tet would result if the two triplets overlap, which in turn would occur if $J(CH_2-CH_2) = J(CH_2-NH)$. Since the broad N-H··O resonance in Bz(tri) (τ -1.39) shows no splitting, this hypothesis is not verifiable from the spectrum of this compound. In the spectrum of the Bz 1,3-diiminopropanol-2 (no. 24), however, the N-H··O resonance appears at τ -1.43 as a triplet (J = 5.5 cps) owing to coupling with the bridge methylene groups. In this compound the CH_2 resonance is also a normal triplet (J = 5.7 cps), and the bridge CH resonance seems to be the expected quintet ($J \sim 5.5$ cps). Accordingly, we may assume that the CH_2 signal is split into a doublet by both the NH and the CH protons and that the two doublets approximately overlap to give a 1:2:1 triplet, since all of the coupling constants are so nearly the same. Treatment of a $CDCl_3$ solution of this compound with two portions of D_2O caused complete deuteration of the N-H··O proton, as evidenced by the disappearance of the absorption peak. The signal for the terminal CH_2 groups of the bridge was now split only by the adjacent CH proton, and the resulting unsymmetrical doublet (J = 5.6 cps) appeared at the same position as the triplet in the nondeuterated compound.

N-H··O Resonance.—All of the Schiff base ligands investigated appear to be almost completely enolized in $CDCl_3$ solution. All show a broad band at about τ -0.8 to -1.7 owing to the N-H··O proton. In some cases the band is featureless, but in others splitting is clearly discernible, and in a few cases the splitting is clear enough to enable the coupling constant to be determined accurately (see Figure 1b). Undoubtedly the explanation of the splitting offered by Dudek and Holm[2] is the correct one, namely, that the enol proton is directly attached to the nitrogen and the splitting is due to coupling with the bridge protons. In acetylacetone the O-H··O resonance appears at τ -5.29. The shift to lower field compared with the resonance of N-H··O may be another indication of better resonance in the symmetrical acetylacetonate ring.

Acknowledgment.—The authors wish to thank Professors David Todd and Ichiro Murase and Mr. Edward Maslowsky for the preparation of several of the compounds used. Thanks are also due to Professor James Van Verth and Dr. James Colson for many helpful discussions, and also to the latter for running a spectrum at 100 Mcps.

CONTRIBUTION FROM THE BIOLOGICAL INORGANIC CHEMISTRY UNIT, JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA

The Stereochemistry and Preparation of Triethylenetetramine-Disubstituted Cobalt(III) Complexes

BY A. M. SARGESON AND G. H. SEARLE

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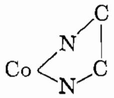
The preparation and resolution of some of the *cis*- and *trans*-$[Co(trien)X_2]^{n+}$ isomers [trien = triethylenetetramine; X = Cl, OH_2, NO_2; 2X = CO_3] are described. The relative stabilities and stereochemical detail are discussed in terms of the directing influences prescribed by the secondary NH groups and the nonbonding interactions between the possible conformers.

Introduction

Although some work has been carried out on the preparation of cobalt(III) triethylenetetramine compounds,[1-4] little is known about the detailed structures of the complexes isolated. This paper concerns the preparation and isolation of isomers of several disubstituted cobalt(III) trien complexes and the assignment of their stereochemical form. It will be followed by papers describing the reactivity of the isomers.

The possible modes of wrapping the triethylenetetramine ligand ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2$-$NH_2$ = trien) about a cobalt(III) ion are given in Figure 1. However, in addition to these topological isomers, several isomeric possibilities arise from the manner in which the secondary N atoms coordinate. For example the *trans*-$[Co(trien)X_2]^{n+}$ ion has three possible forms, Figure 2. All three conformations and configurations may be stable in slightly acidic solutions as interconversion and conformational interchange cannot occur in the *l*-, *d*-, and *meso-trans* isomers unless the secondary N protons dissociate. The *meso* configuration requires at least the central coordinated en unit to be in the envelope conformation



which is observed in some cyclopentane systems but which is not common in M-en chelates. The optically active *trans* isomers however have the usual staggered arrangement of the Co-en rings. Recently the active *trans* isomer has been prepared and its optical proper-

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

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

(3) B. Das Sarma and J. C. Bailar, *J. Am. Chem. Soc.*, **77**, 5480 (1955).

(4) J. Selbin and J. C. Bailar, *ibid.*, **82**, 1524 (1960).

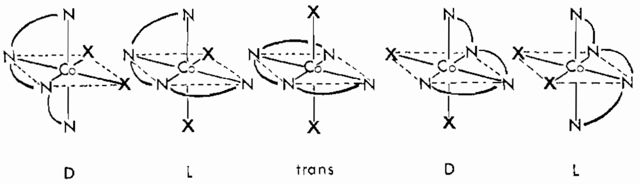

Figure 1.—The modes for coordinating triethylenetetramine about the Co(III) ion.

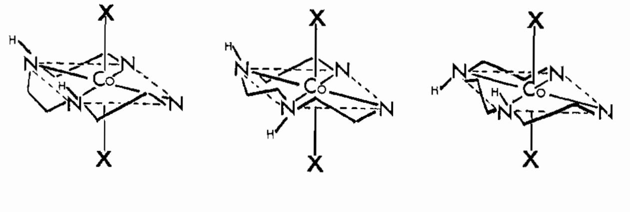
meso d l

Figure 2.—The possible isomers for *trans*-[Co(trien)X_2]$^+$.

ties and reactivities will be described in a subsequent communication.[5] The relative stability of the active and the *meso* forms has not yet been established however.

The optical stability and properties of asymmetric coordinated N atoms where one of the substituents is a proton have been examined recently.[6,7] In acid solution the rates of NH exchange with solvent protons in aqueous solution are slow and the protons can be rendered essentially inert to exchange. The significance of these properties is that the N atom in these fused-ring coordination compounds becomes analogous to asymmetric C atoms in fused-ring alicyclic chemistry since it can introduce further isomerism and may direct the stereochemistry of rearrangements during reactions which the ions may undergo. This is a general principle and should have a wide application to multidentate amine complexes of the type under discussion. For example, it introduces another isomer to the [Co(dien)$_2$]$^{3+}$ system. The form where the three dien N atoms are in the same plane, Figure 3a, should exist in *d* and *l* forms by virtue of the orientation of the secondary N protons whereas Figure 3b has a plane of symmetry and Figure 3c is asymmetric by virtue of the topological arrangement of the tridentates. A simple method now arises for distinguishing the three isomers: that of Figure 3a should racemize in dilute OH^- and that of Figure 3c should be optically stable.

Similarly, the β-[Co(trien)X_2] systems have two possible arrangements for one secondary N atom (Figure 4a and b) while the other secondary N atom has the normal trigonal arrangement, which is forced by the orientation of the C substituents and the Co(III) ion; both of these forms have been detected for the β-[Co(trien)(H_2O)$_2$]$^{3+}$ system and will be discussed in a subsequent paper.[5]

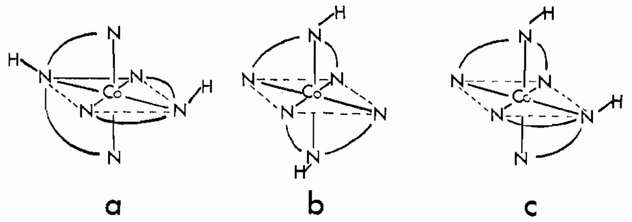
a b c

Figure 3.—Isomeric forms of the bis(diethylenetriamine)cobalt(III) ion.

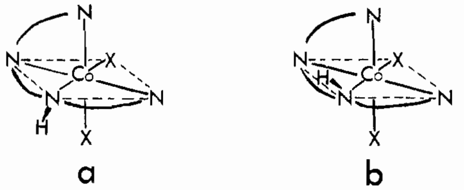
a b

Figure 4.—Internal diastereoisomeric forms of L-β-[Co(trien)X_2]$^+$.

It is not known yet if there is any strain involved in the planar form of dien or trien. If it exists, it is partly alleviated by adjusting the Co–en ring conformations and evidence will be presented to show it is not a dominating influence in determining the stability of the *cis* isomers. In the present series of complexes only one β isomer appears to obtain which our conformational studies suggest is the form in Figure 4b where there is a minimum of nonbonded interaction between the CH protons on different rings and between the terminal NH and the CH protons on the rings in the same plane. A preliminary crystal structure report on β-[Co(trien)CO_3]ClO_4 outlines the β arrangement of the trien skeleton, but it is not refined sufficiently to allow a description of the secondary NH orientation.[8]

The α-[Co(trien)X_2]$^{n+}$ complexes can exist in only one D or one L form since the trigonal stereochemistry of the N atoms in this instance is fixed by the bonding of the terminal NH_2 groups in the 1 and 6 positions.

The experimental results for the preparation and properties of the isomers are now considered in detail for each system.

Experimental Section

Triethylenetetramine (from Carbide and Carbon Chemicals Co., New York, N.Y.) was used without further purification.

Ultraviolet and visible spectra were measured on a Shimadzu RS-27 recording spectrophotometer in 1-cm cells, against water as reference. Dichloro compounds were dissolved in ice-cold 0.01 *N* $HClO_4$ solution, and the spectra were recorded as soon as possible (2–3 min). Chloroaquo spectra were measured after the above solutions had aquated for the appropriate times. Diaquo compounds were measured in 0.01 *N* $HClO_4$ or obtained by dissolving the corresponding carbonato isomers in 0.1 *N* $HClO_4$. Carbonato and dinitro spectra were measured in water.

