
$$[M]_\text{D} +1550^\circ \qquad\qquad\qquad [M]_\text{D} +2950\text{–}3030^\circ$$

which was then converted to the carbonato complex with NaHCO₃ as shown in eq 4. The optical

The isomerization

$$\textit{trans-SS-}[\text{Co(trien)(H}_2\text{O})_2]^{3+} \longrightarrow$$
$$\text{D-}\beta\text{-}SS\text{-}[\text{Co(trien)(H}_2\text{O})_2]^{3+} + \text{D-}\beta\text{-}SR\text{-}[\text{Co(trien)(H}_2\text{O})_2]^{3+} \quad (5)$$
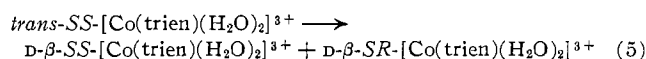
was complete (>99%) and was markedly dependent on [H⁺], temperature, and ionic strength. The first-order rate constants obtained polarimetrically at 640 mμ are given in Table I. Those given in Table II show that reaction 5 is independent of [Hg²⁺]. The product D-β-[Co(trien)(H₂O)₂]³⁺ was shown to be spectrophotometrically indistinguishable (ϵ_{487} 124) from D-β-*SS*-[Co(trien)(H₂O)₂]³⁺ obtained by acidification of D-β-*SS*-[Co(trien)CO₃]ClO₄, but the polarimetric results showed considerable differences at various acid concentrations. The products were optically more active at wavelengths below 560 mμ than optically pure D-β-*SS*-[Co(trien)(H₂O)₂]³⁺ obtained from D-β-*SS*-[Co-(trien)CO₃]ClO₄ (reaction 3). These results are given in Table III. Figure 6 shows the RD curves of the products from reaction 5 after at least 6 half-lives as a function of the HClO₄ concentration. It can be seen that at all acid strengths they are optically more active than the product obtained from reaction 3 with the largest differences occurring at the lowest acid strengths. That these anomalous rotations were due to the presence of some D-β-*SR*-[Co(trien)(H₂O)₂]³⁺ and were not due merely to the presence of Hg²⁺ was established by the experiment illustrated in eq 6.

TABLE I
OBSERVED RATE CONSTANTS FOR THE
trans-SS-[Co(trien)(H₂O)₂]³⁺ ⟶
D-β-*SS*- + D-β-*SR*-[Co(trien)(H₂O)₂]³⁺ REACTION ([Hg(ClO₄)₂] =
0.1 M, FOLLOWED POLARIMETRICALLY AT 640 mμ)

[H⁺], M	μ	Temp, °C	k_obsd, sec⁻¹	k_calcd,[a] sec⁻¹
0.05	1.3	15	3.2×10^{-3}	3.2×10^{-3}
0.10	1.3	15	1.7×10^{-3}	1.7×10^{-3}
	1.3	8	5.9×10^{-4}	
	1.3	1	1.8×10^{-4}	
0.3	1.3	15	6.4×10^{-4}	6.4×10^{-4}
0.5	1.3	15	4.2×10^{-4}	4.4×10^{-4}
1.0	1.3	23	1.0×10^{-3}	
	1.3	15	3.3×10^{-4}	2.9×10^{-4}
	1.3	8	8.7×10^{-5}	
0.10	4.0	15	4.6×10^{-4}	
1.0	4.0	15	2.5×10^{-4}	
2.0	4.0	15	3.2×10^{-4}	
3.0	4.0	15	3.3×10^{-4}	
	4.0	15	3.4×10^{-4}	
	4.5[b]	15	3.8×10^{-4}	
5.89	6.2	15	1.6×10^{-3}	

[a] k_calcd was obtained from the rate law $k = k_1 + k_2/[\text{H}^+]$, using $k_1 = 1.33 \times 10^{-4}$ sec⁻¹, $k_2 = 1.53 \times 10^{-4}$ sec⁻¹. [b] [Hg(ClO₄)₂] = 0.5 M.

purity of the product demonstrates that little or no *meso-trans* isomer is involved in the equilib-

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

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

$$\text{D-}\beta\text{-}SS\text{-[Co(trien)CO}_3]\text{ClO}_4 \xrightarrow[\text{HClO}_4]{0.1\ M} \begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_\text{D}\ +850°,\ [M]_{510}\ +1450° \end{array}$$

$$\begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)CO}_3]\text{ClO}_4 \\ [M]_\text{D}\ +2950° \end{array} \xrightarrow[\substack{0.1\ M \\ \text{Hg}^{2+}}]{} \\ \xrightarrow[\text{HClO}_4]{1.05\ M} \begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_\text{D}\ +850°,\ [M]_{510}\ +1450° \end{array} \tag{6}$$

$$\begin{array}{c} \text{rans-}SS\text{-[Co(trien)Cl}_2]^+ \\ [M]_\text{D}\ +3000° \end{array} \xrightarrow[\substack{30\ \text{min, }30° \\ \text{HCO}_3^-}]{0.01\text{--}1.0\ M\ \text{HClO}_4} \text{D-}\beta\text{-}SS\text{-[Co(trien)Cl(H}_2\text{O)}]^{2+}$$

