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Chemistry, Stereochemistry, and Molecular Dissymmetry of Metal Complexes Containing a Quadridentate Ligand with Chair Six-Membered Chelate Rings

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Received July 5, 1974 AIC404362

The meso and racemic quadridentate ligands produced by the reaction between ethylene dibromide and excess *meso*-2,4-pentanediamine have been separated by means of their cobalt(III) complexes. Both ligands give a rich variety of complexes with varying stereochemistries. Thus it was possible to isolate all three topological isomers, cis-α, cis-β, and trans, of the racemic ligand complexes of cobalt(III) as well as two conformational isomers of each of the cis-β and trans complexes which differed by either having racemic or meso configurations of the inner nitrogen atoms. Similarly, a cis-β isomer with racemic inner nitrogen atoms and the two conformational isomers of the trans topology have been isolated with the meso ligand. In general, the racemic ligand has a strong tendency to form trans complexes with racemic inner nitrogen atoms, and a large number of complexes with this geometry have been isolated. The meso ligand seems to be less restrictive and forms either cis-β or trans complexes depending on the conditions of reaction. Conformational arguments are presented in order to rationalize this behavior. Apart from the trans complex of the meso ligand with meso inner nitrogen atoms, which is conformationally labile, all the complexes of both the meso and racemic ligand have been obtained in pure optical forms. Their absolute configurations have been assigned from the circular dichroism spectra of their cis complexes and through chemical interconversions. The optical, conformational, and topological stability of these complexes are recorded and discussed and their structures have been inferred from a variety of spectroscopic and chemical observations. The ligands appear to be completely stereospecific.

The preceding papers[1,2] left unresolved the origins of the environmental dependence of the circular dichroism spectra of the *trans*-$[Co(3,2,3\text{-tet})XY]^{n+}$ complexes. In particular, the possibility that conformational equilibria exist involving the flipping of the terminal six-membered rings between the achiral chair and chiral skew conformations was not excluded. In order to resolve this problem, we have sought to synthesize complexes with stereospecific ligands of the 3,2,3-tet type in which the conformations of the terminal chelate arms would be fixed because of C-alkylation. For this purpose, we have prepared and isolated several isomers of the tetramethylated 3,2,3-ligand, namely, 2,11-diamino-4,9-dimethyl-5,8-diazadodecane ($NH_2CH(CH_3)CH_2CH(CH_3)NHCH_2CH_2NHCH(CH_3)CH_2CH(CH_3)NH_2$), and in this and subsequent papers we report the preparations, resolutions, and circular dichroism spectra of cobalt(III) complexes with these ligands.

The ligand may exist in six isomeric forms, four racemates and two meso compounds, but because of our synthetic methods using the separate reactions between either the *R*,*S* or the *R*,*R*:*S*,*S* isomers of the 2,4-diaminopentane molecule and ethylene dibromide we have obtained four of these isomers, two at a time. This has simplified the experimental problem of separating the isomers while still providing, as we shall show, a series of complexes in which it is probable that all possible conformational forms of the 3,2,3-tet system have been characterized.

The present paper reports the preparation and characterization of cobalt(III) complexes of the two quadridentate ligands derived from (meso) (*R*,*S*)-2,4-pentanediamine (*R*,*S*-dmtn). Subsequent papers will deal with the preparations of complexes made from *R*,*R*:*S*,*S*-dmtn as well as the circular dichroism spectra of all the complexes made from all the ligands.

1. The Ligands

Both theoretical[3,4] and experimental[5–7] studies suggest that the most stable conformation of the 1,3-diaminopropane-cobalt(III) chelate ring system is the chair. When such a ring system is substituted as in the case of the *R*,*S*-dmtn ligand, the system can adopt several conformations of which only one chair conformation can have equatorially disposed methyl groups; the other conformations as well as the inverted chair

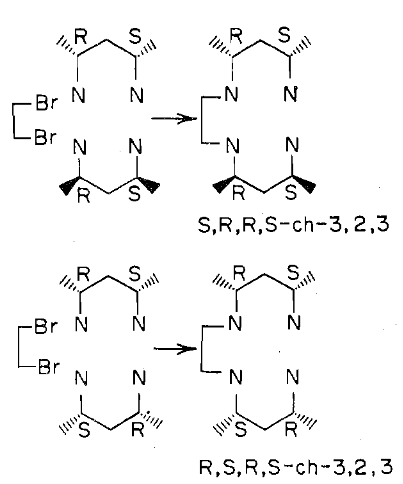

Figure 1. The two possible modes of reaction between *meso*-2,4-pentanediamine and ethylene dibromide where it will be noted that the racemic ligand *S,R,R,S*-ch-3,2,3 has the mirror image form *R,S,S,R*-ch-3,2,3 and that, for the meso ligand, *R,S,R,S*-ch-3,2,3 is the same as *S,R,S,R*-ch-3,2,3.

all have to a greater or lesser degree axially oriented methyl groups. Thus we would expect that the *R,S*-dmtn chelate ring system would be even more stabilized in the chair conformation than its unsubstituted analog. Except in cases where there are very severe bond angle deformations involved, we assume that when the *R,S*-dmtn system is incorporated in a quadridentate ligand, this strong preference for the chair conformation will persist in the *R,S*-dmtn residues. It is for this reason that we designate the two quadridentate ligands derived from *R,S*-dmtn as ch-3,2,3, although we do not wish to imply that in all the complexes we have prepared the ligand will adopt perfect chair chelate rings.

In the reaction between ethylene dibromide and excess *R,S*-dmtn, two ch-3,2,3 ligands are formed depending on the mode of reaction (Figure 1). The two ligands are therefore *R,S,S,R*:*S,R,R,S*-ch-3,2,3 (racemic) and *R,S,R,S*-ch-3,2,3 (meso) where the sequential order of the chiral centers is in conformity with the usual numbering sequence for organic systems. The product of the reaction was a high-boiling colorless viscous oil consisting of a mixture of the two quadridentate amines which we did not attempt to separate by fractional distillation. We have, however, obtained both of them in pure forms, as well as the racemic ligand optically active, by separating and resolving their cobalt(III) complexes.

2. Stereochemistries and Mode of Chelation

The two ligands give complexes displaying a rich variety of stereochemistries, but before we describe these, it is useful to discuss briefly the restrictions and flexibility of coordination that may be important in these systems. We attempt this in semiquantitative terms by imposing the following restrictions to these systems: (a) that the ethylenediamine cobalt chelate ring will prefer an unstrained gauche conformation, (b) that the six-membered chelate rings will prefer unstrained chair conformations, and (c) that all methyl groups will prefer equatorial dispositions. This restricts the number of isomers possible and implies complete stereospecificity of the active ligand. Figure 2 shows the possible stereochemistries of the ligands assuming these limitations, as well as some other topologies which do not comply with the above restrictions but which have actually been isolated.

It seems that for the active *S,R,R,S*-ch-3,2,3 ligand, the trans-*S,S* structure (I) is the most stable of all the geometries that this ligand could adopt. This is borne out by experiment, but this structure presents a problem with respect to the conformation of the inner five-membered chelate ring. Molecular models indicate that for the *S,S* inner nitrogen configurations the shown δ absolute configuration of this ring may only be slightly more stable than the λ configuration. Since the chirality of this ring is probably the major source of dissymmetric perturbation in this system, a serious ambiguity would arise in the interpretation of the circular dichroism spectra of these complexes. There is, however, very strong experimental and theoretical[11] evidence to support our assignment of the δ configuration to this ring. Thus the crystal structures of the *trans*-*R,R*-$[Co(3,2,3\text{-tet})(NO_2)_2]Br$,[8] *trans*-*R,R*-$[Co(3,2,3\text{-tet})Cl_2]NO_3$,[9] and $[Ni(cyclam)Cl_2]$[10] all have chair six-membered rings and δ five-membered rings for the *R,R* nitrogen configurations. Furthermore, recent studies[11] of complexes derived from a 3,2,3-tet ligand prepared from active propylenediamine show that the ligand is stereospecific in the trans geometry and the circular dichroism spectrum of the *trans*-dichloro complex is superimposable on the spectrum of the analogous complex made with the *S,R,R,S*-ch-3,2,3 ligand.