Infrared spectra were obtained over the NaCl region using a Unicam SP-200 double-beam infrared spectrometer. The KBr-disk method was employed for all spectral runs (1 mg of sample in 200 mg of KBr) with either air or a KBr disk in the reference beam.

Samples of the optically active isomers of [Co(trien)(NO_2)$_2$]ClO_4 were deuterated by recrystallization from D_2O (99.7%). The fine structures of the ND absorptions (~2400 cm^{-1}) were

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(5) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, in press.

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

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

(8) B. F. Hoskins, unpublished work.

measured on a Perkin-Elmer 112 single-beam spectrophotometer fitted with an LiF prism and calibrated with HBr gas.

Optical rotations were measured visually with a Bellingham and Stanley polarimeter or a Perkin-Elmer 141 spectropolarimeter in a 1-dm tube at 20° unless otherwise stated. The sign of rotation is described as (+) or (−) for the sodium D line or as $(+)_\lambda$ or $(-)_\lambda$ where λ represents another wavelength used.

***cis*-α-Dinitro(triethylenetetramine)cobalt(III) Chloride Monohydrate.**—Ice-cold solutions of trien·HCl (75 ml in 44 ml of 11.6 *N* HCl) and $CoCl_2\cdot 6H_2O$ (119 g in 100 ml of water) were mixed and added quickly to solid $NaNO_2$ (72.5 g). The mixture was aerated vigorously and the yellow *cis*-dinitro salt commenced to separate (2 min). Aeration was continued for 1.5 hr at 0°. The product was filtered, washed with ice-cold hydrochloric acid (1 *N*), alcohol, and acetone, and air dried; yield, 100 g, 57%.

Additional dinitro product was obtained as the iodide monohydrate by adding excess sodium iodide to the solution; yield, 30 g, 13%.

When the chloride was fractionally recrystallized from hot water (90°), the least soluble material (86 g) was shown to be the *cis*-α isomer. The next fractions (8.3 g), obtained by evaporation of the mother liquor in a stream of air over a steam bath, contained appreciable amounts of the *cis*-β isomer.

The corresponding *cis*-α-dinitro bromide, nitrate, and acetate may be prepared in a similar manner by using the respective cobalt(II) salts and acids. Varying the order of mixing the three constituents, the presence of charcoal, longer aeration times, the presence of a large excess of the respective anion (*i.e.*, NaBr in the preparation of the bromide), or the use of trien·HOAc and excess LiCl to replace trien·HCl in the preparation of the chloride gave no significant improvements in yield.

The analogous preparation of $[Co(trien)(NO_2)_2]ClO_4$ from $Co(ClO_4)_2$ solution (11.9 g of $CoCO_3$ in 206 ml of 1.0 *N* $HClO_4$ evaporated to 50 ml over a steam bath), $[trien\cdot H]ClO_4$ (15 ml in 50 ml of water and 33 ml of 3.1 *N* $HClO_4$), and $NaNO_2$ (14.6 g) also gave a mixture of α and β isomers; yield, 31 g, 77%. Here the order of solubilities was reversed; on fractional recrystallization the least soluble material (2.4 g) was largely the β isomer. The perchlorate was converted to the triiodide by adding excess NaI, 1 drop of glacial acetic acid, and hydrogen peroxide dropwise. A suspension of the triiodide in ethanol was reduced to the iodide with sulfur dioxide. The iodide was converted to the dinitro chloride solution by grinding with AgCl in a little water. *Anal.* Calcd for *dl*-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]Cl\cdot H_2O$: C, 20.54; H, 5.71; N, 23.97. Found: C, 20.65; H, 5.88; N, 23.61. Calcd for *dl*-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]I\cdot H_2O$: C, 16.30; H, 4.52; N, 19.00. Found: C, 16.74; H, 4.64; N, 18.90. Calcd for *dl*-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]Br\cdot H_2O$: C, 18.23; H, 5.06; N, 21.27. Found: C, 18.30; H, 5.03; N, 21.23. Calcd for *dl*-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]NO_3$: C, 20.06; H, 5.05; N, 22.47. Found: C, 20.17; H, 5.36; N, 27.41. Calcd for *dl*-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]ClO_4$: C, 18.17; H, 4.56; N, 21.19. Found: C, 18.26; H, 4.54; N, 20.90.

Resolution of *cis*-α-Dinitro(triethylenetetramine)cobalt(III) Chloride.—To an aqueous solution of *cis*-α-$[Co(trien)(NO_2)_2]Cl\cdot H_2O$ (2.0 g in 30 ml) at 35°, $Na(-)[Co(en)(C_2O_4)_2]\cdot H_2O$ (1.0 g) was added gradually, and red-brown (+)*cis*-α-$[Co(trien)(NO_2)_2](-)[Co(en)(C_2O_4)_2]\cdot H_2O$ commenced to separate immediately. This was filtered after 5 min, washed with small volumes of iced water, alcohol, and acetone, and air dried; yield, 1.3 g, 75%. *Anal.* Calcd for (+)*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2](-)[Co(C_2H_8N_2)(C_2O_4)_2]\cdot H_2O$: C, 23.61; H, 4.62; N, 18.36. Found: C, 23.76; H, 4.54; N, 18.36.

The diastereoisomer was ground with excess NaI (added gradually) in sufficient water to give a mobile slurry. Yellow (+)*cis*-α-$[Co(trien)(NO_2)_2]I\cdot H_2O$ separated and was filtered, washed with ice-cold NaI solution, alcohol, and acetone, and air dried. A 0.32% aqueous solution gave α_{546} +0.15° whence $[\alpha]_{546}$ +47°. *Anal.* Calcd for (+)-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]I\cdot H_2O$: C, 16.30; H, 4.56; N, 19.01. Found: C, 16.40; H, 4.86; N, 18.78.

The (−) isomer was fractionally precipitated from the filtrate as iodide or bromide by gradually adding NaI or NaBr, respectively. The least soluble fractions were optically pure for the iodide, $[\alpha]_{546}$ −50°, and for the bromide, $[\alpha]_{546}$ −55°. *Anal.* Calcd for (−)-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]I\cdot H_2O$: C, 16.30; H, 4.56; N, 19.01. Found: C, 16.24; H, 4.97; N, 18.85. Calcd for (−)-*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]Br\cdot H_2O$: C, 18.24; H, 5.10; N, 21.27. Found: C, 18.40; H, 5.01; N, 21.04.

Racemic *cis*-α-$[Co(trien)(NO_2)_2]^+$ nitrate and acetate were resolved in the same manner as the chloride. The iodide and bromide were too insoluble to be resolved directly and were first converted to the acetate by shaking with a slight deficiency of silver acetate in aqueous solution.

Optical isomers (+)- and (−)*cis*-α-$[Co(trien)(NO_2)_2]^+$ iodide or bromide were fractionally recrystallized from hot water (90°) without racemization. The least soluble fractions were optically pure. The perchlorates of the optical isomers were obtained as fine yellow needles by fractional precipitation with $NaClO_4$ from a solution of active chloride ($[\alpha]_{546}$ ±50°). *Anal.* Calcd for (+)*cis*-α-$[Co(C_6H_{18}N_4)(NO_2)_2]ClO_4$: C, 18.17; H, 4.56; N, 21.19. Found: C, 18.02; H, 4.66; N, 20.7.

***cis*-α-Dichloro(triethylenetetramine)cobalt(III) Chloride.**—A mixture of *cis*-α-$[Co(trien)(NO_2)_2]Cl_2\cdot H_2O$ (97 g in 100 ml of water) and excess HCl (70 ml of 11.6 *N*) was evaporated on a steam bath to dryness (overnight). The purple product was ground in ethanol, filtered, washed with ethanol and acetone, and air dried. The yield of mixed α- and β-$[Co(trien)Cl_2]Cl$ was theoretical (86 g).

The method described by Basolo,[1] aeration of a mixture of triethylenetetramine and excess $CoCl_2$, followed by addition of 10 *N* HCl and evaporation of the solution, gave a crude product which was blue rather than violet. The blue color was probably due to the anion $[CoCl_4]^{2-}$ and was difficult to remove by recrystallization. In Basolo's method, as evaporation proceeded and successive crops of crystals were filtered, the mother liquor became dark olive-green. However, the addition of $LiClO_4$ did not precipitate *trans*-$[Co(trien)Cl_2]ClO_4$.

The product was dissolved in the minimum volume of boiling 3 *N* HCl, filtered through a sintered-glass filter, and allowed to stand in a refrigerator. The crystals were filtered off, washed with ice-cold HCl (1 *N*), alcohol, and acetone, and air dried. Two recrystallizations gave the pure *cis*-α isomer (solubility *ca.* 2.6 g/100 ml). *Anal.* Calcd for *cis*-α-$[Co(C_6H_{18}N_4)Cl_2]Cl$: C, 23.11; H, 5.78; N, 17.98. Found: C, 23.10; H, 5.81; N, 17.75.

Resolution of *cis*-α-Dichloro(triethylenetetramine)cobalt(III) Chloride.—The resolution was carried out in slightly acid solution to suppress hydrolysis. A saturated solution of twice-recrystallized *cis*-α-$[Co(trien)Cl_2]Cl$ (28 g) was made by shaking the complex with 800 ml of acetic acid solution, pH 3, at room temperature for 2 min. The undissolved material (8.1 g) was filtered off. $Na(+)[Co(en)(C_2O_4)_2]\cdot H_2O$ (11.2 g) was then added and the solution was stirred and the beaker scratched with a glass rod. The red-violet diastereoisomeric salt (−)-*cis*-α-$[Co(trien)Cl_2](+)[Co(en)(C_2O_4)_2]\cdot H_2O$ began to separate immediately and was filtered after 5 min, washed with methanol and acetone, and air dried. It was quite insoluble and could not be recrystallized. The yield was not improved by working at lower temperatures nor by allowing the solution to stand for a longer time; yield, 15.3 g, 81%. The specific rotations were: $[\alpha]_D$ −1050° (α_D −0.43° for a 0.0408% solution in 0.01 *N* $HClO_4$), $[\alpha]_{578}$ −1590° (at this wavelength the resolving agent has nearly zero rotation). *Anal.* Calcd for (−)*cis*-α-$[Co(C_6H_{18}N_4)Cl_2](+)[Co(C_2H_4N_2)_2(C_2O_4)_2]\cdot H_2O$: C, 24.44; H, 4.75; N, 14.25. Found: C, 24.57; H, 4.92; N, 14.34.