$$\begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)CO}_3]^+ + \text{Cl}^- + \text{H}^+ \\ [M]_\text{D}\ +2960° \end{array} \xleftarrow[\substack{0.1\ M\ \text{Hg}^{2+} \\ 1\ M\ \text{HClO}_4}]{} \qquad\downarrow$$

$$\begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} + \text{Cl}^- \\ [M]_{510}\ +1450° \\ \epsilon_{486}\ 122 \end{array} \tag{7}$$

$$\begin{array}{c} \text{rans-}SS\text{-[Co(trien)Cl}_2]\text{ClO}_4 \\ [M]_\text{D}\ +3000° \end{array} \xrightarrow[\substack{1\ M\ \text{HClO}_4,\ 15°}]{\text{Hg}^{2+}\ (2\ \text{equiv})} \begin{array}{c} \text{trans-}SS\text{-[Co(trien)Cl(H}_2\text{O)}]^{2+} \\ [M]_\text{D}\ +3040° \\ \text{(after 6 min)} \end{array}$$

$$\downarrow 15°$$

$$\begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_{510}\ +1500° \end{array} \xleftarrow[1\ M\ \text{HClO}_4]{0.1\ M\ \text{Hg}^{2+}} \begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)Cl(H}_2\text{O)}]^{2+} \\ [M]_\text{D}\ +1600° \\ \text{(after 41 min)} \end{array} \tag{8}$$

$$\begin{array}{c} \text{trans-}SS\text{-[Co(trien)Cl}_2]^+ \\ [M]_\text{D}\ +3000° \end{array} \xrightarrow[1\ M\ \text{HClO}_4,\ 15°]{0.1\ M\ \text{Hg}^{2+}} \begin{array}{c} \text{trans-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_\text{D}\ +750° \\ \text{(after 12 min)} \end{array}$$

$$\substack{\text{Hg}^{2+} \\ \text{(2 equiv)}} \downarrow \substack{1\ M\ \text{HClO}_4 \\ 15°} \qquad\qquad\qquad\qquad \downarrow 15°$$

$$\begin{array}{c} \text{trans-}SS\text{-[Co(trien)Cl(H}_2\text{O)}]^{2+} \\ [M]_\text{D}\ +2930° \\ \text{(after 6 min)} \end{array} \xrightarrow[1\ M\ \text{HClO}_4,\ 15°]{0.1\ M\ \text{Hg}^{2+}} \begin{array}{c} \text{D-}\beta\text{-}SS\text{- + D-}\beta\text{-}SR\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_{510}\ +2275° \\ \text{(after 6 hr)} \\ \epsilon_{487}\ 124 \end{array} \tag{9}$$

$$\begin{array}{c} \text{L-}\beta\text{-}RR\text{-[Co(trien)Cl}_2]^+ \\ [M]_\text{D}\ -900° \end{array} \xrightarrow[1\ M\ \text{HClO}_4]{0.1\ M\ \text{Hg}^{2+}} \begin{array}{c} \text{L-}\beta\text{-}RR\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_\text{D}\ -850° \\ [M]_{510}\ -1420° \end{array}$$

$$0.01\text{--}1.0\ M\ \text{HClO}_4 \downarrow \substack{60\ \text{min} \\ 25°}$$

$$\begin{array}{c} \text{L-}\beta\text{-}RR\text{-[Co(trien)Cl(H}_2\text{O)}]^{2+} \\ [M]_\text{D}\ -1550° \end{array} \xrightarrow[]{0.1\ M\ \text{Hg}^{2+}} \begin{array}{c} \text{L-}\beta\text{-}RR\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_{510}\ -1440° \end{array} \tag{10}$$

$$\text{HCO}_3^- \searrow \qquad \nearrow 2\ M\ \text{HClO}_4$$

$$\begin{array}{c} \text{L-}\beta\text{-}RR\text{-[Co(trien)CO}_3]^+ \\ [M]_\text{D}\ -2950° \end{array}$$

It was established also by the following set of experiments that the D-β-SR-[Co(trien)(H$_2$O)$_2$]$^{3+}$ ion is formed only *via* trans-SS-[Co(trien)(H$_2$O)$_2$]$^{3+}$ (eq 7–9).

The RD curves of the trans-SS-[Co(trien)Cl(H$_2$O)]$^{2+}$, trans-SS-[Co(trien)(H$_2$O)$_2$]$^{3+}$, and D-β-SS-[Co(trien)-Cl(H$_2$O)]$^{2+}$ ions formed in reactions 8 and 9 are given in Figure 7. The *trans* products almost certainly contain some of the β species but they are predominantly as stated (>80%).

Furthermore, it was shown that similar treatment of L-β-RR-[Co(trien)Cl$_2$]ClO$_4$ over the acid range 0.01–1.0 M HClO$_4$ gave no evidence for the formation of the "high-rotation" L-β-RS-[Co(trien)(H$_2$O)$_2$]$^{3+}$ product, and only a single product identical spectrophotometrically and polarimetrically with that obtained from optically pure L-β-RR-[Co(trien)CO$_3$]ClO$_4$ was formed (eq 10).