The relationships between the various geometries of the coordinated *S,R,R,S*-ch-3,2,3 ligand present a number of

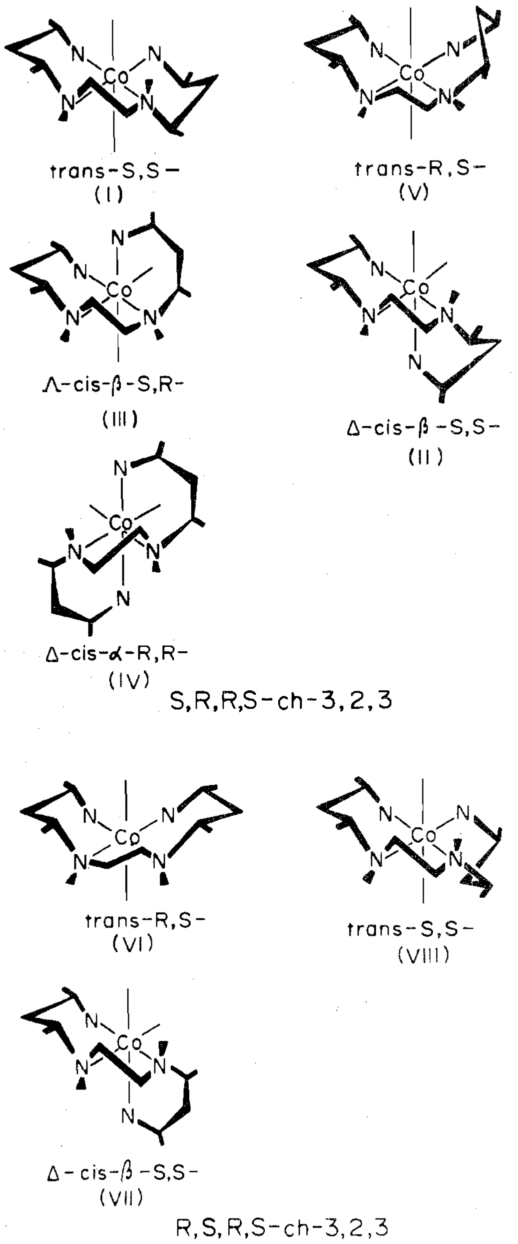

Figure 2. Some of the topologies and possible conformations of complexes derived from the active ligand *S,R,R,S*-ch-3,2,3 (I-V) and those of the meso ligand *R,S,R,S*-ch-3,2,3 (VI-VIII).

unusual features and we briefly discuss these. In generating the Δ-cis-β-*S,S* geometry II from I, that is, without inverting any of the inner nitrogen configurations, the moved chelate arm cannot adopt a chair ring with equatorial methyl groups. The choice seems to be between having a chair conformation with two axial methyl groups or a boat conformation in which the methyl groups can adopt pseudoequatorial dispositions. We suspect the system will prefer the latter as shown in II. If, however, the nitrogen atom associated with the moved chelate arm is inverted to give a meso inner nitrogen configuration and the opposite cis-β absolute configuration is adopted, then a reasonably strain-free Λ-cis-β-*S,R* geometry (III) is obtained where both six-membered rings are in the chair conformation with equatorial methyl groups. The same considerations apply in obtaining a stable cis-α geometry: it will be seen in Figure 2 that both inner nitrogen configurations must be inverted relative to the trans geometry in order that the cis-α complex may have both six-membered rings in the chair conformation with equatorial methyl groups. Thus the *S,R,R,S*-ch-3,2,3 ligand stereoselects the Δ-cis-α-*R,R* geometry (IV). The origins of these restrictions are connected with the fixed axial and equatorial positions of the bonds of the inner nitrogen atoms, and because a given six-membered ring is prevented from flipping between two chair forms, the process would involve an equatorial–axial interchange of the methyl groups. That these considerations are real is borne out by experiment where it is found that the ligand is completely stereospecific and that, for example, the cis-α complex cannot be converted to the trans without amino proton exchange despite the fact that the trans topology is more stable. Finally, the trans-*R,S* complex (V) has been prepared, and although one terminal ring can adopt a chair conformation with equatorial methyl groups, the other must be highly distorted, either as a chair with two axial methyl groups or as a distorted skew with one axial and one equatorial methyl group or a boat with both methyl groups pseudoequatorially disposed. We prefer the last as shown in V.

For the *ms-R,S,R,S*-ch-3,2,3 ligand only two isomers exist where the six-membered rings can be chair and the methyl groups equatorial, namely, the structures trans-*R,S* (VI) and Δ-cis-β-*S,S* (VII) (or Λ-cis-β-*R,R*). We have also obtained the trans-*S,S* complex (VIII) where we assume that the ring on the right will be a boat since this is the only conformation which allows the methyl groups to be "equatorial."

Thus the above semiquantitative arguments suggest that structures I, III, IV, VII, and possibly VI would be stable and that structures II, V, and VIII would be unstable. This is confirmed by experiment.

3. General Chemistry

A. Separation of the Ligands. A methanol solution of the mixed ch-3,2,3 quadridentate ligands and cobalt chloride is efficiently oxidized by air to give a mixture of brown peroxo complexes. When the methanol solvent is removed, the brown residue reacts with dilute HCl to give a sparingly soluble green *trans*-dichloro complex in about 50% yield. The filtrate is red, and when it is allowed to evaporate to dryness, a crystalline blue *cis*-dichloro complex is obtained in approximately 30% yield. The green and blue complexes cannot be converted into one another which suggests that the two complexes contain different amines. That this is true has been established by the isolation of the two amines from their optically active complexes after reduction with $\mathrm{SnCl_2}$ in HCl. The amine derived from the optically active trans complex was found to be optically active while the amine from the optically active cis complex was found to be without optical rotation. And when the active amine was complexed again, only the (optically active) trans complex was obtained with an identical rotation to the original material; no other species were detected. The inactive amine gave only the (inactive) blue cis complex. The amines give identical analyses and we conclude that the trans complex contains only the racemic ligand *R,S,S,R*:*S,R,R,S*-ch-3,2,3 which appears to be stereospecific (Figure 2 (I)) and that the cis complex contains only the meso ligand *R,S,R,S*-ch-3,2,3 (Figure 2 (VII)).

B. Complexes of the Racemic Ligand. The rather insoluble (racemic) *trans-R,R*:*S,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]Cl complex reacts readily in hot water with nitrite, azide, and thiocyanate ions to give *trans*-di-X complexes in high yields. A rapid reaction occurs with $\mathrm{Li_2CO_3}$ in water to give a mixture of carbonato complexes (see later) one of which, the *cis*-β-*R,R*:*S,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{CO_3}$]$^+$ ion, forms an insoluble perchlorate salt; this solid may be reacted with nitric acid to produce the very insoluble *trans*-(*R,R*:*S,S*)-dinitrato complex. The *trans*-(*R,R*:*S,S*)-dicyano complex is obtained in high yield from the reaction between the *trans*-dichloro perchlorate salt and sodium cyanide in dimethyl sulfoxide solution, and the *trans*-(*R,R*:*S,S*)-diammine complex is obtained by dissolution of the *trans*-dichloro chloride in liquid ammonia. The reaction between the *trans*-(*R,R*:*S,S*)-dinitro complex and dilute HCl can be controlled so that the maroon *trans*-(*R,R*:*S,S*)-nitrochloro complex is obtained, and by the use of this complex the *trans*-(*R,R*:*S,S*)-nitroazido and nitroisothiocyanato complexes can be obtained by simple anation reactions. All these compounds are of similar aqueous solubility to the unsubstituted analogs but tend to be more soluble in organic solvents.

We have resolved the *trans*-(*R,R*:*S,S*)-dinitro complex by means of its α-bromocamphor-π-sulfonate salt. Using this resolved *trans*-dinitro complex we have been able to convert it into all the above complexes with full retention of optical activity.

In order to investigate the stereochemistry of the complexes of the racemic ligand, we have allowed the *trans-R,R*:*S,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]Cl complex to react with $\mathrm{Li_2CO_3}$ in water in the presence of activated charcoal. The reaction appears to reach equilibrium after about 1 hr at 100°, and if the filtered red solution is treated with hydrochloric acid, a 60% recovery of the original *trans*-(*R,R*:*S,S*)-dichloro complex is obtained; the remaining solution is violet. The violet solution may be evaporated to dryness to give a blue residue which is partly soluble in 5 *M* HCl, leaving the blue complex *cis*-α-*R,R*:*S,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]Cl. Addition of $\mathrm{HClO_4}$ to the blue extract results in the precipitation of the blue-violet *cis*-β-*R,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]$\mathrm{ClO_4}$ complex. This last compound may be dissolved in hot acidified (HCl) methanol (or ethanol) to give a green solution containing predominantly the *trans-R,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]$^+$ ion which can be isolated as green crystals of the $\mathrm{ClO_4^-}$ salt. The corresponding optically active complexes of these last three isomers have been obtained in low yield and with great difficulty because of their much greater solubility compared to their racemic analogs and because the active cis-β-*R,S* and the trans-*R,S* complexes are of similar solubility in relation to their proportions in alcoholic solutions. We have been unable to prepare the *cis*-β-*R,R*:*S,S*-[Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{Cl_2}$]$^+$ ion because, even at −5°, the only solid produced by the reaction of the carbonato complex with methanolic HCl is the green *trans*-(*R,R*:*S,S*)-dichloro complex.

Numerous other [Co(*R,S,S,R*:*S,R,R,S*-ch-3,2,3)$\mathrm{X_2}$]$^{n+}$ complexes, *e.g.*, the dibromo, hydroxoaquo, dihydroxo, diaquo, and the acetylacetonato species, are readily prepared; the *trans*-(*R,R*:*S,S*)-dihydroxo cation, perhaps surprisingly, is readily precipitated from aqueous solution as its perchlorate salt. We have not studied these complexes in any detail.