(−)*cis*-α-Dichloro(triethylenetetramine)cobalt(III) Iodide Hemihydrate.—The diastereoisomeric salt was ground (twice) in an ice-cold mortar with NaI (excess) and a little ice-cold water containing 1 drop of glacial acetic acid. The slightly soluble $(-)[Co(trien)Cl_2]I$ was filtered off, washed with ice-cold NaI solution, alcohol, and acetone, and air dried. The grinding of the slurry was carried out as quickly as possible.

The $(-)[Co(trien)Cl_2]I$ was converted to the chloride by shaking it vigorously with excess AgCl in water containing a drop of acetic acid. AgI was filtered off and the *cis*-α isomer was fractionally crystallized as the iodide or perchlorate by adding NaI or $NaClO_4$. Both iodide and perchlorate crystallized as deep violet needles and the optical forms were less soluble than the racemates.

Alternatively, the iodide was transformed to the acetate by shaking it vigorously for 3 min with a slight deficiency of silver acetate in a small volume of ice water containing 1 drop of acetic acid. AgI was filtered off and the iodide or perchlorate fractionally crystallized as before.

The maximum rotations were: iodide, $[\alpha]_D$ +2100, −2130° (α_D = −1.06° for 0.05% solution in acetic acid), $[\alpha]_{578}$ +2320, −2340°; perchlorate, $[\alpha]_D$ +2330, −2350° (α_D +0.93° for a 0.04% solution in acetic acid). *Anal.* Calcd for *cis*-α-$[Co(C_6H_{18}N_4)Cl_2]I\cdot 0.5H_2O$: C, 17.52; H, 4.61; N, 13.59. Found (for (+) isomer): C, 17.48; H, 4.59; N, 13.28. Found (for (−) isomer): C, 17.59; H, 4.59; N, 13.59. Calcd for *cis*-α-$[Co(C_6H_{18}N_4)Cl_2]ClO_4$: C, 19.16; H, 4.82; N, 14.91. Found (for (+) isomer): C, 19.06; H, 4.75; N, 14.55. Found (for (−) isomer): C, 19.38; H, 4.81; N, 14.80. Active *cis*-α-$[Co(trien)Cl_2]I$ was converted to the perchlorate by grinding twice in an ice-cold mortar with a little water containing 1 drop of acetic acid and excess $NaClO_4$.

In another resolution the diastereoisomeric salt (15.3 g) was ground twice in an ice-cold mortar with a little water containing 1 drop of 5 *N* $HClO_4$ and excess $NaClO_4$ (added in small portions). The (−)-*cis*-α-$[Co(trien)Cl_2]ClO_4$ which crystallized was filtered, washed with ice-cold $NaClO_4$ solution, methanol, and ether, and air dried; yield, 10.3 g. The following rotations were observed: $[\alpha]_D$ −1780° (α_D −0.73° for a 0.0411% solution in 0.01 *N* $HClO_4$), $[\alpha]_{578}$ −2030° (76% optically pure).

(+)*cis*-α-Dichloro(triethylenetetramine)cobalt(III) Perchlorate.—The remaining antimer (+)-*cis*-α-$[Co(trien)Cl_2]Cl$ and excess resolving agent were totally precipitated from the filtrate by adding a large excess of acetone (10 l.). This product was ground with $HClO_4$ and $NaClO_4$ as described for the diastereoisomer, and the (+)*cis*-α-$[Co(trien)Cl_2]ClO_4$ was filtered off; yield, 10.3 g, 86%; $[\alpha]_D$ +1790°, $[\alpha]_{578}$ +2090°.

The (+) isomer could not be precipitated from the filtrate using ClO_4^- or I^- ion. The resolving agent was recovered from the filtrates by precipitating it with excess ethanol.

(±)α-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate.—Twice recrystallized *cis*-α-$[Co(trien)Cl_2]Cl$ (20.7 g) was added to $HClO_4$ solution (150 ml of 0.013 *M*), and the solution was stirred for a time sufficient for the dichloro chloride to dissolve and aquate completely to the chloroaquo stage (30 hr). Excess $NaHCO_3$ (12.6 g) was added, followed by $NaClO_4$ (14 g). The mixture was then evaporated in a current of air at room temperature and (±)α-$[Co(trien)CO_3]ClO_4$ soon began to crystallize. It was filtered off and recrystallized fractionally from hot water (80°) by cooling and adding $NaClO_4$. The fractions were filtered off, washed with methanol containing a little water, ethanol, and acetone, and dried at 50°. By their visible spectra, the first two fractions (yield, 8.7 g, 34%) were shown to be pure α-$[Co(trien)CO_3]ClO_4\cdot H_2O$.

A resolution of the compound was attempted by adding K(+)-$[Co(en)(mal)_2]\cdot 2H_2O$ (1 mole) to a solution of (±)α-Co(trien)-$CO_3]ClO_4\cdot H_2O$ (1 mole) at 50°. However, on evaporation at room temperature (±)α-$[Co(trien)CO_3]ClO_4$ separated as the least soluble component.

(+)α-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate.—This was prepared in a similar manner to the racemic perchlorate, by transforming the active *cis*-α-dichloro perchlorate with full retention of configuration. (+)*cis*-α-$[Co(trien)Cl_2]ClO_4$ (11.5 g, $[\alpha]_D$ +1800°, 77% optically pure) was aquated in 0.01 *M* $HClO_4$ (200 ml) for 15 hr. $NaHCO_3$ (5.7 g) was added, and after 15 min $NaClO_4$ (8.4 g) was added. Orange-red crystals of (+)-α-$[Co(trien)CO_3]ClO_4\cdot H_2O$ began to crystallize in a few minutes and were filtered off after 1 hr. They were washed with methanol–water, ethanol, and acetone and dried at 50°; yield, 5.4 g, 46%. This fraction gave $[\alpha]_D$ +1200° [α_D +1.24° for a 0.103% aqueous solution), $[\alpha]_{578}$ +1430°. *Anal.* Calcd for (+)α-$[Co(C_6H_{18}N_4)CO_3]ClO_4\cdot H_2O$: C, 21.97; H, 5.27; N, 14.64. Found: C, 21.99; H, 5.21; N, 14.71. A further fraction (4.1 g), obtained by reducing the volume of solution to 50 ml in a rotatory evaporator, gave $[\alpha]_D$ +1050° and $[\alpha]_{578}$ +1300°. On recrystallization from warm water (50°) as described for the racemic isomer, the measured rotation could not be increased above $[\alpha]_D$ +1230°, and the optical isomers were less soluble than the racemate. The α-$[Co(trien)CO_3]ClO_4\cdot H_2O$ crystallized as plates or prisms; the corresponding β isomer was obtained only as needles.

$(+)_{546}$*cis*-α-Diaquo(triethylenetetramine)cobalt(III) Perchlorate.—To (+)α-$[Co(trien)CO_3]ClO_4\cdot H_2O$ (2.59 g, $[\alpha]_D$ +1200°) 10% excess of $HClO_4$ (3.0 ml of 5 *M*) was added drop by drop with stirring at 0°. After effervescence was complete, the solution in a beaker was placed in a vacuum desiccator. When the solution had evaporated nearly to dryness (1 week) the well-formed, deep reddish carmine crystals of $(+)_{546}$*cis*-α-$[Co(trien)(H_2O)_2](ClO_4)_3$ were filtered off in a sintered-glass filter, washed twice with ether, and quickly placed in the vacuum desiccator. They were analyzed after 3 days; yield, 3.13 g, 86%. *Anal.* Calcd for $(+)_{546}$*cis*-α-$[Co(C_6H_{18}N_4)(H_2O)_2](ClO_4)_3$: C, 13.35; H, 4.11; N, 10.39. Found: C, 13.29; H, 4.02; N, 10.22. The measured rotation was $[\alpha]_D$ −168° (α_D −0.19° for a 0.0566% solution in 0.01 *M* $HClO_4$, in a 2-dm tube).

The (+)*cis*-α-$[Co(trien)(H_2O)_2](ClO_4)_3$ was slightly hygroscopic. Also the complex decomposed when kept under vacuum for an extended period.

α-Dibromo(triethylenetetramine)cobalt(III) Bromide.—This was prepared in a manner similar to that described for *cis*-α-$[Co(trien)Cl_2]Cl$. *cis*-α-$[Co(trien)(NO_2)_2]Br\cdot H_2O$ (79.0 g in 100 ml of water) was treated with excess HBr (77 ml of 5.8 *N*) and after evaporation the olive-green product was ground in ethanol, filtered, washed with ethanol and ether, and dried at 50°; yield, 85 g, 95%. The product contained a little unreacted *cis*-α-$[Co(trien)(NO_2)_2]Br\cdot H_2O$.