From the above sequence of experiments (eq 7–10), it is evident that the D-β-SR-[Co(trien)(H$_2$O)$_2$]$^{3+}$ ion is produced only during the isomerization of trans-SS-

[Co(trien)(H$_2$O)$_2$]$^{3+}$. This "high-rotation" D-β-SR form was found to mutarotate completely (>99%) to the "low-rotation" (D-β-SS) isomer

$$\begin{array}{c} \text{D-}\beta\text{-}SR\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \longrightarrow \\ [M]_{510}\ +2750° \end{array}$$

$$\begin{array}{c} \text{D-}\beta\text{-}SS\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} \\ [M]_{510}\ +1400° \end{array} \tag{11}$$

and the rate of this reaction was shown to be acid dependent, Table IV. The optical rotation of the final diaquo product, $[M]_{510}$ +1400–1550°, may be compared with that obtained on acidification of optically pure D-β-SS-[Co(trien)CO$_3$]ClO$_4$, $[M]_{510}$ +1440°, and it should be noted that β-SS-[Co(trien)(OH$_2$)$_2$]$^{3+}$ racemizes too slowly to affect the mutarotation significantly (k_rac = 1.4 × 10^{-6} sec^{-1} in 1.0 M HClO$_4$ at 40°, μ = 1).

The polarimetric rate data for the isomerization of trans-SS-[Co(trien)(H$_2$O)$_2$]$^{3+}$ (Table I) fit the rate law k_obsd = k_1 + k_2/[H$^+$], and the last column in

TABLE II

RATE CONSTANTS FOR THE ISOMERIZATION OF
trans-SS-[Co(trien)(H$_2$O)$_2$]$^{3+}$ IN 1 *M* HClO$_4$ AT 15°
([Co] = 1.33 × 10^{-3} *M*)

[Hg^{2+}],^{a} *M*	μ	10$^4 k_{obsd}$, sec^{-1}
0.1 (p)	1.3	3.3
0.1 (s)	1.3	2.7
0.1 (s)	1.3	3.0
0.5 (s)	2.5	2.5
1.0 (s)	4.0	2.6
0.1 (p)	4.0	2.5

^{a} s = obtained spectrophotometrically at 415 mμ; p = obtained polarimetrically at 510 mμ.

TABLE III

FINAL MOLECULAR ROTATIONS AT 510 mμ FOR THE
ISOMERIZATION REACTION *trans-SS*-[Co(trien)(H$_2$O)$_2$]$^{3+}$ ⟶
D-β-*SS*- + D-β-*SR*-[Co(trien)(H$_2$O)$_2$]$^{3+}$
([Hg^{2+}] = 0.1 *M*)

[H$^+$], *M*	Temp, °C	μ	Time of measurement, min	$-[M]_{510}$, deg M^{-1} cm^{-1} Obsd	Calcd
0.05	15	1.3	26	2700	2700
0.10	15	1.3	38	2720	2640
0.10	8	1.3	95	2750	
0.10	1	1.3	236	2740	
0.3	15	1.3	80	2490	2470
0.5	15	1.3	233	2240	2340
1.0	15	1.3	360	2275	2130
1.0	8	1.3	300	2190	
0.10	15	4.0	130	2030	
1.0	15	4.0	360	1990	
2.0	15	4.0	180	1580	
3.0	15	4.0	100	1490	
3.0	15	4.0	107	1570	
3.0	15	4.0	270	1430	
3.0	15	4.5^a	105	1500	
5.89	15	6.2	50	1580	

^{a} [Hg^{2+}] = 0.5 *M*.

TABLE IV

OBSERVED RATE CONSTANTS FOR THE
D-β-*SR*-[Co(trien)(H$_2$O)$_2$]$^{3+}$ ⟶ D-β-*SS*-[Co(trien)(H$_2$O)$_2$]$^{3+}$
REACTION ([Hg(ClO$_4$)$_2$] = 0.1 *M*, μ = 1.3,
FOLLOWED POLARIMETRICALLY AT 510 mμ)

[H$^+$], *M*	Temp, °C	k_{obsd}, sec^{-1}	k_{calcd},^{a} sec^{-1}
0.05	40.0	1.7 × 10^{-3}	1.7 × 10^{-3}
0.10	40.0	9.2 × 10^{-4}	9.1 × 10^{-4}
	34.3	4.1 × 10^{-4}	
	25.0	8.2 × 10^{-5}	
0.30	40.0	3.9 × 10^{-4}	3.6 × 10^{-4}
1.0	50.0	4.9 × 10^{-4}	
	40.0	1.4 × 10^{-4}	1.7 × 10^{-4}
	34.3	6.5 × 10^{-5}	

^{a} k_{calcd} was obtained from the rate law $k = k'_1 + k'_2/[H^+]$, where k'_1 = 0.83 × 10^{-4} sec^{-1} and k'_2 = 0.83 × 10^{-4} sec^{-1}.