C. Complexes of the Meso Ligand. The *cis*-β-*R,R*:*S,S*-

[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl$_2$]Cl dissolves in hot aqueous HCl to give a dull violet solution which, upon the addition of HClO$_4$, slowly deposits green needles of *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl$_2$]ClO$_4$. This trans complex dissolves in neutral water to give a pink-violet solution of the *cis*-β-chloroaquo species, which reacts with N$_3^-$ ions to give the very insoluble brown-red complex *cis*-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)(N$_3$)$_2$]N$_3$. It appears that in the cis-β geometry the racemic nitrogen configuration is the most stable since the *cis*-β-dichloro complex may be heated in strong sodium hydroxide solution from which, by the addition of sufficient HCl, the identical *cis*-β-dichloro complex may be isolated in quantitative yield. Although the cis-β topology is more stable in water, where the ion exists mainly as the *cis*-β-chloroaquo species, an acidified methanol solution of the *cis*-β-dichloro species gives an equilibrium mixture of *cis*-β-dichloro and *trans*-dichloro species both with racemic inner nitrogen configurations. This equilibrium is strongly dependent on the Cl$^-$ ion concentration, being displaced to the cis species with increasing Cl$^-$ ions. While the racemic inner nitrogen configuration is the most stable for the cis-β geometry in both methanol and water, this is not so for the trans species in methanol. Thus in hot neutral methanol proton exchange occurs and an equilibrium between the *trans*-(*R*,*R*:*S*,*S*)-dichloro and the *trans*-*R*,*S*-dichloro species is set up; the latter has been isolated. A clean equilibrium cannot be obtained for the two trans isomers since *cis*-β-(*R*,*R*:*S*,*S*)-dichloro species is always present but about 50% of the starting material is converted to the *trans*-(*R*,*S*)-dichloro isomer. Unlike the *trans*-(*R*,*R*:*S*,*S*)-dichloro complex, the *trans*-(*R*,*S*)-dichloro species prefers to remain trans in dilute aqueous HCl solutions. In aqueous basic solutions proton exchange occurs and upon acidification a quantitative recovery of the *cis*-β-*R*,*R*:*S*,*S*-dichloro isomer is generated.

The *cis*-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl$_2$]Cl complex readily reacts with CO$_3^{2-}$ ions in water to give the sparingly soluble *cis*-β-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO$_3$]Cl complex which can be resolved into enantiomeric forms by precipitation with the active α-bromocamphor-π-sulfonate ion. The active carbonato complex can be converted to the active *cis*-β-dichloro and *trans*-dichloro complex. The active *cis*-β-diazido species has also been prepared.

Though possible, we have not investigated the generation of the cis-β-*R*,*S* complexes by, for example, treating the *trans*-*R*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl$_2$]Cl complex with oxalic acid.[1]

4. Stereochemistry and Diastereoisomerism

A. Racemic Ligand. The general topology and the stereochemistry of the complexes have been determined by means of nmr spectra, visible absorption spectra, circular dichroism spectra, and a number of chemical interconversions. For most of the complexes a combination of these techniques is sufficient to establish the stereochemistry; for the others, where some ambiguity remains, the physical data are consistent with the proposed stereochemistry. The nmr spectra, which were carried out in (CD$_3$)$_2$SO–DCl and/or D$_2$O–DCl, in principle can distinguish complexes possessing a twofold axis (cis-α and trans complexes with racemic inner nitrogen configurations) from those having C_1 symmetry (cis-β and trans complexes, the latter with meso inner nitrogen configurations). Thus the nmr signals of amino protons of C_2 complexes should integrate as even ratios and there should only be two equally intense methyl proton resonances. The resolution of the methyl resonances, particularly in DMSO, is not always good although they tend to sharpen in water, but we have found the amino proton resonances to be generally useful.

The visible absorption spectra of the trans complexes of the racemic ligand are almost superimposable on those of the *trans*-[Co(3,2,3-tet)XY]$^{n+}$ complexes which we described previously.[1] The absorption spectra of the *trans*-dinitrato, -dichloro, and -diazido complexes are quite diagnostic of the trans configuration.[1] The *trans*-dinitro, -diammino, -diisothiocyanato, and -dicyano complexes, the visible absorption spectra of which are not totally unambiguous, show nmr spectra which indicate a twofold axis in the molecule. Thus the diammino complex shows two clearly resolved methyl doublets around τ 8.2 in D$_2$O–DCl. Similarly the dicyano complex shows two reasonably well-resolved methyl doublets around τ 8.8 as well as an isolated amino proton doublet of area 2 at τ 5.3 in (CD$_3$)$_2$SO–DCl. The methyl resonances of the *trans*-dinitro and -diisothiocyanato complexes which appear at τ 8.8 and 8.7, respectively, in (CD$_3$)$_2$SO–DCl are not clearly resolved into two doublets but the dinitro shows two amino proton resonances at τ 5.1 and 6.2 of areas 4:2, respectively, while the diisothiocyanato species shows three amino proton resonances at τ 4.2, 4.7, and 5.5 of area ratios 2:2:2. In all cases the amino proton resonances show some splitting and are broad, presumably because of quadrupolar interaction of the nitrogen nucleus, but the chemical shifts are sufficiently large so that the integration of the broad manifolds does not lead to ambiguity in identifying sets of protons. Thus all the above complexes possess a twofold axis and are assigned the trans-*R*,*R*:*S*,*S* configuration because of not only their consistent visible absorption spectra but also, as we shall see in the next paper, their circular dichroism spectra which are characteristic of trans species being weak in intensity and showing splittings of the d-electron manifold consistent with the trans formulation.

The remaining unsymmetrical trans complexes, namely, nitro-X, X$^-$ = Cl$^-$, NCS$^-$, N$_3^-$, have been assigned the trans configuration because of their visible spectra and the magnitude and splitting patterns shown by their circular dichroism spectra.

The three cis complexes of the racemic ligand, namely, the *cis*-β-carbonato with racemic inner nitrogens, the *cis*-β-dichloro with meso inner nitrogens, and the *cis*-α-dichloro (which is geometrically constrained to have racemic inner nitrogens) all have visible absorption and circular dichroism spectra (see later) which are characteristic of cis complexes. Their topologies are assigned and distinguished by nmr; the C_2 *cis*-α-dichloro complex shows three sets of amino proton resonances at τ 3.0, 3.9, and 5.3 in (CD$_3$)$_2$SO–DCl solution in the ratio 2:2:2. The methyl resonances, although sharp, are overlayed by methylene protons. The two cis-β isomers both show complex methyl resonances in DMSO or water indicating the unsymmetrical disposition of the chelate arms, and, in addition in (CD$_3$)$_2$SO–DCl, the *cis*-β-*R*,*S*-dichloro complex shows an isolated amino proton resonance at τ 3.5 of area 1, while the *cis*-β-*R*,*R*:*S*,*S*-carbonato complex shows an isolated amino proton resonance of unit area at τ 5.

The remaining complex of this ligand, namely, the green *trans*-dichloro complex with meso inner nitrogen atoms, shows, in (CD$_3$)$_2$SO–DCl, a well-isolated amino proton resonance of unit area at τ 3.4, indicating that the molecule is devoid of a twofold axis. This nmr spectrum is quite distinct from that observed for the C_2 *trans*-*R*,*R*:*S*,*S*-dichloro complex which, in (CD$_3$)$_2$SO–DCl, shows two well-resolved methyl resonance doublets at around τ 8.8 and two amino proton resonances at τ 4.5 and 5.7 having area ratios of 4:2, respectively.

In all the above experiments the amino proton resonances were identified by deuteration. These deuteration studies have also helped in the assignment of the relative absolute configurations of the trans complexes (see later) as well as in identifying the geometrical isomerism of the inner nitrogen configurations of the cis complexes.

Figure 3 shows the various interconversions performed with these complexes of the racemic ligand. Of particular interest is the fact that the dinitro, diazido, dinitrato, nitroacido (Cl$^-$, N$_3^-$, NCS$^-$), and the *cis*-β-*R*,*R*:*S*,*S* carbonato complexes can

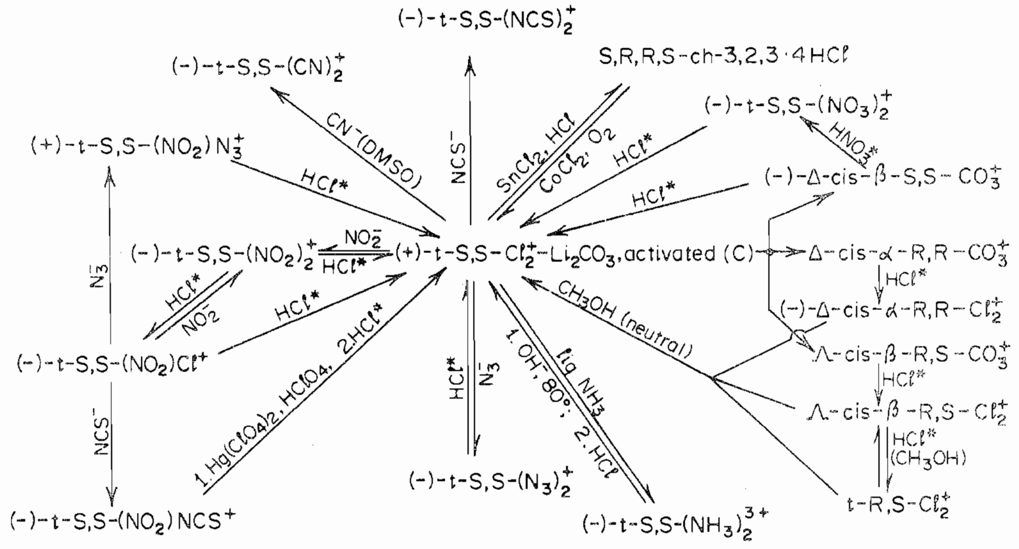

Figure 3. Chemical interconversions of complexes containing the optically active *S,R,R,S*-ch-3,2,3 ligand. Reactions marked with an asterisk proceed without proton exchange; t = *trans*. All conversions regenerate identical optical activity.

all be converted to the *trans-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)Cl$_2$]$^+$ ion without proton exchange. This was shown by nmr and establishes the racemic inner nitrogen configuration of the starting complexes. Although the *trans*-diammino, -dicyano, and -diisothiocyanato complexes could not be converted to the *trans*-dichloro complex without concomitant proton exchange, their nmr spectra establish their racemic inner nitrogen configurations.