β-Carbonato(triethylenetetramine)cobalt(III) Chloride Sesquihydrate.—A mixture of *cis*-α-$[Co(trien)Cl_2]Cl$ (85 g of crude) and Li_2CO_3 (25 g) in water (170 ml) was heated on a steam bath with occasional stirring. The violet color soon changed to red, and after the solution had become alkaline (60 min), the excess Li_2CO_3 was filtered from the hot solution. After cooling, $CaCl_2$ (4 g) was added to eliminate carbonate ion and the solution was filtered again. From the filtrate, β-$[Co(trien)CO_3]Cl\cdot 1.5H_2O$ was crystallized by carefully adding ethanol. After standing, the red crystals were filtered, washed with ethanol and acetone, and air dried; yield, 79 g, 89%. The visible spectrum of this crude product showed that it contained about 80% of the β isomer. The product was recrystallized from a small volume of warm water by carefully adding ethanol. *Anal.* Calcd for β-$[Co(C_6H_{18}N_4)CO_3]Cl\cdot 1.5H_2O$: C, 25.65; H, 6.41; N, 17.10. Found: C, 25.52; H, 6.33; N, 17.19. The β-carbonato perchlorate was obtained as well-formed red needles by adding $NaClO_4$ to a solution of β-$[Co(trien)CO_3]Cl$. It was recrystallized slowly from hot water (50°) by leaving the solution to stand (3 days). The large crystals which first separated had a visible spectrum identical with that of optically pure (−)β-$[Co(trien)CO_3]ClO_4\cdot H_2O$.

β-$[Co(trien)CO_3]Br\cdot 0.5H_2O\cdot 0.5C_2H_5OH$ was prepared from α-$[Co(trien)Br_2]Br$ (89 g in 180 ml of water) and Li_2CO_3 (20 g) in a manner similar to that above. After removing excess Li_2CO_3, the solution was cooled in an ice bath for 1 hr. Ethanol was added to the filtrate and the deep red product crystallized on standing; yield, 57 g, 83%. It was recrystallized from water by the addition of ethanol. *Anal.* Calcd for β-$[Co(C_6H_{18}N_4)CO_3]Br\cdot 0.5H_2O\cdot 0.5C_2H_5OH$: C, 25.48; H, 5.89; N, 14.86. Found: C, 25.48; H, 5.71; N, 15.18. The same sample was also recrystallized from water with methanol. *Anal.* Calcd for β-$[Co(C_6H_{18}N_4)CO_3]Br\cdot 0.5H_2O\cdot 0.5CH_3OH$: C, 24.33; H, 5.72; N, 15.14. Found: C, 24.45; H, 5.48; N, 15.21.

(+)Silver Bis(malonato)ethylenediaminecobalt(III) Dihydrate.—To an aqueous solution of (+)K$[Co(en)(mal)_2]\cdot 2H_2O$

(38.8 g in 70 ml) a warm solution containing a slight excess of $AgNO_3$ (17.4 g in 25 ml) was added; on cooling $(+)Ag[Co(en)(mal)_2]\cdot 2H_2O$ precipitated. It was filtered off, washed with small volumes of ice water, methanol, and acetone, and air dried. From the filtrate more product was precipitated by adding ethanol. The second fraction was recrystallized from hot water (60°) by the addition of ethanol and added to the main crop; yield, 43.1 g, 94%. The product had the following rotations: $[\alpha]_D$ +1430° (α_D +0.73° for a 0.0511% aqueous solution), $[\alpha]_{578}$ +2080°, $[\alpha]_{546}$ +1060°. *Anal.* Calcd for $(+)Ag[Co(C_2H_8N_2)(C_3H_2O_4)_2]\cdot 2H_2O$: C, 20.57; H, 3.45; N, 6.00. Found: C, 20.76; H, 3.56; N, 5.96.

Resolution of β-Carbonato(triethylenetetramine)cobalt(III) Bromide.—$(+)Ag[Co(en)(mal)_2]\cdot 2H_2O$ (43.1 g) was shaken with a slight excess of β-$[Co(trien)CO_3]Br\cdot 0.5H_2O\cdot 0.5C_2H_5OH$ (32.6 g in 100 ml of water) for 5 min in a stoppered flask. The silver bromide was filtered off and washed with water, and the filtrate and washings (which were free of Ag^+ ion) were evaporated in a rotatory evaporator to 100 ml. Methanol and ethanol were added, and on standing overnight the diastereoisomer (+)β-$[Co(trien)CO_3](+)[Co(en)(mal)_2]\cdot 4H_2O$ crystallized as fine silvery pink plates. It was filtered off, washed with methanol and acetone, and air dried; yield, 23.7 g, 78%. The product gave the following rotations: $[\alpha]_D$ +1500° (α_D +0.66° for a 0.044% aqueous solution), $[\alpha]_{578}$ +2230°. On evaporating the filtrate further, to 60 ml, and repeating the precipitation with methanol–ethanol, very little more diastereoisomer was obtained (0.3 g having $[\alpha]_D$ +1440°).

The diastereoisomer was recrystallized from the minimum volume of water, by adding methanol (or dimethylformamide) to incipient crystallization and allowing the solution to stand. The maximum rotation obtained was $[\alpha]_D$ +1540°, so that the diastereoisomer obtained in the above resolution was almost optically pure. *Anal.* Calcd for (+)β-$[Co(C_6H_{18}N_4)CO_3](+)[Co(C_2H_8N_2)(C_3H_2O_4)_2]\cdot 4H_2O$: C, 27.27; H, 5.76; N, 12.73. Found: C, 27.35; H, 5.88; N, 12.50.

(+)β-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate.—The diastereoisomer (22.5 g, $[\alpha]_D$ +1540°) was dissolved in the minimum volume of water (50 ml) and treated with excess $NaClO_4$; orange-red (+)β-$[Co(trien)CO_3]ClO_4\cdot H_2O$ began to crystallize immediately. It was filtered after 5 min, washed with methanol containing a little water, methanol, and acetone, and air dried; yield, 12.0 g, 88%. The product was recrystallized from warm water (50°) by adding ethanol until incipient crystallization occurred.

(+)β-$[Co(trien)CO_3]ClO_4\cdot H_2O$ was fractionally crystallized as orange-red needles, filtered, washed with ice-cold $NaClO_4$ solution, methanol, and acetone, and air dried at 50°. The optical isomers were less soluble than the racemate. The yield of pure isomer, $[\alpha]_D$ +770° (α_D +0.73° for a 0.0957% aqueous solution), was 11.3 g. *Anal.* Calcd for (+)β-$[Co(C_6H_{18}N_4)CO_3]ClO_4\cdot H_2O$: C, 21.97; H, 5.27; N, 14.64. Found: C, 21.91; H, 5.37; N, 14.55.

The diastereoisomer was also converted to the carbonato iodide (through the triiodide and reduction with Na_2SO_3) and to the tetraphenylborate derivative, which was acetone soluble. *Anal.* Calcd for (+)β-$[Co(C_6H_{18}N_4)CO_3][B(C_6H_5)_4]\cdot 1.5H_2O$: C, 60.91; H, 6.55. Found: C, 60.63; H, 6.62.

(−)β-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate.—The filtrate from the separation of diastereoisomer was reduced in volume on a rotatory evaporator to 50 ml. On addition of excess $NaClO_4$, (−)β-$[Co(trien)CO_3]ClO_4\cdot H_2O$ crystallized immediately and this was recrystallized as described above. The pure product had the following rotations: $[\alpha]_D$ −780°, $[\alpha]_{578}$ −930°; yield, 9.5 g, 54%. *Anal.* Calcd for (−)β-$[Co(C_6H_{18}N_4)CO_3]ClO_4\cdot H_2O$: C, 21.97; H, 5.27; N, 14.64. Found: C, 22.08; H, 5.31; N, 14.64. The resolving agent $Na(+)[Co(en)(mal)_2]\cdot 2H_2O$ was precipitated from the combined filtrates with ethanol.

$(-)_{546}$*cis*-β-Diaquo(triethylenetetramine)cobalt(III) Perchlorate.—This was prepared in a manner similar to that described for the corresponding *cis*-α isomer. (−)β-$[Co(trien)CO_3]ClO_4\cdot H_2O$ (1.3 g, $[\alpha]_D$ −730°) was carefully treated with excess $HClO_4$ (2.0 ml of 5 *N*), and the solution was placed in a vacuum desiccator. The orange-red product slowly crystallized and after standing (4 hr) was filtered off on a sintered-glass filter, washed with ether, and dried in a vacuum desiccator (3 days). It was very soluble in water, soluble in alcohol and acetone, but insoluble in ether. *Anal.* Calcd for $(-)_{546}$*cis*-β-$[Co(C_6H_{18}N_4)(H_2O)_2](ClO_4)_3$: C, 13.35; H, 10.39; N, 4.11. Found: C, 13.40; H, 10.30; N, 4.16. A 0.205% solution in 0.01 *M* $HClO_4$ gave α_D −0.38° whence $[\alpha]_D$ −186°, $[\alpha]_{578}$ −200°. It was shown to be optically pure by transforming the above solution to optically pure (−)β-$[Co(trien)CO_3]^+$ with excess $NaHCO_3$. The carbonato solution had α_D −1.12°, whence $[M]_D$ −2970°. The diaquo perchlorate was hygroscopic.

Decomposition of *cis*-α- and *cis*-β-Diaquo(triethylenetetramine)cobalt(III) Perchlorates.—When samples of both the *cis*-α and *cis*-β isomers were kept in a desiccator (over calcium chloride) for a long period (3 months), both isomers darkened (the α form changed from reddish carmine to violet-red; the β form changed from reddish orange to brownish orange), they were much less hygroscopic than the original samples, and both contained some dark brown or dark green-brown material, insoluble in water. However, they were completely soluble in ethanol and acetone. The dry, freshly prepared samples were normally stored in stoppered bottles, and under these conditions they were quite stable.