Table I gives values of k_{calcd}, at 15° and an ionic strength of 1.3, using k_1 = 1.33 × 10^{-4} sec^{-1} and k_2 = 1.53 × 10^{-4} sec^{-1}. The agreement obtained and the insensitivity to [H$^+$] for 1.0 ≤ [H$^+$] ≤ 3.0 *M* at the higher ionic strength (μ = 4.0) eliminate the possibility of a term directly proportional to [H$^+$], except possibly at the highest acid strengths. Furthermore, the final product distribution (column 5, Table III) agrees with this rate law where k_1 corresponds to that path leading
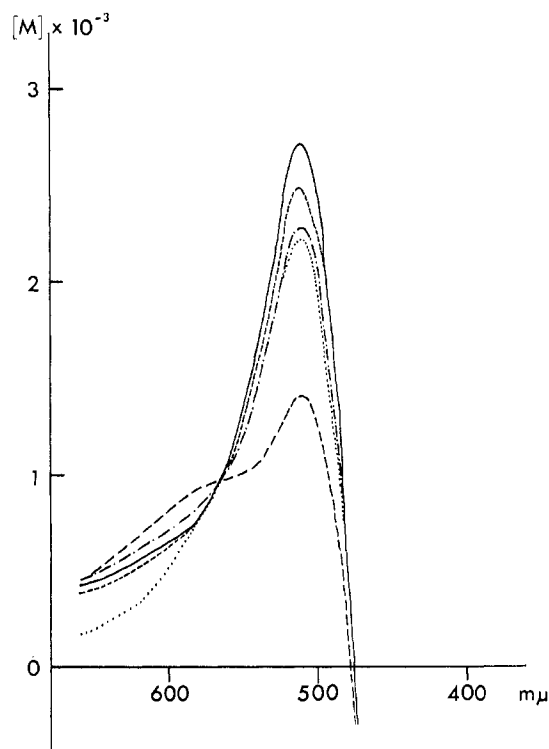
Figure 6.—RD curves for the D-β-*SS*-[Co(trien)(OH$_2$)$_2$]$^{3+}$ and D-β-*SR*-[Co(trien)(OH$_2$)$_2$]$^{3+}$ products of reaction 5 as a function of [HClO$_4$]: 1.0 *M*, – · – ·; 0.1 and 0.05 *M*, ———; 0.3 *M*, – – – –; 0.5 *M*, · · · ·; at μ = 1.3, 15°, and 6$t_{1/2}$. The 0.1 *M* curve (———) mutarotates to the 0.1 *M* curve (— —) at 40°.
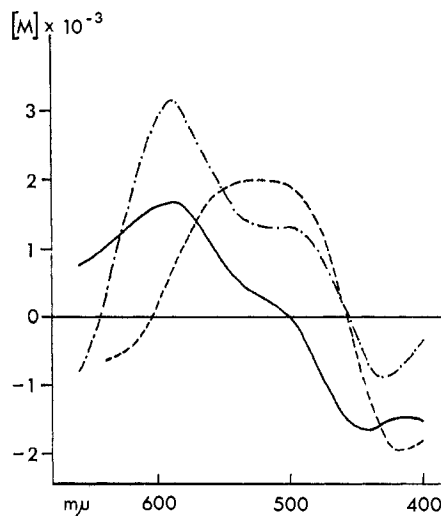
Figure 7.—RD curves of the *trans-SS*-[Co(trien)Cl(OH$_2$)]$^{2+}$ (· – · –), *trans-SS*-[Co(trien)(OH$_2$)$_2$]$^{3+}$ (– – – –), and D-β-*SS*-[Co(trien)Cl(OH$_2$)]$^{2+}$ (———) ions formed in reactions 8 and 9 ([*M*] in deg M^{-1} cm^{-1}).

to the D-β-*SS* isomer and k_2 to that producing D-β-*SR*-[Co(trien)(H$_2$O)$_2$]$^{3+}$. Column 6 of Table III lists [*M*]$_{510}$ values for the final product calculated using the above values of k_1 and k_2 and assuming [*M*]$_{510}$ for the D-β-*SS* and D-β-*SR* isomers are +1400 and +2750°, respectively. However, it is possible that the k_2 path yields a constant ratio of D-β-*SR* and D-β-*SS* isomers which requires [*M*]$_{510}$ for the pure D-β-*SR* isomer to be greater than 2750°. This question has not yet been

resolved, although the magnitude of the rotation suggests that the D-β-SR isomer is by far the largest component.

The temperature dependence of the rate in 0.1 and 1.0 M acid allows a separation of the individual activation parameters for the two paths giving $\Delta H_1^{\ddagger} = 28.0$ kcal mole^{-1} and $\Delta H_2^{\ddagger} = 10.1$ kcal mole^{-1}. The value of $\Delta H_2^{\ddagger}$ has been corrected for ΔH for the dissociation of water.

Similarly, the rate data for the mutarotation of the D-β-SR-[Co(trien)(H$_2$O)$_2$]$^{3+}$ to the D-β-SS isomer (Table IV) fit the rate law $k_{obsd} = k'_1 + k'_2/[H^+]$, and the last column in Table IV gives values of k_{calcd} at 40° and an ionic strength of 1.3 using $k'_1 = k'_2 = 0.83 \times 10^{-4}$ sec^{-1}. The temperature dependence of the rate in 0.1 and 1.0 M acid results in $\Delta H_1^{\ddagger} = 18.9$ kcal mole^{-1} and $\Delta H_2^{\ddagger} = 16.2$ kcal mole^{-1}.