The blue *cis-α*-dichloro complex must have racemic inner nitrogen configurations for steric reasons (Figure 2) and in addition these must be of the opposite configuration to the more stable trans isomer. We present evidence later to support this assertion.

The blue-violet *cis-β-*(*R,S*)-dichloro complex is converted in acidic methanol without proton exchange to the *trans*-(*R,S*)-dichloro complex, the structure of which has been established by nmr and hence the carbonato complex has a meso configuration of its inner nitrogen atoms.

B. Meso Ligand. The visible absorption spectra establish the gross stereochemical features of these complexes; thus the two green complexes have spectra characteristic of *trans*-dichlorotetraamine complexes, while the blue dichloro, pink carbonato and chloroaquo, and brown-violet diazido complexes show characteristic *cis*-tetraamine spectra. Unlike the racemic ligand complexes, only the *trans-R,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl$_2$]$^+$ complex ion formed by the meso ligand has a plane of symmetry (provided the inner ring is flipping); all the other stereochemistries are devoid of any elements of symmetry (Figure 2). The *trans*-dichloro complex with meso inner nitrogen atoms shows two well-resolved methyl proton doublets around τ 8.8 in (CD$_3$)$_2$SO–DCl as well as two well-separated amino proton resonances at τ 4.0 and 4.7 of areas 2:2. This establishes the stereochemistry of the complex as well as indicates that if the inner five-membered ring is puckered, it is rapidly flipping. The other *trans*-dichloro complex must have racemic inner nitrogen atoms since it has been resolved and its nmr spectrum, as well as those of the cis complexes, shows its lack of symmetry in both amino proton and methyl proton nmr resonances.

Our assignment of the cis-*β* geometry to the other cis complexes is not unambiguous and is based on the assumption that the two terminal chelate arms will prefer to adopt chair conformations with equatorial methyl groups; this is possible in the cis-*β* but not the cis-*α* geometry (Figure 2). The general tendency of these complexes to prefer a cis geometry, in contrast to most other 3,2,3-tet complexes, suggests that the steric demands of the rings are important: if this is so then the cis-*β* will be preferred over the cis-*α* geometry. Since these cis complexes are converted without proton exchange to the *trans*-(*R,R:S,S*)-dichloro complex, the inner nitrogen atom configurations of these complexes must also be racemic; this allows the two terminal rings to adopt stable conformations in the cis-*β* geometry. As we shall see, the circular dichroism spectra of these complexes are suggestive of the cis-*β* geometry but are not conclusive.

5. Optical Stability and Stereochemical Equilibria

A. Racemic Ligand. In basic media the trans complexes of the racemic ligand with racemic inner nitrogen atoms exchange their amino protons rapidly but the optical activity does not change. We have obtained no evidence for any other diastereomers and we assume the ligand to be completely stereospecific. The *cis-α*-dichloro complex can be substituted with OH$^-$ and N$_3^-$ ions with complete retention of optical activity and topology, but, as in the cases of the *cis-β-*(*R,S*)-dichloro and the *trans*-(*R,S*)-dichloro species, it eventually reverts back to *trans*-(*R,R:S,S*)-dichloro complex in neutral or basic solutions. This strong preference for the trans configuration with racemic inner nitrogen atoms is similar to the preferences shown by the 3,2,3-tet ligand; but unlike the latter, where only the *cis-β-R,R:S,S*-[Co(3,2,3-tet)CO$_3$]$^+$ species was detected at equilibrium, an equilibrated solution of the carbonato complex of the substituted racemic ligand gives the three isomers *cis-β-R,R:S,S*-, *cis-β-R,S*-, and *cis-α-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)CO$_3$]$^+$ in the ratio 3:1:1, respectively. As we have pointed out previously the *cis-β-*(*R,R:S,S*)-dichloro complex appears to be very unstable and reverts to the trans while the *cis-β-*(*R,S*)-dichloro species forms a chloride-dependent equilibrium with the *trans*-(*R,S*)-dichloro isomer in acidic methanol and the *cis-α*-(*R,R:S,S*)-dichloro complex is indefinitely stable in acid solutions.

B. Meso Ligand. The meso ligand shows quite different behavior in its complexes. In neutral water (where aquation is rapid and extensive and the complex exists as the cis-*β* isomer) and also in basic aqueous solution only isomers with racemic nitrogen atoms could be detected. In neutral methanol, however, where trans complexes tend to be favored, the [Co(*R,S,R,S*-ch-3,2,3)Cl$_2$]$^+$ ion forms an equilibrium mixture of species containing racemic inner nitrogen atoms (both cis-*β* and trans) and species having meso nitrogen configurations (only trans) in about equal proportions. Of the two trans

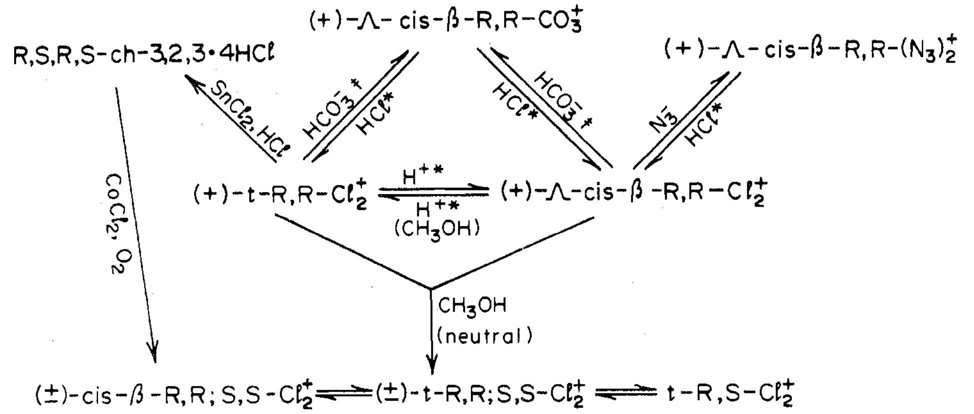

Figure 4. Chemical interconversions of complexes containing the meso ligand *R,S,R,S*-ch-3,2,3. Reactions marked ‡ proceed with greater than 95% retention of chirality; those marked with an asterisk proceed without proton exchange. The equilibrium in neutral methanol, where amino proton exchange and racemization occur, is shown on the bottom line.

complexes, the complex with the meso inner nitrogen configurations is preferred while the one with racemic nitrogen atoms tends to isomerize to the *cis*-β-(*R,R*:*S,S*)-dichloro complex in methanol. Thus using the perchlorate salt, the *trans*-(*R,R*:*S,S*)-dichloro predominates in methanol over the *cis*-β-(*R,R*:*S,S*)-dichloro isomer, but as chloride ions are added to the solution, the concentration of the cis-β-*R,R*:*S,S* isomer increases until it becomes the predominant species. The *trans*-(*R,S*)-dichloro ion appears to be insensitive to chloride ion concentration and remains trans under these conditions.

The cis-β complexes are slow to racemize in basic aqueous solution where amino proton exchange occurs. This is presumably related to the probability that racemization occurs most easily through the trans complex of which there must be very little in dilute aqueous solutions. As a consequence the *cis*-β-chloroaquo species can be substituted with basic anions such as CO_3^{2-}, NO_2^-, OH^-, and N_3^- with very little racemization (Figure 4). In methanol, however, the active *trans*-*R,R*-[Co(*R,S,R,S*-ch-3,2,3)Cl_2]ClO_4 is substituted by the (basic) N_3^- ion with extensive racemization but in neutral room-temperature methanol the half-life of racemization is of the order of hours which is an optical stability comparable to that of the active *trans*-*R,R*-[Co(3,2,3-tet)Cl_2]$^+$ ion.

6. Optical Purity and Absolute Configurations

A. Racemic Ligand. All the optically active complexes of the racemic ligand were prepared by chemical conversions from the resolved *trans*-dinitro species and the optical purity of the derived complexes is in part related to the extent of the initial resolution. We have made no quantitative determination of the optical purity but the generation of antipodes of the dinitro salt of equal and opposite rotation and the regeneration of the original rotations after exhaustive chemical interconversions (Figure 3) of a large number of species which have been crystallized several times leave little doubt that all the complexes are optically pure.