***cis*-β-Dinitro(triethylenetetramine)cobalt(III) Nitrate.**—A slight excess of HNO_3 (101 ml of 2 *N*) was slowly added to β-$[Co(trien)CO_3]Cl\cdot 1.5H_2O$ (32.7 g). After 30 min, $NaNO_2$ (15.0 g) was added to the diaquo compound and yellow-orange crystals of *cis*-β-$[Co(trien)(NO_2)_2]NO_3$ slowly separated (1 hr). The product was filtered off after 1 day, washed quickly with ice-cold HNO_3 (1 *N*), alcohol, and acetone, and air dried; yield, 28 g, 80%. It was recrystallized from hot water (90°). *Anal.* Calcd for *cis*-β-$[Co(C_6H_{18}N_4)(NO_2)_2]NO_3$: C, 20.06; H, 5.05; N, 27.47. Found: C, 20.29; H, 5.13; N, 27.36.

***cis*-β-Dinitro(triethylenetetramine)cobalt(III) Iodide.**—NaI was added to a hot solution of *cis*-β-$[Co(trien)(NO_2)_2]NO_3$ (4.4 g in 90 ml of water at 80°) and the corresponding iodide crystallized out. It was filtered off, washed with ice-cold NaI solution, alcohol, and acetone, and air dried; yield, 4.8 g, 90%. The complex was recrystallized quickly from hot water (90°). *Anal.* Calcd for *cis*-β-$[Co(C_6H_{18}N_4)(NO_2)_2]I$: C, 16.99; H, 4.28; N, 19.82. Found: C, 17.06; H, 4.27; N, 19.84.

Resolution of *cis*-β-Dinitro(triethylenetetramine)cobalt(III) Iodide.—*cis*-β-$[Co(trien)(NO_2)_2]I$ (10.0 g in 80 ml of water containing 1 drop of glacial acetic acid) was transformed to the acetate, by shaking the suspension with a slight deficiency of silver acetate (3.9 g). The AgI was filtered off and sodium (+)-antimonyl tartrate (3.6 g) was added slowly to the solution. On scratching the sides of the vessel the yellow diastereoisomer $(+)_{546}$*cis*-β-$[Co(trien)(NO_2)_2](+)[SbO(C_4H_4O_6)]$ commenced to separate; yield, 6.4 g. The diastereoisomer was recrystallized fractionally from hot water (70°). The least soluble fractions had the highest optical purity, and the highest rotations measured were: $[\alpha]_D$ +138° (α_D +0.41° for a 0.30% aqueous solution), $[\alpha]_{578}$ +142°, $[\alpha]_{546}$ +198°. *Anal.* Calcd for $(+)_{546}$*cis*-β-$[Co(C_6H_{18}N_4)(NO_2)_2](+)[SbO(C_4H_4O_6)]$: C, 20.60; H, 3.80; N, 14.42. Found: C, 20.63; H, 3.89; N, 14.25 The diastereoisomer was shaken in solution with excess NaI, and $(+)_{546}$*cis*-β-$[Co(trien)(NO_2)_2]I$ precipitated. The (−) isomer was precipitated as the iodide by the addition of NaI to the diastereoisomer filtrate.

Both optically active dinitro iodides were purified by rapid fractional recrystallization from hot water (95°). The fractions were filtered, washed with ice-cold NaI solution, ethanol, and acetone, and air dried. The optical isomers were less soluble than the racemate, and the maximum rotations measured were: $[\alpha]_D$ +149, −156°, $[\alpha]_{578}$ +160, −167°, $[\alpha]_{546}$ +255, −255°. *Anal.* Calcd for *cis*-β-$[Co(C_6H_{18}N_4)(NO_2)_2]I$: C, 16.99; H, 4.28; N, 19.82. Found ((+) isomer): C, 17.03; H, 4.24; N, 19.70. Found ((−) isomer): C, 17.01; H, 4.26; N, 19.53.

Active *cis*-β-dinitro perchlorates were prepared by shaking the corresponding active iodides with excess AgCl in water. The silver halides were filtered off and the perchlorates were fractionally precipitated as yellow plates, by adding $NaClO_4$ solution slowly. The active isomers which were less soluble than the racemate were filtered, washed with ice-cold $NaClO_4$ solution, ethanol, and acetone, and air dried. The optically pure (−) perchlorate gave the following rotations: $[\alpha]_D$ −156° (α_D −0.31° for a 0.198% aqueous solution), $[\alpha]_{578}$ −181°, $[\alpha]_{546}$ −282°. *Anal.* Calcd for $(-)_{546}$*cis*-β-$[Co(C_6H_{18}N_4)(NO_2)_2]ClO_4$: C, 18.17; H, 4.56; N, 21.19. Found: C, 18.30; H, 4.71; N, 21.20. Although not quite so stable optically as the *cis*-α isomer, the *cis*-β-dinitro perchlorate and iodide were recrystallized from hot water by cooling and adding $NaClO_4$ or NaI without appreciable change in rotation.

***cis*-β-Dichloro(triethylenetetramine)cobalt(III) Chloride Hemihydrate.**—β-$[Co(trien)CO_3]Cl\cdot1.5H_2O$ (16.1 g) was suspended in ethanol (500 ml) saturated with dry hydrogen chloride and stirred. There was a slow effervescence, and, in the early stage, more HCl was bubbled through the solution periodically. After standing overnight, *cis*-β-$[Co(trien)Cl_2)Cl$ was filtered off as a fine, reddish violet powder, washed with ethanol and acetone, and air dried; yield, 12.5 g, 82%.

This product was resolved without purification. However, for analysis, a saturated solution was made up quickly in dilute acetic acid (pH 3) at room temperature, and the compound was recrystallized quickly by cooling in an ice bath and adding hydrochloric acid (12 *N*). *Anal.* Calcd for *cis*-β-$[Co(C_6H_{18}N_4)Cl_2]Cl\cdot0.5H_2O$: C, 22.46; H, 5.93; N, 17.47. Found: C, 22.16; H, 5.83; N, 17.38.

Resolution of *cis*-β-Dichloro(triethylenetetramine)cobalt(III) Chloride.—This isomer aquated rapidly ($t_{1/2}$ in acid solution 8 min at 25°) and the resolution was therefore carried out quickly and at low temperatures.

A saturated solution of the dichloro isomer, prepared by shaking the solid with dilute acetic acid solution (pH 3) at 20° for 2 min, was filtered quickly into a flask cooled in an ice bath. A solution thus prepared (8.2 g in 300 ml) was immediately treated with Na(+)$[(Co(en)(C_2O_4)_2]\cdot H_2O$ (5.0 g). The diastereoisomer (−)*cis*-β-$[Co(trien)Cl_2]$(+)$[Co(en)(C_2O_4)_2]\cdot H_2O$ separated immediately and was filtered off after 4 min. It was washed with a little iced water, alcohol, and acetone and air dried; yield, 5.0 g, 65%. A 0.066% solution in cold 0.01 *N* $HClO_4$ gave α_D +0.09° and α_{578} −0.09 ± 0.02°, whence $[M]_D \backsim +800°$ and $[M]_{578}$ $\backsim -800°$. The optical purity of the complex was determined more accurately by converting the above solution, after it had aquated to the chloroaquo ion (1 hr at 25°), to the carbonato complex with excess $NaHCO_3$. The rotation measured was α_{578} −0.35°, whence $[M]_{578}$ −3100°. At this wavelength the (+)$[Co(en)(C_2O_4)_2]^-$ ion has nearly zero rotation, and the resolved carbonato compound has $[M]_{578}$ −3700°. No diastereoisomer separated when the resolution was carried out at room temperature. *Anal.* Calcd for (−)-*cis*-β-$[Co(C_6H_{18}N_4)Cl_2]$(+)-$[Co(C_2H_8N_2)(C_2O_4)_2]\cdot H_2O$: C, 24.44; H, 4.75; N, 14.25. Found: C, 24.25; H, 4.86; N, 14.04.

(−)*cis*-β-$[Co(trien)Cl_2]I$ was recovered from the diastereoisomer by a procedure identical with that described for the *cis*-α isomer. The grinding with NaI was carried out quickly at 0°. The isomer was purified by shaking the iodide (3 g) in an ice-cold dilute acetic acid solution (60 ml) with an excess of AgCl. The silver halides were filtered off (2 min) and $NaClO_4$ was added in small portions to the filtrate to precipitate fractionally (−)-*cis*-β-$[Co(trien)Cl_2]ClO_4$ as violet plates. These were washed with ice-cold $NaClO_4$ solution, ethanol, and acetone and air dried. The optical isomer was less soluble than the racemate, and the rotation measured for the least soluble fraction was α_D −0.12° for a 0.051% solution, whence $[\alpha]_D$ −230°. The solution was transformed to β-$[Co(trien)CO_3]^+$ whence α_D −0.42° and $[M]_D$ −3100°. *Anal.* Calcd for (−)*cis*-β-$[Co(C_6H_{18}N_4)Cl_2]ClO_4$: C, 19.16; H, 4.82; N, 14.91. Found: C, 19.28; H, 4.82; N, 14.96.

After removal of the diastereoisomer, (+)-*cis*-β-$[Co(trien)Cl_2]ClO_4$ was precipitated fractionally from the filtrate by adding $NaClO_4$; total yield, 3.9 g, 80%. A 0.057% solution of the least soluble fraction (1 g) gave α_D +0.15° whence $[\alpha]_D$ +240° (±10°). The solution converted to the β-$[Co(trien)CO_3]^+$ ion gave $[M]_D$ +2650°. Fractions 2 (1.4 g) and 3 (1.5 g) gave $[M]_D$ +1800 and +450°, respectively, for the carbonato complex.