Finally, *trans*-[Co(trien)Cl$_2$]Cl·H$_2$O in the solid state at 90° is converted to pure β-[Co(trien)Cl$_2$]Cl as evidenced by comparisons of infrared[8] and visible absorption[6] spectra. This result is in direct contradiction with the reported conversion of moist β-[Co(trien)-Cl$_2$]Cl·H$_2$O into *trans*-[Co(trien)Cl$_2$]Cl by heating at 180°.[9] We find the latter experiment gives rise chiefly to reduction to cobalt(II). Heating anhydrous *trans*-[Co(trien)Cl$_2$]ClO$_4$ at 110° results in no observable isomerization.

Pmr Studies.—Integration of the NH absorptions for the products of the reactions

$$\textit{trans-}[Co(trien)Cl_2]^+ \xrightarrow[\text{1.8 } M \text{ Hg}^{2+}]{\text{2.2 } M \text{ DClO}_4} \textit{trans-}[Co(trien)(H_2O)_2]^{3+} \quad (12)$$

$$\textit{trans-}[Co(trien)Cl_2]^+ \xrightarrow[5°]{1.5 \times 10^{-8} M \text{ DCl}}$$
$$\beta\text{-}[Co(trien)Cl(H_2O)]^{2+} \quad (13)$$
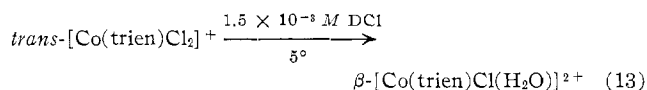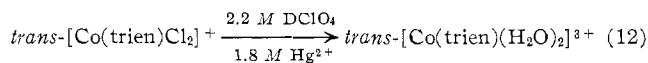
indicated that no significant NH proton exchange occurred during the reactions. However for the reactions

$$\textit{trans-}[Co(trien)(H_2O)_2]^{3+} \xrightarrow[\substack{\text{1.8 } M \text{ Hg}^{2+} \\ \text{20 min, 40°}}]{\text{2.2 } M \text{ DClO}_4}$$
$$\beta\text{-}[Co(trien)(H_2O)_2]^{3+} \quad (14)$$

$$\textit{trans-}[Co(trien)Cl_2]^+ \xrightarrow[\substack{\text{0.38 } M \text{ Hg}^{2+} \\ \text{45 min, 5°}}]{\text{0.1 } M \text{ DClO}_4} \beta\text{-}[Co(trien)(H_2O)_2]^{3+} \quad (15)$$
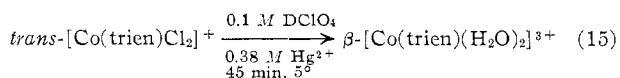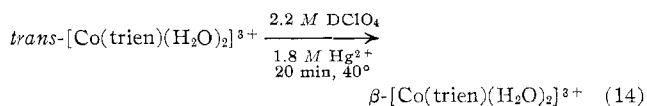
integration of the β-product spectra showed that approximately half of the protons at $\delta = 6.8$ ppm had been lost to the solvent for reaction 14 and all of the protons at $\delta = 6.8$ ppm for reaction 15. An analysis of the rate data for reaction 14 indicated that the partial proton exchange was due to subsequent exchange in the product and not to exchange during the reaction. Conversely, an analysis of the rate data for reaction 15 indicated that N-proton exchange must have occurred during the reaction. For the β-SS-[Co(trien)(OH$_2$)$_2$]$^{3+}$ ion the rate of exchange of the N proton at $\delta = 6.8$ ppm was followed in 1.18 N D$_2$SO$_4$ at 34.3°, $\mu = 4.3$ (Figure 8), and the observed rate constant, $k = 3.8 \times 10^{-4}$ sec^{-1}, was obtained from the linear plot of log (integrated peak) *vs. t*. The enthalpy of activation for
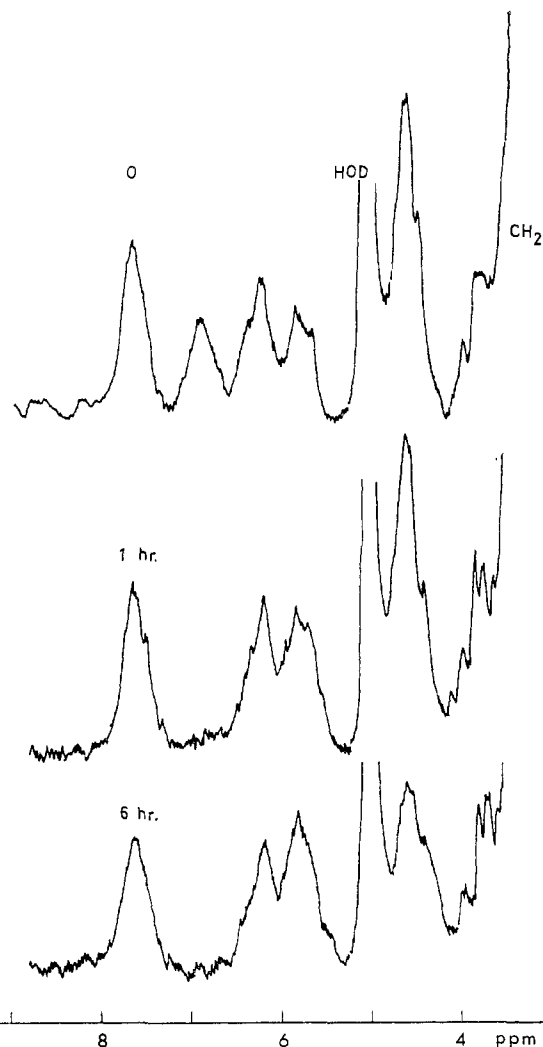
Figure 8.—Rate of N-proton exchange of the β-SS-[Co(trien)-(OH$_2$)$_2$]$^{3+}$ ion followed by pmr in 1.18 N D$_2$SO$_4$.