The absolute configurations of these complexes have been assigned on the basis of the circular dichroism spectra shown by both their cis and trans isomers and from these assignments the absolute configuration of the ligand may be inferred from the conformational arguments given previously and from the fact that we have shown the ligand to be stereospecific. The circular dichroism spectra of the trans complexes derived from the levorotatory dinitro complex bear a remarkable similarity to those shown by the corresponding *trans*-*R,R*-[Co(3,2,3-tet)X_2]$^{n+}$ analogs. (The two sets of spectra are shown in the preceding and following papers.) This suggests that the two series of complexes have the same absolute configurations provided we make the assumption that the two sets of compounds have the same conformations, which appears to be the case because, as we shall see in subsequent papers, the corresponding systems of the 3,2,3-tet type where substituents force the terminal rings into skew conformations show circular dichroism spectra completely different for these two series. Since the *trans*-*R,R*-[Co(3,2,3-tet)X_2]$^{n+}$ ions have a δ inner five-membered ring[8,9] and, bearing in mind the stereospecificity of the ch-3,2,3 ligand, it follows that the complexes derived from the levorotatory dinitro complex have the absolute configuration *trans*-*S,S*-[Co(*S,R,R,S*-ch-3,2,3)X_2]$^{n+}$.[12]

These assignments are supported by the circular dichroism spectra of the cis complexes. From the chemical interconversions shown in Figure 3, it follows that if the inner nitrogen configurations are *S,S*, the cis-β carbonato complex with racemic inner nitrogen atoms must have the Δ configuration (Figure 2). Furthermore, from the considerations shown in Figure 2 and the supporting chemical evidence, the *S,R,R,S*-ch-3,2,3 ligand will give a cis-α complex with a Δ absolute configuration and an (inverted) *R,R* configuration for the inner nitrogen atoms and a cis-β-*R,S* complex with a Λ absolute configuration.

In Figure 5 we show the absorption and circular dichroism spectra of the Δ-*cis*-β-*S,S*-[Co(*S,R,R,S*-ch-3,2,3)CO_3]$^+$, Λ-*cis*-β-*R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$, and Δ-*cis*-α-*R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ ions. It will be seen that the Δ-cis-β-*S,S* carbonato complex shows a circular dichroism spectrum under the $^1A_{1g} \rightarrow {}^1T_{1g}$ manifold very similar to that of the Δ-*cis*-β-*R,R*-[Co(3,2,3-tet)CO_3]$^+$ ion, the absolute configuration of which is known unambiguously.[1,2] The Δ-*cis*-α-(*R,R*)-dichloro complex shows a circular dichroism which has a plus–minus pattern under the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition characteristic of Δ-cis-α quadridentate amine systems of known absolute configuration.[13-15] The circular dichroism spectrum of the Λ-*cis*-β-(*R,S*)-dichloro complex is perhaps not as definitive but its minus–plus pattern under the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is consistent with its assigned Λ configuration.[13-15]

Thus the circular dichroism spectra of the cis and trans complexes are internally consistent and each correlates with similar systems of known configuration and hence the assignments of both the complexes and the ligand may be put forward with some confidence.

B. Meso Ligand. The optically active cis-β-*R,R* and cis-β-*S,S* carbonato complexes of the meso ligand were fractionally crystallized to constant equal and opposite rotation. The same was done with the *trans*-dichloro enantiomers derived from the active carbonato complexes. The resultant carbonato and dichloro complexes were then converted to the *cis*-β-dichloro complex under acid conditions where no proton exchange occurs; the products had identical (opposite) rotations from either starting material. We therefore conclude that these three complexes were prepared optically pure.

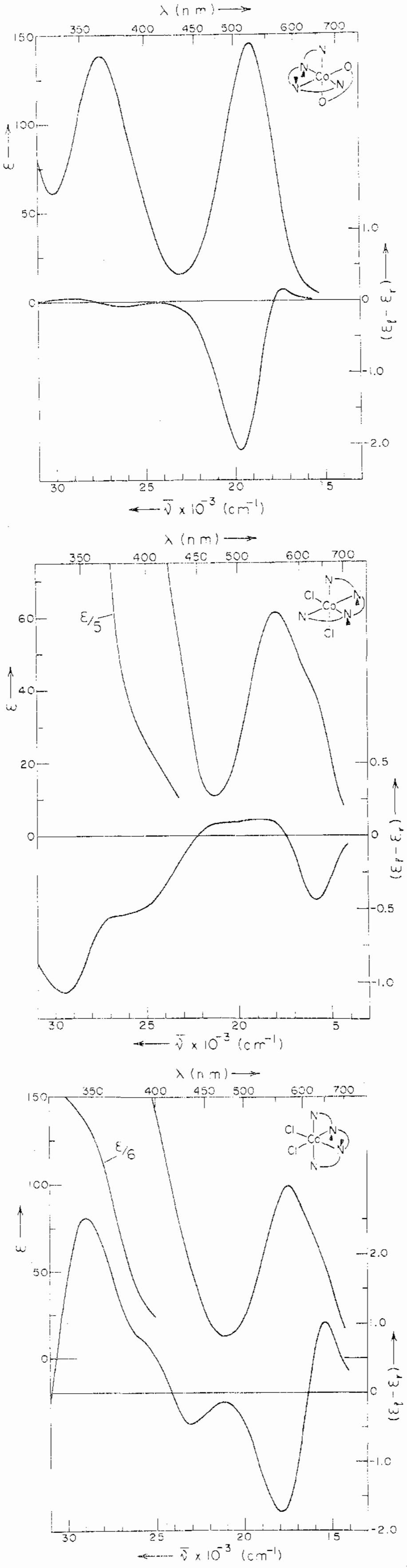

Figure 5. The absorption and circular dichroism spectra, from top to bottom: Δ-*cis*-β-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)CO_3]ClO_4 in H_2O, Λ-*cis*-β-*R*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4 in DMSO (HCl), and Δ-*cis*-α-*R*,*R*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]Cl in CH_3OH (HCl).

The assignment of the absolute configurations of these complexes is dependent on our original topological assignment of the cis-β complexes which we assigned on the basis of conformational arguments and consistent physical properties.

In Figure 6 we show the absorption and circular dichroism spectra of the Δ-*cis*-β-*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)X_2]$^+$ where X = Cl^-, N_3^-, CO_3^{2-}. It will be seen that all show a minus-plus pattern under the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition with a major negative band. The Δ-*cis*-β-*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]$^+$ ion shows a circular dichroism spectrum almost identical with that shown by the Δ-*cis*-β-*R*,*R*-[Co(3,2,3-tet)CO_3]$^+$ ion of established[1] absolute configuration and it is on this basis that we assign the Δ absolute configuration to these complexes; the *S*,*S* absolute configuration of the inner nitrogen atoms follows from stereospecificity arguments (Figure 2). We include the diazido spectrum because of the very large circular dichroism shown by the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The magnitude of this Cotton effect is almost an order of magnitude greater than that of any polyamine system so far recorded. We are uncertain as to the precise reason for this.

Since the Δ-cis-β-*S*,*S* carbonato complex can be converted to the (−)-*trans*-dichloro complex without proton exchange (Figure 4), it follows that the (−)-*trans*-dichloro complex has an absolute configuration specified as *trans*-*S*,*S*-(δ)-[Co-(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]$^+$ (Figure 2).

7. Experimental Section

The instruments used in obtaining the physical measurements were as follows: nmr, Varian T60 and HA100 using TMS as an internal reference; visible and ultraviolet spectra, Unicam SP820 (series 2) recording spectrometer; circular dichroism, Roussell-Jouan Dichrographe Mark II; conductance, Yellow Springs Instrument Co. Model 31 conductivity bridge (all solutions 1×10^{-3} *M*); optical rotations, Perkin-Elmer 141 digital recording polarimeter.

In all these measurements due care was taken with respect to complications that may arise from dissociation, isomerism, and ion association. The inferences drawn from the measurements are reliable insofar as these effects have been eliminated.

A. Preparation of *R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*- and *R*,*S*,*R*,*S*-ch-3,2,3. (*R*,*S*)-2,4-Diaminopentane (75 g) was heated on the steam bath as 1,2-dibromoethane (8 ml) was slowly added over a period of 45 min. The reaction mixture was heated another 30 min and then cooled before distilling out the bulk of excess diamine under water pump vacuum. KOH (11 g) in methanol (75 ml) was added to the viscous pale yellow residue remaining after the distillation temperature had reached 65°. On cooling, ether (150 ml) was added and the mixture was allowed to stand 30 min to allow KBr to settle. The solution was filtered and fractionally distilled under water pump vacuum, the mixed quadridentates being collected as a well-isolated fraction between 160 and 200°; yield 14.5 g (74%). Redistillation gave a colorless, viscous liquid.

B. Separation of *R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*- and *R*,*S*,*R*,*S*-ch-3,2,3. Solutions of the quadridentates (12.0 g) in methanol (50 ml) and $CoCl_2 \cdot 6H_2O$ (12.0 g) in methanol (200 ml) were mixed and oxidized by vigorous passage of air for 2 hr. The methanol was removed under vacuum and the brown residue slurried with water (75 ml, 80°). HCl (12 *M*, 25 ml) was added and the resulting solution was heated on the steam bath for 10 min. The resultant mixture of green solid and violet solution was allowed to cool for 90 min at room temperature and then filtered, the green precipitate being washed with HCl (2 *M*, 25 ml), absolute ethanol, and ether; yield 9.8 g (47%). This *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]Cl complex may be recrystallized from dilute HCl but, because of its rather small temperature gradient of solubility, is reprecipitated in only fair recovery and a more convenient procedure is simply to dissolve the solid in a slight excess of warm 1 *M* NaOH, filter, and add HCl (12 *M*) to precipitate small, yellow-green needles; Λ_M = 85.0 $cm^2\ ohm^{-1}\ mol^{-1}$ (in methanol).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)Cl_2]Cl·0.5H_2O: C, 35.6; H, 7.7; N, 13.8; Cl, 26.3. Found: C, 35.7; H, 7.8; N, 13.9; Cl, 26.2.