The combined filtrates were reduced to a small volume and the resolving agent was recovered by adding ethanol.

***trans*-Dichloro(triethylenetetramine)cobalt(III) Chloride and Perchlorate.**—β-$[Co(trien)CO_3]Cl\cdot1.5H_2O$ (20 g) was treated with excess ice-cold HCl (50 ml of 12 *N*). The solution was placed in the refrigerator, and as the product crystallized, it was filtered fractionally in a sintered-glass filter, washed with acetone, and air dried. The first two fractions (7.0 g), which separated after 1 day, were red-violet. The next fraction obtained (0.2 g, after 2 days) was all green *trans*-$[Co(trien)Cl_2]Cl\cdot HCl\cdot H_2O$. *Anal.* Calcd for *trans*-$[Co(C_6H_{18}N_4)Cl_2]Cl\cdot HCl\cdot H_2O$: C, 19.69; H, 5.78; N, 15.31. Found: C, 19.51; H, 6.07; N, 15.25. More violet product was filtered off over the next 7 days, and this was shown to be largely the β isomer. A microscopic examination showed that all fractions contained some green crystals of the *trans* isomer.

The violet product (about 10 g) was refluxed in methanol (300 ml) for 1 hr. The residue was filtered off and excess dry $LiClO_4$ was then added to the green solution. On cooling in an ice bath and scratching the vessel walls with a glass rod, green crystals of *trans*-$[Co(trien)Cl_2]ClO_4$ were obtained. These were filtered off after 10 min to avoid contamination with the *cis* isomers, washed with ethanol and ether, and air dried. The residue was extracted again and more of the *trans* isomer was obtained; total yield, 1.5 g. *Anal.* Calcd for *trans*-$[Co(C_6H_{18}N_4)Cl_2]ClO_4$: C, 19.16; H, 4.82; N, 14.91. Found: C, 19.23; H, 4.72; N, 14.82.

Results and Discussion

$[Co(trien)Cl_2]^+$ Isomers.—Purple α-$[Co(trien)Cl_2]Cl$ was prepared quantitatively by treating α-$[Co(trien)(NO_2)_2]Cl$ with excess HCl. This isomer was the same as that described by Basolo[1] and it showed only one rate for the loss of the first Cl^- ion by aquation in acid solution. The red-violet β isomer was prepared by treating β-$[Co(trien)CO_3]Cl\cdot1.5H_2O$ in ethanol saturated with HCl. This isomer was identified by acid hydrolysis of the first Cl^- ion and the detection of the two chloroaquo isomers formed.[9] It is apparent that α-$[Co(trien)Cl_2]^+$ has a twofold axis of symmetry which makes the two Cl^- ions equivalent whereas the β isomer has nonequivalent coordinated Cl^- ions. Both dichloro isomers were resolved and gave for the α form $[\alpha]^{20}_D$ ±2330° and for β $[\alpha]^{10}_D$ ±230°. These rotations may be compared with that recorded by Das Sarma and Bailar,[3] $[\alpha]_D$ −100°, but it is not clear in their preparation which isomer was involved. The visible absorption spectra of the optically pure α- and β-$[Co(trien)Cl_2]ClO_4$ salts are given in Figure 5 along with that of the *trans* isomer. The rotatory dispersion, circular dichroism curves, and absolute configurations have been reported and discussed elsewhere.[10] Green *trans*-$[Co(trien)Cl_2]Cl$ was obtained from the crude β-$[Co(trien)Cl_2]Cl$ by heating it in methanol; both *trans*-$[Co(trien)Cl_2]Cl$ and *trans*-$[Co(trien)Cl_2]ClO_4$ were obtained. The reactions in methanol were not extensively investigated, but it appeared that α-$[Co(trien)Cl_2]Cl$ did not isomerize to *trans*, whereas the β isomer gave both *trans* and some α. The apparent

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(9) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).
(10) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

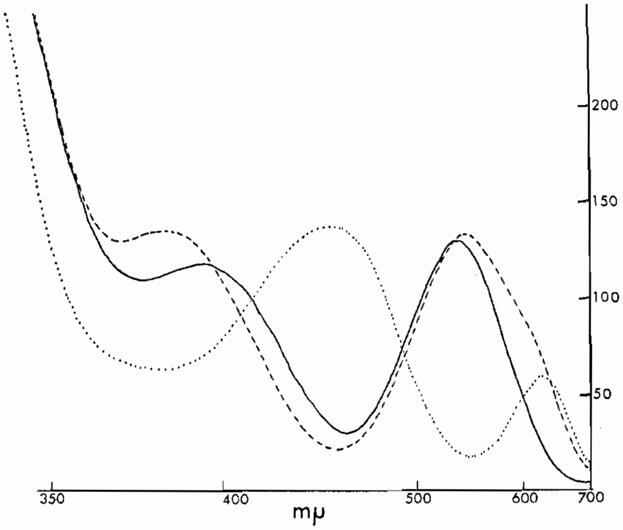

Figure 5.—Visible spectra for α- (-- – – –), β- (———), and *trans*- (. . . .) [Co(trien)Cl_2]ClO_4 in 10^{-2} *M* $HClO_4$.

order of stability of these isomers in methanol appears to be α(?) > *trans* > β. In aqueous solution the thermodynamic stability was more difficult to ascertain owing to the presence of substantial amounts of the chloroaquo ions. However, it is known that the concentration of *trans* is small and it appears that α is more stable than β since a concentrated solution of the red-violet β-[Co(trien)Cl_2]Cl in HCl slowly changed to the purple color of the α form.

The α and β isomers have similar visible spectra except that the more symmetrical (C_2) α form absorbs more strongly about 650 mμ. The pronounced shoulder at this wavelength has been attributed to a partial splitting of the $^1A_1 \rightarrow$ A, B, B levels in the first ligand field absorption band.[10] The principal absorption has been identified with the $^1A_2 + B$ levels derived from the $^1A_1 \rightarrow E_a$ absorption in D_3 symmetry. The absorption at longer wavelengths was identified with the second B transition derived from the $^1A_1 \rightarrow {}^1A_2$ transition in D_3 symmetry. The spectrum of the *trans* isomer has the general appearance of *trans*-[N_4CoCl_2]$^+$ spectra and this and the CD curve of the active isomer will be discussed elsewhere.

It was thought that the infrared spectra in the vicinity of 3500 cm^{-1} would allow the isomers to be distinguished. The β isomer has different site symmetries for the two NH_2 groups as well as the two secondary NH groups but the α and *trans* isomers have a symmetrical arrangement for these groups. Although the NH stretching region was more complex for the β than for α and *trans* isomers, the absorptions were not clearly resolved and did not allow an unequivocal assignment of the NH spectra to the α and β isomers. It has since been established that in the region 1110–950 cm^{-1} a clear distinction between the *cis* isomers may be made in the absence of an absorbing anion such as ClO_4^-.[11]

[Co(trien)ClOH$_2$]$^{2+}$ Isomers.—The α- and β-chloroaquo ions were not isolated but were obtained by aquating the dichloro complexes in dilute acid solution. Both reactions take place with full retention, and the visible spectra of these ions are given in Figure 6. Solid products were obtained with the anions [B(C_6H_5)$_4$]$^-$, [$PtCl_6$]$^{2-}$, [Cr(NH_3)$_2$(NCS)$_4$]$^-$, and [C_2O_4]$^{2-}$, but they were not analytically pure.

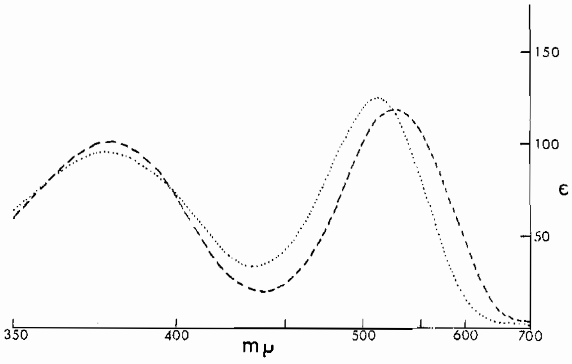

Figure 6.—Visible spectra for α- (– – – –) and β- (. . . .) [Co(trien)ClOH_2]$^{2+}$ ions in 10^{-2} *M* $HClO_4$.

[Co(trien)CO$_3$] Isomers.—[Co(trien)Cl_2]Cl heated with Li_2CO_3 in aqueous solution gave red β-[Co(trien)-CO_3]Cl which was isolated with ethanol. The crude complex contained a small amount of the α form. The pure β isomer was resolved into optical forms using the (+)[Co(en)(mal)$_2$]$^-$ ion (mal = malonate). The pure optical isomers were converted with acid to the diaquo complexes and then with NO_2^- to the β-dinitro ion with full retention of configuration. Since in the mode of preparation, aquation of the Cl$^-$ ions precedes the addition of CO_3^{2-} to the complex, it follows that the β-diaquo or -hydroxo species are the most stable under these conditions and this agrees with other observations in acid solution where the β-diaquo ion is more stable than the α form in the ratio ∽5.6:1. This complex provides access to the β series of complexes, Figure 7.

The α-[Co(trien)CO_3]$^+$ complex was prepared by aquating the α-[Co(trien)Cl_2]$^+$ ion in dilute acid followed by addition of HCO_3^-. Both active and inactive samples were obtained this way since the optically active complexes showed that the conversion dichloro → chloroaquo → carbonato takes place with full retention of configuration. Both of the carbonato complexes had large rotations, α[*M*]D ±4740° and β[*M*]D ±2980°, and substantial extinction coefficients at 505 mμ, ϵ_α 120 and ϵ_β 178, Figure 8. These properties were used to measure the degree of α → β isomerization in the kinetic studies to be described later.