NH exchange in cobalt(III) complexes has been found to be remarkably constant,[1-3] 28 ± 1 kcal mole^{-1}, and this value was used to estimate the rates at different temperatures. One of the two N protons at 4.6 ppm also exchanges with the solvent under the conditions used above with a rate constant $k = 3.3 \times 10^{-5}$ sec^{-1}.

Discussion

The isolation of the optically active forms of the *trans*-[Co(trien)Cl$_2$]$^+$ ion allows a description of the configurations of these ions in some detail. Both the configurations about the sec-N atoms in each ion must be the same and the conformation of the central ring must be *gauche, i.e., k'* or *k*.[10] The conformations of the terminal rings are not so clearly indicated, although a distorted *gauche* form appears to be favored. The conformational arrangement follows from the stereochemistry about the sec-N atoms and the properties of these asymmetric N centers is therefore relevant. They have been discussed in detail elsewhere[1,2] and briefly in the Introduction, where it was inferred that in acid solutions the proton remains intact. It follows

(8) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).
(9) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963).

(10) For nomenclature see E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

that under these conditions the asymmetric N centers are akin to asymmetric carbon atoms in fused-ring alicyclic systems and should exert a directing influence on the stereochemistry of the reactions of the complexes. For example, for *trans-SS*-[Co(trien)X₂]⁺ to racemize to the *trans-RR*-[Co(trien)X₂]⁺ ion it is necessary that both *sec*-NH groups exchange their protons and invert, presumably through the *meso* form as an intermediate. In this context the acid hydrolysis of *trans*-[Co(trien)-Cl₂]⁺ was reexamined with the optically active isomer.

It was shown previously[7] that *trans*-[Co(trien)Cl₂]⁺ aquated stereospecifically to β-[Co(trien)ClOH₂]²⁺ and that the aquation rate was synchronous with the rearrangement. Moreover, it was shown that *trans*-[Co(trien)ClOH₂]²⁺ did not isomerize fast enough to be involved as a labile intermediate. Also it was argued that the reaction of Hg²⁺ ion with the *trans*-[Co(trien)Cl₂]⁺ ion gave a five-coordinate intermediate which reacted with solvent to give predominantly *trans*-[Co(trien)ClOH₂]²⁺. Considerable evidence has now been collected to show that the Hg²⁺ ion does produce intermediates of the nature proposed.[11-15] The elimination of these possible routes for the rearrangement led to the conclusion that H₂O was actively involved in bond making at an octahedral face in the normal aquation and that isomerization was effected by an edge displacement reaction of the type shown in Figure 9.

The alternative to this SN2 mechanism is that a five-coordinate intermediate different from that formed by the induced aquation with Hg²⁺ ion leads exclusively to β-[Co(trien)ClOH₂]²⁺. An objection to the alternative however arises from the fact that in the uncatalyzed aquation reactions anions do not compete for the possible intermediate,[16] whereas in the induced aquations anated products appear synchronously with the aquo product, for a variety of anions.[11,14] In short, the bulk of evidence favors at least some bond making by water in the normal aquation reactions.

In relation to the present study the SN2 mechanism requires that only one possible isomer form, since the optically active N center drives the bridge in one direction, provided proton exchange does not occur at the *sec*-N atom. Experimentally it was shown that (+)₅₈₉-*trans*-[Co(trien)Cl₂]⁺ gave (+)₅₈₉-β-[Co(trien)-ClOH₂]²⁺ optically pure and that isomerization was independent of the planar *sec*-N proton exchange. This result is significant because it not only bears out the foregoing arguments but it allows a more detailed description of the *trans*- and β-chloroaquo configurations.

The absolute configuration of the (+)₅₈₉-β-[Co(trien)-ClOH₂]²⁺ ion has been evaluated previously[6] as that in Figure 9b and it is required from the present results that the proton on the "planar" *sec*-N be directed up

(11) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).
(12) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).
(13) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).
(14) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *ibid.*, **6**, 1027 (1967).
(15) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, to be published.
(16) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).
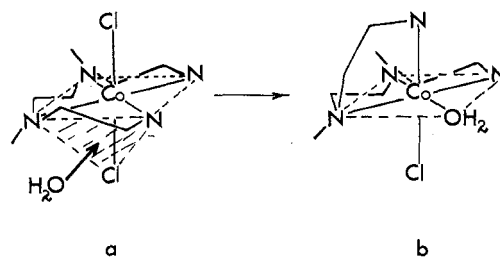
Figure 9.—SN2 mechanism for the aquation and isomerization of the (a) *trans*-[Co(trien)Cl₂]⁺ ion to (b) β-[Co(trien)ClOH₂]²⁺.