The violet filtrate from the green precipitate began to deposit a flocculent violet solid immediately after filtration, but this *cis*-chloroaquo complex could not be obtained in good yield without

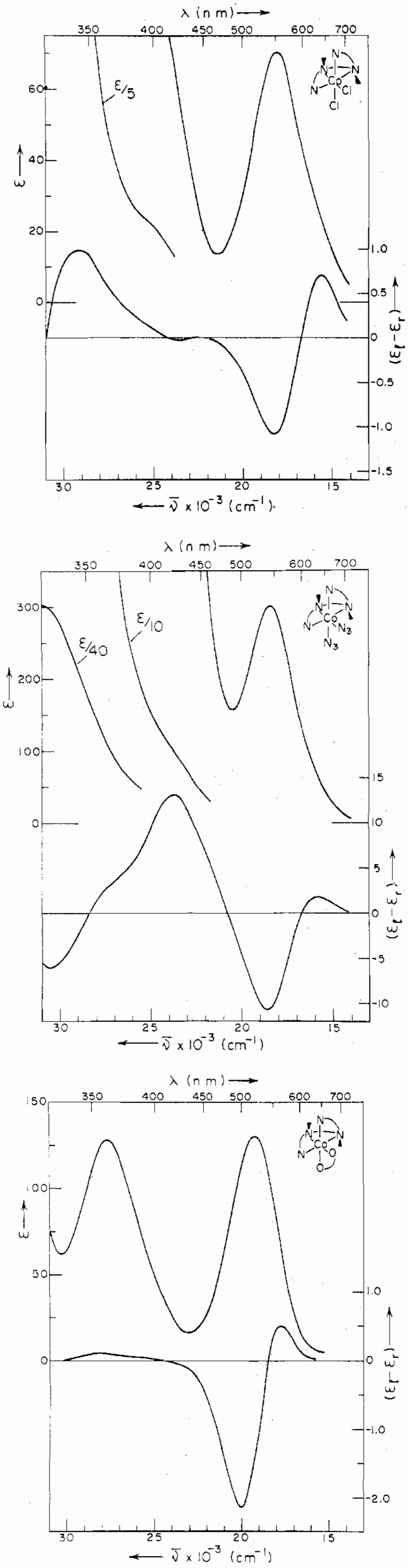

Figure 6. The absorption and circular dichroism spectra of the three complexes Δ-*cis*-β-*S,S*-$[Co(R,S,R,S\text{-ch-}3,2,3)X_2]^+$, X = Cl^-, N_3^-, CO_3^{2-}. The dichloro complex is in DMSO–HCl solution as the Cl^- salt, the diazido complex is in methanol as the NO_3^- salt, and the carbonato complex is in water solution as the Cl^- salt.

reduction of the filtrate volume and consequent contamination with its blue *cis*-dichloro anation product and this in turn could not be obtained free of Co(II). Hence, the filtrate was taken to dryness under vacuum and the blue crystalline residue was redissolved in HCl (5 *M*, 50 ml, 80°). The dull violet solution was mixed with $HClO_4$ (12 *M*, 10 ml) and allowed to stand at 0° for 12 hr to deposit fine green needles of *trans-R,R:S,S*-$[Co(R,S,R,S\text{-ch-}3,2,3)Cl_2]ClO_4$ (7.2 g), slightly contaminated with residual *trans-R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]ClO_4$. This solid was heated with methanol (50 ml) containing HCl (12 *M*, 5 ml); its rapid dissolution was followed by rapid precipitation of small, deep blue crystals of *cis*-β-*R,R:S,S*-$[Co(R,S,R,S\text{-ch-}3,2,3)Cl_2]Cl$ which, after cooling for 3 hr at 0°, were filtered off and washed with methanol and ether; yield 6.0 g (29%). The complex was recrystallized from boiling methanol (in which it gives a green solution) by cooling and slowly adding an equal volume of ether; Λ_M = 61 $cm^2\ ohm^{-1}\ mol^{-1}$ (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl$: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.5; H, 7.8; N, 13.9; Cl, 26.4.

C. Co(III) Complexes of *R,S,S,R:S,R,R,S*-ch-3,2,3. ***cis*-β-*R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)CO_3]ClO_4$.** *trans-R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]Cl\cdot0.5H_2O$ (0.70 g) and Na_2CO_3 (0.30 g) in water (20 ml) were heated on the steam bath for 30 min. The deep pink-violet solution formed was filtered, $NaClO_4$ (2.0 g) was dissolved in, and the mixture was allowed to stand at 0° for 12 hr. The precipitate of pink-violet needles was collected and washed with methanol (5 ml), ethanol, and ether (0.50 g, 64%). Some additional solid could be obtained by reducing the filtrate volume on the steam bath and again allowing the mixture to stand. The complex recrystallized from water as thin plates; Λ_M = 85 $cm^2\ ohm^{-1}\ mol^{-1}$ (in water).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)CO_3]ClO_4$: C, 34.7; H, 6.7; N, 12.5. Found: C, 34.4; H, 6.7; N, 12.2.

Even at −5° the only solid obtained on treatment of this complex with HCl was *trans-R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]Cl$. However, treatment of its preparative solution filtrate with HCl does not lead to regeneration of solely this dichloro complex and in fact three other diastereoisomeric forms can eventually be isolated from this solution. We now describe these.

***cis*-α-*R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]Cl$.** A mixture of *trans-R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]Cl$ (4.0 g), Li_2CO_3 (1.5 g), and activated charcoal (0.2 g) in water (30 ml) was heated on the steam bath for 1 hr. The violet solution formed was filtered, mixed with HCl (12 *M*, 10 ml), and heated on the steam bath for 5 min partially reprecipitating the starting complex. After cooling at 0° for 12 hr, this precipitate (2.6 g, 65%) was filtered off and the violet filtrate was taken to dryness under vacuum. The blue residue was extracted with HCl (6 *M*, 10 ml) by heating on the steam bath for 15 min and then allowed to cool at room temperature for 2 hr. The insoluble blue powder (0.6 g, 15%) thus remaining was filtered off and extracted a second time with boiling methanol (50 ml) containing HCl (12 *M*, 5 ml) to ensure freedom from residual starting complex. The remaining blue solid was the *cis*-α-*R,R:S,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]Cl$ complex. This was recrystallized (in poor recovery) from dilute HCl (1 *M*, 30 ml, 80°) by adding concentrated HCl (12 *M*, 30 ml) and heating until precipitation was initiated. Very small blue crystals were thereby obtained; Λ_M = 66 $cm^2\ ohm^{-1}\ mol^{-1}$ (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl$: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.5; H, 7.5; N, 14.3; Cl, 27.2.

***cis*-β-*R,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]ClO_4$.** The first HCl extract was mixed with $HClO_4$ (6 *M*, 10 ml) and gently warmed to cause rapid precipitation of a violet powder (0.6 g, 13%). After standing at room temperature for 1 hr this was collected and washed with $HClO_4$ (2 *M*, 10 ml), ethanol, and ether. Recrystallization from HCl (6 *M*, 25 ml, 80°) by the addition of $HClO_4$ (12 *M*, 1 ml) gave clusters of long, blue-violet needles; Λ_M = 86 $cm^2\ ohm^{-1}\ mol^{-1}$ (in methanol, extrapolated).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]ClO_4$: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.5; H, 6.6; N, 12.3; Cl, 23.5.

***trans-R,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]ClO_4$.** *cis*-β-*R,S*-$[Co(R,S,S,R:S,R,R,S\text{-ch-}3,2,3)Cl_2]ClO_4$ (0.30 g) and absolute ethanol (30 ml) containing HCl (12 *M*, 0.3 ml) were heated on the steam bath until a green solution had formed (*ca.* 10 min). This was cooled, filtered, mixed with $HClO_4$ (12 *M*, 0.5 ml), and diluted with ether (150 ml). A powdery green solid, slightly contaminated with the starting complex, quickly deposited and, after storage at 0° for 30 min, was filtered off and washed with ether. To remove the cis complex contaminant the solid was extracted with ice-cold acidified (HCl) ethanol (two 5-ml portions) and quickly filtered into ether (100 ml) and $HClO_4$ (12 *M*, 0.5 ml). This procedure was repeated finally to provide fine, pale green needles (0.10 g, 33%); Λ_M = 82 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]ClO_4$: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.2; H, 6.8; N, 12.1; Cl, 23.4.

***trans-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)(NO$_2$)$_2$]I.** *trans-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)Cl$_2$]Cl (14.2 g) was added in portions to a boiling solution of $NaNO_2$ (14.2 g) in water (500 ml). A rapid reaction occurred to give a deep yellow-orange solution. This was filtered hot and then treated with excess NaI to precipitate small golden needles, after cooling at 0° for 1 hr. These were collected and washed with water, ethanol–ether (1:1), and ether (16.7 g, 94%). The complex was recrystallized from methanol; Λ_M = 76 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)(NO_2)_2]I$: C, 28.4; H, 5.9; N, 16.5. Found: C, 28.3; H, 6.2; N, 16.8.