An X-ray crystallographic analysis has been carried out on (−)[Co(trien)CO_3]$ClO_4 \cdot H_2O$ and the skeletal arrangement of the ligand ascribed to the β complexes has been confirmed.[8] Also the X-ray study led to a molecular weight of 387 for the complex (calcd 382.7).

[Co(trien)(H$_2$O)$_2$]$^{3+}$ Isomers.—The optically active α- and β-[Co(trien)(H_2O)$_2$](ClO_4)$_3$ salts were isolated by treating the respective carbonato complexes with a slight excess of $HClO_4$ and evaporating them slowly in a vacuum desiccator. The complexes were very soluble and hygroscopic and decomposed slowly in the desic-

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(11) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

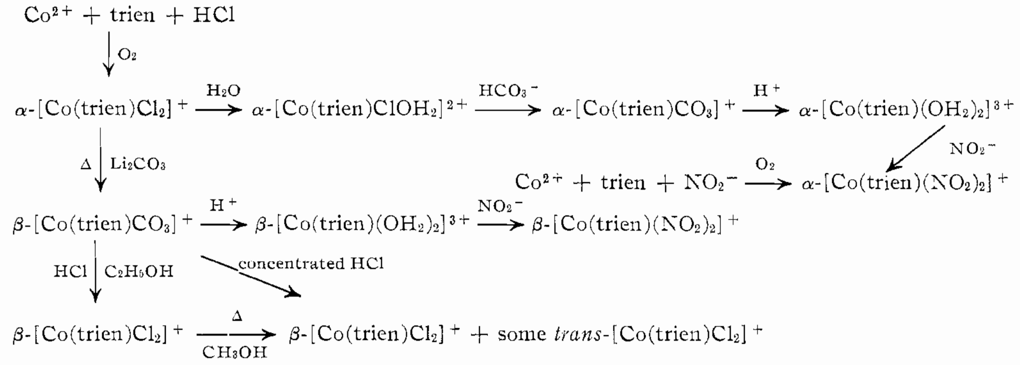


Figure 7.—Preparative routes for cobalt(III) triethylenetetramine complexes.

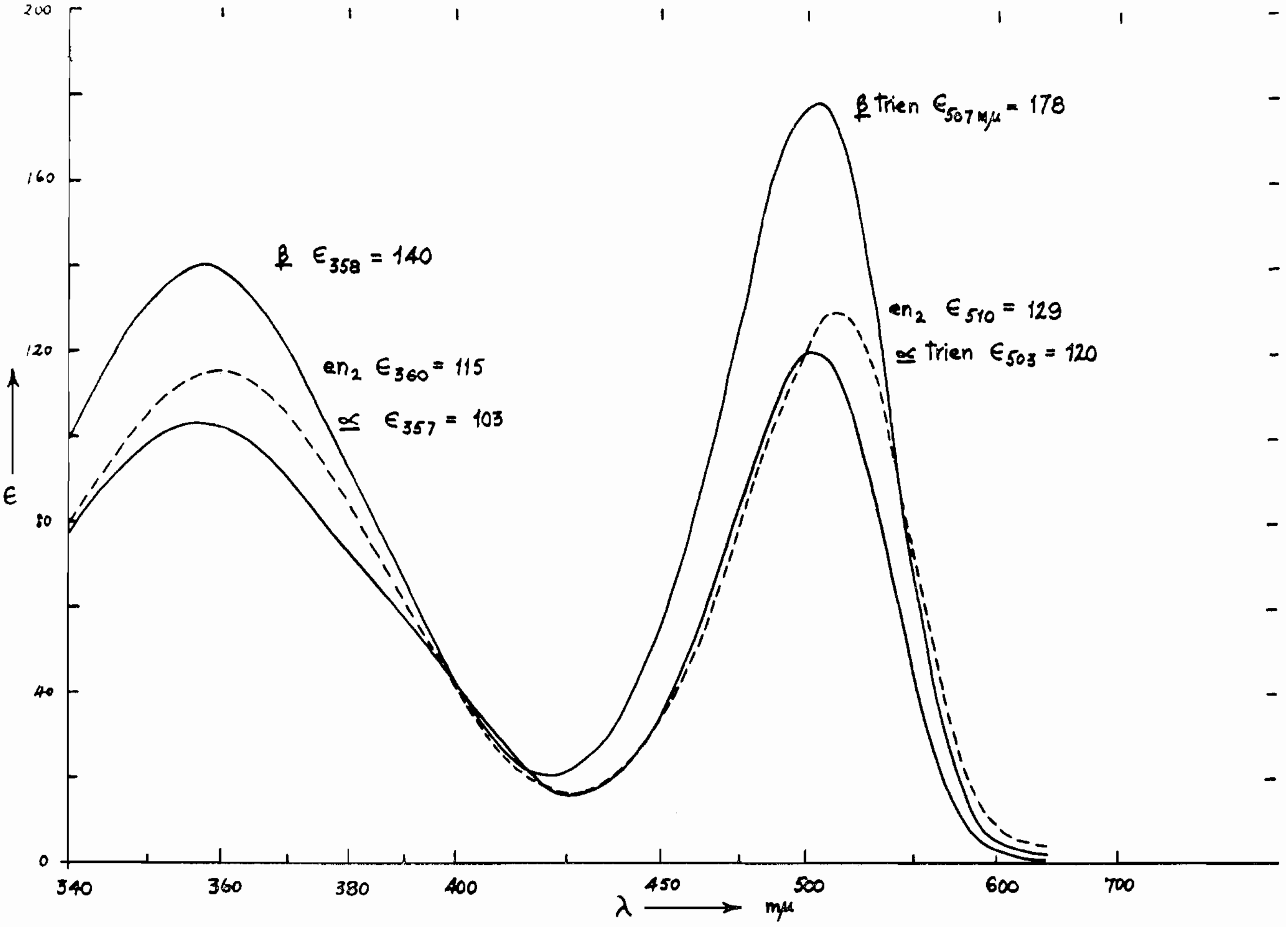
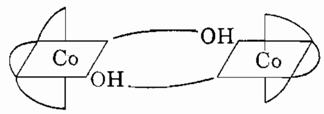


Figure 8.—Visible spectra for α- and β-[Co(trien)CO$_3$]ClO$_4$ compared with [Co(en)$_2$CO$_3$]ClO$_4$ (aqueous solution).

cator. There is some evidence for the formation of the binuclear diol complex



and its β equivalent. The optical purity of the isolated salts was confirmed by reconverting them to the respective carbonato or dinitro isomers.

The different colors of the two *cis* isomers (α, scarlet-carmine; β, light orange) are reflected in the spectral differences for the first ligand field bands, Figure 9 (β, ϵ_{max} 122 at 487 mμ; α, ϵ_{max} 87 at 500 mμ). No evidence was found for the *trans* isomer in either preparation but subsequent studies have shown that the *trans*-diaquo complex can be prepared in solution but it isomerizes completely to the β isomer (>98%). The α-diaquo ion isomerizes to an equilibrium mixture of 85% β–15% α and since the *trans*-diaquo ion isomerizes to β, the order of stability is β > α > *trans*.

The pmr spectra of the α and β ions are striking for the resolution observed in both the NH and CH regions, Figure 10. It is apparent from Figure 10 that the large number of broad NH peaks for the β complex is consistent with the different site symmetries for all the N protons (1,1,1,1,2). In contrast, the α isomer has three NH bands of equal intensity (2:2:2),

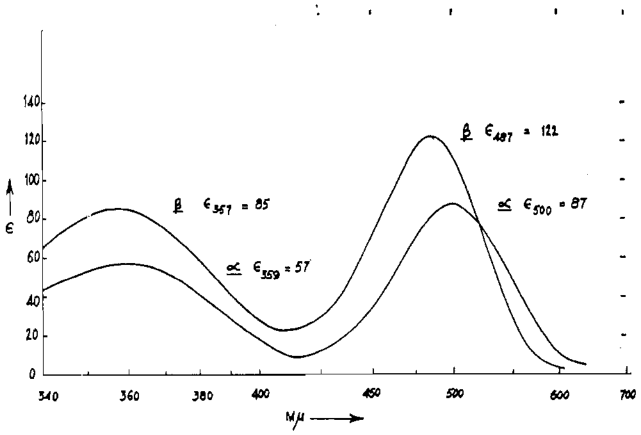


Figure 9.—Visible spectra for α- and β-[Co(trien)(OH$_2$)$_2$](ClO$_4$)$_3$ in 0.1 M HClO$_4$.

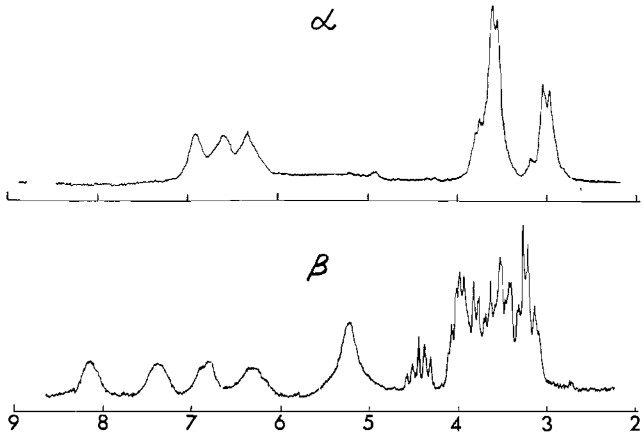


Figure 10.—Pmr spectra (100 Mc) for α- and β-[Co(trien)(OH$_2$)$_2$](ClO$_4$)$_3$ (in 1.8 M D$_2$SO$_4$ relative to TMS (external), using a Varian HR-100 spectrometer) (sample concentration 40 mg/ml).