toward the apical bridge. The β-chloroaquo ion produced from the aquation of *trans*-dichloro ion has the same spectrum and RD curve as that obtained by aquating (+)₅₈₉-β-[Co(trien)Cl₂]⁺ and it follows[7] that the (+)₅₈₉-*trans*-[Co(trien)Cl₂]⁺, (+)₅₈₉-β-[Co(trien)-Cl₂]⁺, (+)₅₈₉-β-[Co(trien)ClOH₂]²⁺, (+)₅₈₉-β-[Co-(trien)(OH₂)₂]³⁺, (+)₅₈₉-β-[Co(trien)CO₃]⁺, and (+)₅₈₉-β-[Co(trien)(NO₂)₂]⁺ ions all have the same configurations about the *sec*-N atoms, namely *SS*. This argument requires the absolute configuration of (+)₅₈₉-*trans*-[Co(trien)Cl₂]⁺ to be that shown in Figure 9a. Also the configurations described above are the most stable since the resolved β-[Co(trien)CO₃]⁺ ion prepared under conditions where the N protons exchange rapidly gave β-[Co(trien)(OH₂)₂]³⁺ with the same RD curve and spectrum as that prepared from β-[Co(trien)ClOH₂]²⁺ (obtained from *trans*-[Co(trien)-Cl₂]⁺ and also from β-[Co(trien)Cl₂]⁺) with Hg²⁺. In addition a conformational analysis has been carried out for the two orientations of the proton in the β-[Co-(trien)X₂]ⁿ⁺ complex.

An examination of the Dreiding stereo models shows that there is a substantial difference in the orientation of the protons on the chelate rings in the two forms and the difference is reflected in the calculated conformational energy difference of 3.0 kcal mole⁻¹ in favor of the D-β-*SS* isomer, Figure 10A, over the D-β-*SR* isomer, Figure 10B, where X = Cl. In arriving at this value all H–H, C–H, N–H, C–C, C–N, and H–Cl interactions were considered. The H–Cl interactions were attractive and equal in the two structures considered and therefore do not contribute to the energy difference. It is also probable that the same situation pertains for other substituents such as H₂O, Br, CO₃, and NO₂ and that Figure 10A is for practical purposes formed exclusively. The following interactions (distances in Ångstroms) were found the most significant: Figure 10A: H₈–C₂ (2.4); Figure 10B: H₁–H₁₃ (1.8), H₁–H₁₀ (1.8), H₅–H₈ (1.8), H₈–C₂ (2.4), H₅–C₃ (2.4). The configurations in Figure 10 were chosen for the analysis as those with the maximum distances between the most significant nonbonding interactions, and the expression derived by Hill[17] was used to calculate the interaction energies.

The isomerization of *trans-SS*-[Co(trien)(H₂O)₂]³⁺ in acid solution gives rise to a mixture of D-β-*SS*- and D-β-*SR*-[Co(trien)(H₂O)₂]³⁺ products, with the rate and product distributions being both acid and ionic strength dependent (Table III). The D-β-*SR* isomer is

(17) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

Figure 10.—Configurations of the (A) D-β-*SS*- and (B) D-β-*SR*-[Co(trien)X₂]ⁿ⁺ isomers used in the conformational analysis calculations.

favored at low acid concentrations and low ionic strengths. Temperature or Hg^{2+} concentration has little effect on the product distribution. The absorption spectra of the products show no dependence on [H^+] and show that little or no α-[Co(trien)(H₂O)₂]³⁺ is formed (for α-[Co(trien)(H₂O)₂]³⁺ ϵ_{500} is 87 and for β-[Co(trien)(H₂O)₂]³⁺ ϵ_{487} is 122). Furthermore, if some α-diaquo product was formed in the isomerization, this would necessarily be L-α-*SS*-[Co(trien)(H₂O)₂]³⁺ leading to a decrease in optical activity at 510 mμ.[7] The observed large increase over that for the D-β-*SS* isomer at this wavelength and the very much slower rate of isomerization[18] of α-[Co(trien)(H₂O)₂]³⁺, when compared with the mutarotation rates observed here (Table IV), also eliminate the possibility of α-diaquo participation.

The above data are in agreement with the reaction scheme given in Figure 11, where k_1 governs that path leading to the formation of D-β-*SS*-[Co(trien)(H₂O)₂]³⁺ with retention of configuration at the N centers and k_2 governs the base-catalyzed path leading to the D-β-*SR* isomer with inversion of configuration about the "planar" N atom. The D-β-*SR* isomer then mutarotates to the thermodynamically more stable D-β-*SS* isomer by both acid-independent and base-catalyzed paths. Figure 12 shows RD curves for the D-β-*SS* and D-β-*SR* configurations.