Resolution of *trans-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)(NO$_2$)$_2$]I. *trans-R,R:S,S*-[Co(*R,S,S,R:S,R,R,S*-ch-3,2,3)(NO$_2$)$_2$]I (4.01 g) was added to a boiling solution of Ag(+)BCS (3.30 g) in methanol (100 ml), and the mixture was shaken vigorously for 5 min, while being kept hot. The AgI was filtered off and washed with boiling methanol (five 10-ml portions), and the filtrate–wash was taken to dryness under vacuum. The yellow residue was taken up in water (70 ml, 100°), filtered, and allowed to stand at 0° for 12 hr to precipitate flaky, golden crystals, 1.1 g [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = +0.357$ in water]; Na D line rotations of the diastereoisomers are similar, so that the resolution is not conveniently monitored by this method. These were washed with water (10 ml), acetone, and ether. Successive reductions of the filtrate volume to 50, 35, 25, and 15 ml gave crystalline precipitates of 1.3 g [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = -0.171$], 0.4 g [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = +0.149$], 0.8 g [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = -0.393$], and 0.3 g [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = +0.385$], respectively. No further diastereoisomer precipitates could be obtained without a large degree of contamination with a yellow decomposition product formed during the repeated crystallization. The (+) CD diastereoisomer fractions were recrystallized (separately) from water (100°, *ca.* 20 ml g^{-1}) and the (−) isomer from methanol (66°, *ca.* 10 ml g^{-1}). All precipitates then showed CD of the same magnitude and this was not increased by repeated recrystallization. Impure diastereoisomers were recovered from the recrystallization filtrates and fractionated again from water and methanol to provide eventually total yields of *ca.* 1.5 g (27%) of each diastereoisomer. Pure *trans-R,R*-[Co(*R,S,S,R*-ch-3,2,3)(NO$_2$)$_2$](+)BCS formed as very large golden-brown blocks [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = +0.398$, $[\alpha]_D$ 44 ± 1°, 2 × 10^{-3} *M* in water] and pure *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_2$)$_2$](+)BCS as lustrous, golden flakes [$(\epsilon_l - \epsilon_r)_{443\text{nm}} = -0.398$, $[\alpha]_D$ +35 ± 1°, 2 × 10^{-3} *M* in water].

Anal. Calcd for $[Co(C_{12}H_{30}N_4)(NO_2)_2]C_{10}H_{14}BrO_4S$: C, 38.2; H, 6.4; N, 12.2. Found for (+) CD: C, 38.3; H, 6.4; N, 12.2. Found for (−) CD: C, 38.3; H, 6.1; N, 12.3.

Addition of excess $NaClO_4$ to saturated aqueous solutions of the diastereoisomers caused immediate precipitation of the perchlorate salts, which were recrystallized from boiling water to give broad golden needles, $[\alpha]_D$ ±5 ± 1° (rotation and 443-nm CD have the same sign).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)(NO_2)_2]ClO_4$: C, 30.0; H, 6.3; N, 17.5. Found for the (+) isomer: C, 29.7; H, 6.1; N, 17.8. Found for the (−) isomer: C, 30.1; H, 6.4; N, 17.4.

The resolution may be carried out from methanol alone with similar results, though the higher solubility of the diastereoisomers necessitates the use of inconveniently small volumes at the later stages of fractionation. In the resolution described, the (−) CD diastereoisomer was recrystallized from methanol because its temperature gradient of solubility in this solvent is much greater than that of the (+) CD diastereoisomer. Methanol may be used to effect a crude initial separation of the bulk diastereoisomers, because when deposited slowly from a concentrated solution, separate crystals of quite distinct morphologies are formed and may be easily separated mechanically.

(+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl·H$_2$O. (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_2$)$_2$]ClO$_4$ (2.0 g) was added in portions, with stirring, to hot HCl (12 *M*, 200 ml, 80°). A red solution formed very rapidly and over 30 min of heating on the steam bath changed to a clear green (if a large volume of HCl is not used, the nitrochloro complex precipitates out and complete reaction is greatly retarded). After 45 min the solution was diluted with water (200 ml) and stored at 0° for 12 hr to precipitate small yellow-green crystals (1.6 g), which were collected and washed with water, ethanol, and ether. The complex was recrystallized from boiling methanol to give small green plates, $[\alpha]_D$ +49° (5 × 10^{-3} *M* in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl \cdot H_2O$: C, 34.8; H, 7.8; N, 13.5; Cl, 25.7. Found: C, 35.0; H, 7.8; N, 13.4; Cl, 26.0.

Addition of $HClO_4$ to a solution of the chloride in boiling HCl (4 *M*) resulted in essentially quantitative precipitation of the perchlorate salt. This was recrystallized from boiling methanol as elongated deep green plates, $[\alpha]_D$ +41° (2 × 10^{-3} *M* in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]ClO_4$: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.2; H, 6.6; N, 12.3; Cl, 23.0.

***S,R,R,S*-ch-3,2,3·4HCl.** (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl·H$_2$O (0.75 g) and $SnCl_2 \cdot 2H_2O$ (0.45 g) were heated in boiling methanol (50 ml) containing HCl (12 *M*, 5 ml) for 30 min. The deep blue solution formed was evaporated to dryness under vacuum and the residue was taken up in methanolic HCl (1 *M*, 20 ml). This solution was percolated through a column of Dowex 2-X8 Cl$^-$ form anion-exchange resin and washed off with methanolic HCl (1 *M*), and the colorless effluent was again taken to dryness. The oily white residue could be induced to crystallize by addition of acetone to its solution in ethanol, but these crystals were very deliquescent and a stable solid could not be obtained. (The nitrate and bromide salts apparently have similar properties.) In methanolic solution the material showed a small negative rotation and on neutralization with NaOH, addition of $CoCl_2$, oxidation by air, and readdition of HCl, fully active (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl was regenerated as the sole product.

(−)-Δ-*cis-β-S,S*-[Co(*S,R,R,S*-ch-3,2,3)CO$_3$]ClO$_4$·H$_2$O. (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl·H$_2$O (0.59 g) and Na_2CO_3 (0.20 g) in water (20 ml) were heated on the steam bath for 15 min. On filtration, addition of excess $NaClO_4$ caused rapid precipitation of glittering violet needles. The mixture was kept at 0° for 12 hr and the filtered complex was washed with water, ethanol, and ether (0.44 g, 66%). Recrystallization from boiling water (15 ml) gave broad pink-violet needles, $[\alpha]_D$ −320° (5 × 10^{-3} *M* in water). (The yield of this complex may be made almost quantitative by repeatedly filtering it out after thermally equilibrating the supernatant mixture of carbonato species.)

Anal. Calcd for $[Co(C_{12}H_{30}N_4)CO_3]ClO_4 \cdot H_2O$: C, 33.4; H, 6.9; N, 12.0. Found: C, 33.1; H, 6.6; N, 11.9.

On warming in methanolic HCl the complex gave a CD spectrum identical with that of the pure (+)-*trans-R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]$^+$ ion.

(−)-Δ-*cis-α-R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl. (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl·H$_2$O (1.6 g), Na_2CO_3 (0.6 g), and activated charcoal (0.2 g) were heated in water (50 ml, 80°) for 60 min. The resulting violet solution was filtered, mixed with HCl (12 *M*, 50 ml), and allowed to stand at 0° for 12 hr to reprecipitate some starting complex (1.0 g), which was recycled using Na_2CO_3 (0.4 g) and activated charcoal (0.1 g) to return finally 0.65 g. The two violet HCl-soluble filtrates were combined and evaporated to dryness under vacuum. The blue residue was extracted with boiling ethanol (45 ml) containing HCl (12 *M*, 5 ml). The NaCl plus a very small amount of starting complex was filtered and the blue solution was again taken to dryness under vacuum. The residue was redissolved in boiling methanol (100 ml) containing HCl (12 *M*, 1 ml). Filtration, addition of ether (100 ml), and storage at 0° for 12 hr provided clusters of fine, pale blue needles (0.30 g), which were washed with ether. The filtrate–wash was taken to dryness and more cis-α complex (0.09 g) was obtained by dissolution of the residue in acidified methanol (25 ml) and addition of ether (50 ml). The two precipitates were combined and recrystallized from HCl (12 *M*, 5 ml) by adding water (5 ml) and heating until the formation of clusters of dark blue needles was initiated; $[\alpha]_D$ −1210° (5 × 10^{-4} *M* in acid methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl$: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.5; H, 7.6; N, 13.9; Cl, 26.4.

On heating a *neutral* methanolic solution of the complex for 5 min, conversion to (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$ was complete.

Λ-*cis-β-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$ and *trans-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$. The filtrate from the second precipitate of the Δ-cis-α complex was diluted with more ether (100 ml) and allowed to stand at 0° for 4 hr to precipitate a little flocculent blue-green material which was filtered off and discarded. The filtrate was taken to dryness under vacuum and the oily, blue-green residue, now obviously contaminated with Co(II), was dissolved in acidified (HCl) methanol (10 ml, 25°). The solution was filtered, mixed with $HClO_4$ (12 *M*, 0.2 ml), diluted with ether (150 ml), and allowed to stand for 12 hr at 0° to deposit small clusters of violet needles (0.06 g). These were washed with ethanol–ether (1:4) and ether. No convenient recrystallization procedure was found for this *cis-β-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]ClO_4.