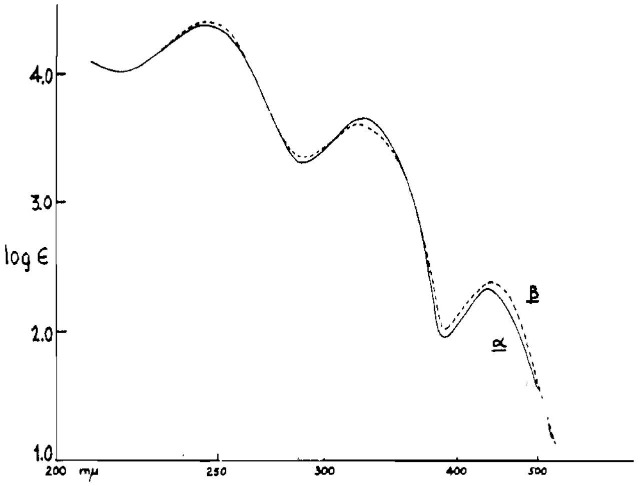


Figure 11.—Visible and ultraviolet spectra of α- and β-[Co(trien)(NO$_2$)$_2$]ClO$_4$ in aqueous solution.

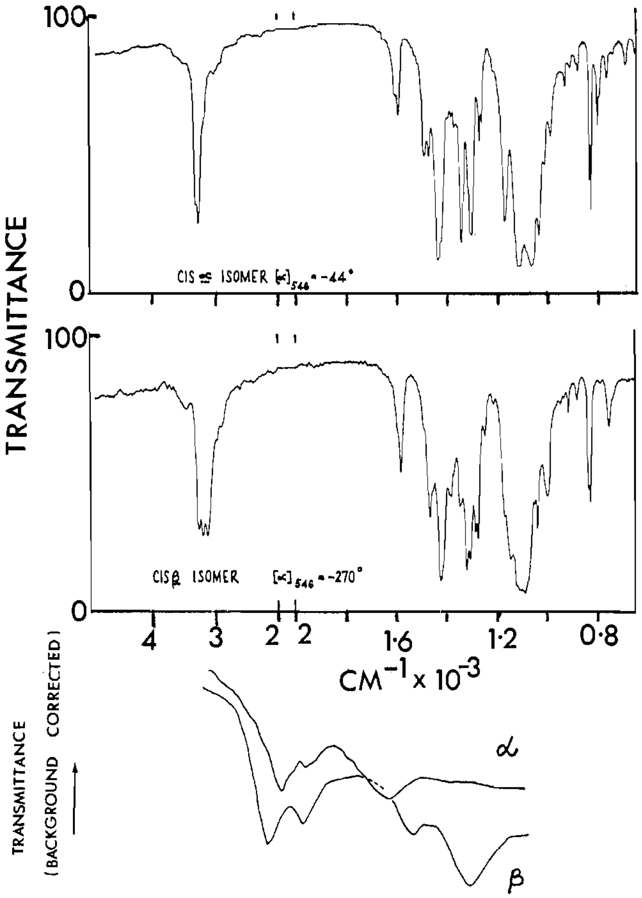


Figure 12.—Infrared spectra of α- and β-[Co(trien)(NO$_2$)$_2$]ClO$_4$ (KBr disk). Upper two curves measured on a Unicam SP-200 spectrometer. Lowest curves are for N–D stretching bands at 2400–2500 cm^{-1}, measured on a Perkin Elmer 112 spectrometer. From left to right the peaks are: α, 2467.0, 2459.0, 2429.3 cm^{-1}; β, 2471.8, 2459.5, 2421.4, 2402.3 cm^{-1}.

consistent with the pairs of N protons related by the twofold axis of symmetry. The CH region is well resolved in the β complex but we have been unable to solve the spectrum. The α CH region is more symmetrical than the β and the two sets of signals (2:1) might be rationalized by the fact that the terminal ethylene bridges are equivalent and different from the central span. If the conformational interchange in these rings is slow compared with the frequency of the band width, an ABCD pattern should appear for the terminal ethylene links and an A$_2$B$_2$ pattern for the central link. However it seems certain that these patterns will be complicated also by NH–CH coupling leading to a broad envelope of bands.[12] For these reasons the CH region does not give an unequivocal choice between α and β beyond the point that the α spectra are less complicated than the β where none of the ethylene links are equivalent.

[Co(trien)(NO$_2$)$_2$]$^+$ Isomers.—The α isomer was prepared by aerial oxidation of a mixture of CoX$_2$, trien·HX, and 2NaNO$_2$ where X = Cl, Br, NO$_3$, OAc. The product α-[Co(trien)(NO$_2$)$_2$]X precipitated in yields of 60–80% and always contained some β isomer. However, the pure β-dinitro salts were obtained from the carbonato complex using acid and then NaNO$_2$. The two isomers were separated and characterized by chromatographing the chlorides or acetates on paper with 1-butanol–pyridine–water–acetic acid (4:3:2:1) or 1-butanol–water–acetic acid (7:2:1). In this way the

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[12] D. A. Buckingham, L. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

geometrical purity of the various products was established. Also a preparation where no precipitate was formed gave the α/β ratio as 2.7 which established the α form as the thermodynamically stable form. This preparative procedure was assumed to be equilibrium controlled since in the analogous $[Co(en)_2(NO_2)_2]^+$ system either the *cis* or *trans* isomer can be precipitated depending on the anion present.

The visible and ultraviolet absorption spectra of the α and β forms are very similar, Figure 11, and are of little use in distinguishing the isomers. However the infrared specta, Figure 12, confirm the α and β assignments of configuration which have been made by converting the other complexes to the dinitro species with retention of configuration.[10] The NH absorptions ~3300 cm^{-1} are not well resolved, but the less symmetrical β isomer gives a more complex spectrum which is consistent with the lower site symmetry of the β NH groups. This is also evident in the infrared spectra of the deuterated complexes in the vicinity of 2400 cm^{-1}, Figure 12.

The α isomer was resolved with the $(-)[Co(en)(C_2O_4)_2]^-$ ion, and the β isomer, with (+)antimonyl tartrate. The iodide, bromide, or perchlorate salts gave, for α, $[M]_{546}$ ±220° and, for β, $[M]_{546}$ ±1100°. The optical purities of these resolved complexes was confirmed by transforming the resolved dichloro and carbonato isomers to the dinitro salts with retention of configuration.

Careful fractionation of large amounts of these dinitro isomers failed to reveal any trace of the *trans* form. The infrared, visible, and ultraviolet spectra, powder diffraction patterns, and chromatographic behavior were always consistent with either the α or the β isomer. The β-dinitro isomer, as well as being less stable than the α form, was also more reactive. An aqueous solution of the β isomer lost 10% of its rotation in 5 hr at 50° whereas the α form showed no change in 30 hr under the same conditions.

General Stability.—It is apparent from the foregoing results that the relative stability of the α and β isomers is a function of the substituent rather than of the possible strain associated with coordination of the secondary N atoms in the two configurations. The dichloro and dinitro complexes appear to favor the α form whereas the diaquo ion favors the β configuration and there appears to be no obvious correlation between either the size or the electronic properties of these substituents to account for the variation in stability of the geometrical form.

Assignment of Configuration.—This has been discussed to some extent for each isomer in this paper and has been expounded also in a previous article.[10] The stereochemical detail in these systems will also be developed in subsequent papers for compounds in which the stereochemistry is closely related to the reactivity of the isomers.[5]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

Asymmetric Synthesis of Alanine *via* the Template Action of a Dissymmetric Cobalt(III) Complex

BY ROBERT G. ASPERGER[1] AND CHUI FAN LIU

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The complex ion α-amino-α-methylmalonato-L,L-α,α'-dimethyltriethylenetetraminecobalt(III) has been isolated and decarboxylated in aqueous solution to yield the L-*cis*-β-[Co(L,L-α,α'-dimethyltrien)(L-alan)$]^{2+}$ ion. The configuration of the alanine is ascertained by decomposition of the complex ion, isolation of the resulting alanine, and measurement of its optical rotation. A high degree of stereospecificity in the formation of the alanine is indicated by the comparison of the ORD curve of the decarboxylated complex with those of the L-*cis*-β-[Co(L,L-β,β'-dimethyltrien)(L-alan)$]^{2+}$ and the L-*cis*-β-[Co(L,L-α,α'-dimethyltrien)(D-alan)$]^{2+}$ ions obtained from standard L-alanine and D-alanine, respectively.

Introduction

In a previous paper[2] the synthesis of a new optically active tetradentate ligand L,L-α,α'-dimethyltriethylenetetramine[3] was reported. This ligand was found to form complexes with the cobalt(III) ion in a fashion analogous to that of triethylenetetramine.[4] The two *cis* isomers (α and β) were found to form in a stereospecific manner (with the D and L absolute configuration, respectively). Both of the *cis* isomers and the *trans* isomers were isolated, and their absolute configurations were assigned. In the present investigation the D-

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[1] Edgar C. Britton Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640.

[2] R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).

[3] Abbreviations used here are: 2,9-diamino-4,7-diazadecane (L,L-α,α'-dimethylethylenetetramine), L,L-α,α'-dimethyltrien; D-alanate, D-alan; L-alanate, L-alan; $(CH_3C(NH_2)(CO_2^-)_2H$, HMAM; the exact protonation site is not implied.

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