Although the sequence of events in the isomerization is clear, the mechanism for the formation of the two diaquo isomers is less apparent. It seems reasonable however that the acid-independent path is associated with the water-exchange process in a manner similar to that found[19] for the *trans* → *cis* isomerization of [Co(en)₂(OH₂)₂]³⁺, especially since the isomerization by this path does not lead to inversion at either of the *sec*-N atoms and the N proton does not exchange. The base-catalyzed path however does lead to inversion at one of the *sec*-N atoms and it is likely therefore that this path arises by extracting the proton from the
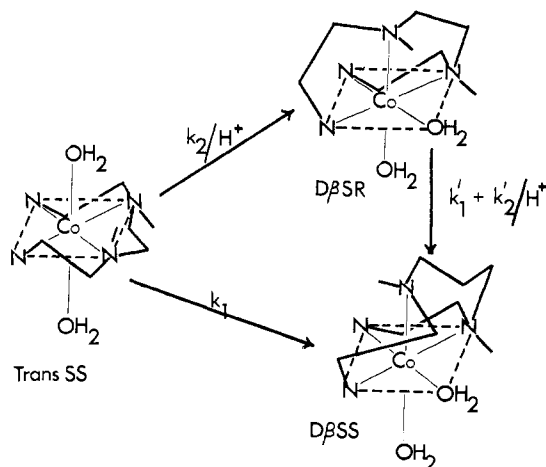

Figure 11.—Reaction scheme for the isomerization of the *trans*-*SS*-[Co(trien)(OH₂)₂]³⁺ ion.
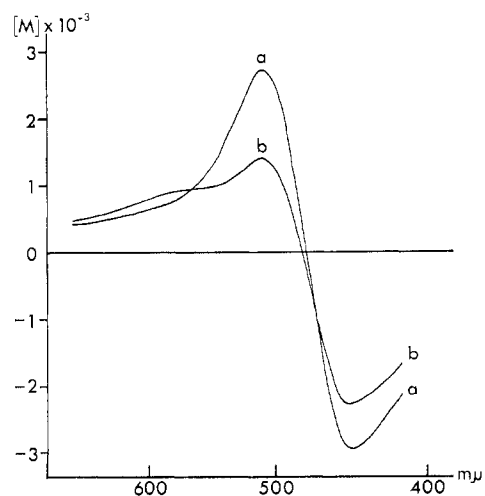
Figure 12.—RD curves for the (a) D-β-*SR*-[Co(trien)(OH₂)₂]³⁺ and (b) D-β-*SS*-[Co(trien)(OH₂)₂]³⁺ ions.

sec-N atom with OH⁻. The pmr spectra showed that the proton exchange at the *sec*-N atoms was not rapid ($k < 10^{-3}$ M^{-1} sec⁻¹ at 40°, $k < 4 \times 10^{-6}$ M^{-1} sec⁻¹ at 5°) for the *trans*-[Co(trien)(OH₂)₂]³⁺ ion, and also

(18) A. M. Sargeson and G. H. Searle, to be published.
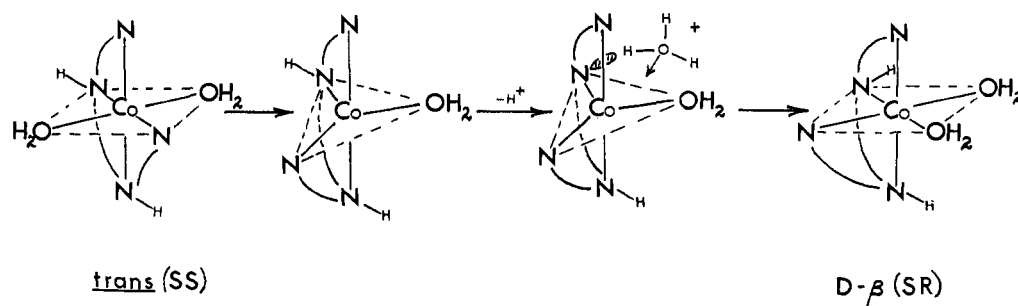(19) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

Figure 13.—Possible mechanism of isomerization of the *trans-SS*-[Co(trien)(OH₂)₂]³⁺ ion to the D-β-SR-[Co(trien)(OH₂)₂]³⁺ ion involving a five-coordinate intermediate

no detectable racemization was observed for this complex. The implication of all this rationale is that water exchange in the *trans*-diaquo ion is faster than the inversion process and it is tempting to suggest that the D-β-*SR* isomer arises by proton abstraction from a five-coordinate intermediate followed by addition of H_3O^+ to give the diaquo ion, Figure 13. Intermediates of this nature have been proposed[19] for the isomerization in the [Co(en)₂(OH₂)₂]³⁺ system, but as yet there is no proof of their existence.

The complete mutarotation of D-β-*SR*- to D-β-*SS*-[Co(trien)(OH₂)₂]³⁺ is consistent with the conformational analysis of the β-[Co(trien)X₂]ⁿ⁺ systems since the 3-kcal mole⁻¹ difference calculated between the two conformational forms requires essentially complete mutarotation. The mutarotation also involves an acid-independent and an inverse [H⁺] path, but the rates are much slower than the isomerization of *trans* → β. Since both paths lead to inversion at the N center, it is proposed that the N proton is abstracted by both H_2O and OH^- in this reaction. Although N–H

exchange effected by H_2O has not been observed before for cobalt(III) complexes, it does occur in the simple amines and quaternary ammonium salts. It should be noted however that this cobalt(III) complex has a considerably more labile N proton than those examined previously[1-3] and presumably is more acidic.

This preliminary analysis of the data obviously depends acutely on the water-exchange rates in the *trans*- and β-diaquo isomers and these are at present being examined along with additional N-proton magnetic resonance data. It is also obvious that these results have some bearing on the mechanism of racemization of α- and β-[Co(trien)(OH₂)₂]³⁺ ions, and both of these aspects will be discussed in detail in subsequent communications.