Anal. Calcd for [Co($C_{12}H_{30}N_4$)Cl_2]ClO_4: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.6; H, 6.7; N, 12.2; Cl, 22.9.

The filtrate from the violet needles was further diluted with ether (100 ml) and again allowed to stand at 0° for 12 hr. The precipitate formed was a mixture of green needles and a small amount of violet powder. On dissolution in cold acidified ethanol (5 ml containing 0.05 ml of 12 *M* HCl and 0.1 ml of 12 *M* $HClO_4$) and filtration directly into ether (100 ml), bright green crystals (0.005 g) were rapidly deposited. These were washed with ether. Due to the presence of considerable amounts of decomposition products no further quantity of either complex could be isolated pure.

Because of the small quantity of material we were unable to obtain analytical data on this compound, but its absorption spectrum is superimposable, in both intensity and position, on that of the racemic material under identical conditions. There is no doubt about the purity or identity of the material.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(N_3)_2$]ClO_4. (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]Cl·H_2O (0.30 g) and NaN_3 (0.25 g) in water (20 ml) were heated on the steam bath for 20 min; a deep blue solution was formed within 2 min. Excess $NaClO_4$ was added and the solution was allowed to stand 1 hr at room temperature to precipitate fine, blue-black needles (0.32 g, 94%), which were washed with water, ethanol, and ether. The complex was recrystallized from boiling water; $[\alpha]_D$ ~−40° (10^{-4} *M* in water—the rotation was too small and the absorption too great at 589 nm and several other wavelengths to allow accurate determination of [α]); Λ_M = 84 cm^2 ohm^{-1} mol^{-1}.

Anal. Calcd for [Co($C_{12}H_{30}N_4$)$(N_3)_2$]ClO_4: C, 30.5; H, 6.4; N, 29.6. Found: C, 30.8; H, 6.4; N, 29.5.

A known mass of the complex was heated on the steam bath in HCl (12 *M*) for 5 min and then made up to an exact volume with methanol. The green solution showed a CD spectrum identical with that of the *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ ion.

$(-)_{436}$-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(NCS)_2$]ClO_4. (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]Cl·H_2O (0.53 g) in boiling methanol (50 ml) was mixed with NaNCS (0.50 g) in water (25 ml) and heated on the steam bath for 1 hr. (In pure aqueous medium the intermediate chloroisothiocyanato complex precipitates out and reaction is difficult to drive to completion.) The deep red solution was taken to dryness under vacuum and the crystalline residue dissolved in water (50 ml, 100°), filtered, and mixed with $HClO_4$ (12 *M*, 5 ml). On standing at room temperature, long red needles were deposited (0.48 g, 74%). The complex was recrystallized from boiling water; $[\alpha]_{436nm}$ −60° (10^{-4} *M* in methanol); Λ_M = 72 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)$(NCS)_2$]ClO_4: C, 33.3; H, 6.0; N, 16.7; S, 12.7. Found: C, 33.3; H, 6.1; N, 16.8; S, 12.6.

No simple method for converting this complex to other diacido species was found.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(NO_3)_2$]NO_3. (−)-Δ-*cis-β-S,S*-[Co(*S,R,R,S*-ch-3,2,3)CO_3]ClO_4·H_2O (0.34 g) was dissolved in HNO_3 (7 *M*, 5 ml) and the solution stood at 0° for 12 hr. Small green crystals deposited (0.32 g, 93%) which were washed with water, ethanol, and ether and recrystallized from water (75 ml, 100°) by the addition of HNO_3 (14 *M*, 25 ml); $[\alpha]_D$ −1010° (10^{-4} *M* in methanol); Λ_M = 82 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)$(NO_3)_2$]NO_3: C, 30.3; H, 6.4; N, 20.7. Found: C, 30.1; H, 6.2; N, 20.7.

Dissolution of the complex in dilute methanolic HCl resulted in slow anation to the pure (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ ion.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(CN)_2$]ClO_4. Finely ground NaCN (0.065 g) was added to a magnetically stirred solution of (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]ClO_4 (0.300 g) in DMSO (10 ml). The solution rapidly turned yellow and, as stirring was continued, began to deposit a yellow solid. After 5 min, ethanol (20 ml) and ether (50 ml) were added to complete precipitation and the yellow powder was filtered off and washed with ethanol–ether (1:1) and ether. It was then dissolved in water (30 ml, 80°) and excess $NaClO_4$ was added to precipitate small yellow needles (0.15 g, 52%), which were washed with water, ethanol, and ether. The complex was recrystallized from boiling water; $[\alpha]_D$ −49° (6 × 10^{-3} *M* in water); Λ_M = 81 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)$(CN)_2$]ClO_4: C, 38.2; H, 6.9; N, 19.1. Found: C, 38.0; H, 6.9; N, 19.0.

No means of converting this complex to any other diacido species was found.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(NH_3)_2$]Cl_3. (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]Cl·H_2O (0.40 g) was added to liquid ammonia (200 ml) and the mixture was magnetically stirred as the NH_3 was allowed to evaporate. The complex slowly reacted to give a pale orange precipitate and the pink-orange residue finally obtained was taken up in water (20 ml) and mixed with ethanol (100 ml) to precipitate an orange powder, leaving a pink-violet supernatant solution. The solid was dissolved in water (20 ml, 80°), filtered, mixed with HCl (12 *M*, 5 ml) and ethanol (20 ml), and allowed to stand at room temperature for 4 hr. Very fine orange needles (0.21 g, 51%) slowly deposited and were washed with ethanol and ether; $[\alpha]_D$ −47° (10^{-2} *M* in water); Λ_M = 310 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)$(NH_3)_2$]Cl_3: C, 33.5; H, 8.4; N, 19.6; Cl, 24.7. Found: C, 33.4; H, 8.4; N, 19.7; Cl, 24.7.

A known mass of the complex was heated with excess dilute NaOH solution for 5 min, then acidified with HCl, heated 1 min, and made up to an exact volume with methanol to give a CD spectrum identical with that of the pure (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ ion.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO_2)Cl]ClO_4. HCl (12 *M*, 0.4 ml) and urea (0.06 g) were added to a solution of (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)$(NO_2)_2$]ClO_4 (1.0 g) in water (175 ml, 100°) and the mixture was heated on the steam bath for 1 hr. Excess $NaClO_4$ was added and the red-brown solution was allowed to stand at 0° for 12 hr to deposit small red crystals (0.9 g, 92%). The complex was freed of very small amounts of both the dichloro and dinitro complexes by recrystallization from boiling methanol (250 ml), forming then as glistening red needles; $[\alpha]_D$ −92° (2 × 10^{-3} *M* in methanol); Λ_M = 80 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)(NO_2)Cl]ClO_4: C, 30.6; H, 6.4; N, 14.9; Cl, 15.1. Found: C, 30.7; H, 6.7; N, 14.9; Cl, 15.0.

On heating a known mass of the complex in HCl (12 *M*) for 30 min and then making up the green solution to an exact volume with methanol, the CD spectrum of pure (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ was observed.

(+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO_2)N_3]ClO_4. (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO_2)Cl]ClO_4 (0.300 g) was dissolved in water (40 ml, 100°), giving an orange solution. NaN_3 (0.045 g) was added, causing a rapid color change to deep brown-red, and the mixture was heated on the steam bath for 5 min without further obvious color change occurring. On filtration, addition of $NaClO_4$, and storage at 0° for 4 hr, small burgundy-colored crystals (0.24 g, 79%) were deposited. These were washed with water, ethanol, and ether. To remove a small amount of the diazido complex contaminant, the product was dissolved in water (10 ml, 100°) and allowed to stand for 2 hr at room temperature to reprecipitate the bulk of the diazido and some of the nitroazido complex. Addition of $NaClO_4$ to the filtrate from these solids gave lustrous, red-brown plates of essentially pure nitroazido compound (0.15 g), which was recrystallized from methanol (15 ml) by the addition of ether (15 ml); $[\alpha]_D$ +80° (10^{-3} *M* in water); Λ_M = 86 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for [Co($C_{12}H_{30}N_4$)(NO_2)N_3]ClO_4: C, 30.2; H, 6.3; N, 23.5. Found: C, 30.3; H, 6.3; N, 23.5.

The complex was quantitatively converted to the optically pure (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl_2]$^+$ ion by the same procedure as described for the nitrochloro species.

(−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO_2)NCS]ClO_4. NaNCS (0.055 g) was added to a hot solution of (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO_2)Cl]ClO_4 (0.300 g) in water (40 ml, 100°), causing a slight color change to clear orange. The solution was heated for 5 min on the steam bath then reduced to a volume of *ca.* 10 ml by vacuum evaporation. Addition of excess $NaClO_4$ and storage at 0° for 2 hr gave an orange powder (0.18 g, 57%), which was washed with water (2 ml), ethanol–ether (1:10), and ether. To free the complex of small amounts of dinitro- and diisothiocyanato complexes it was twice recrystallized from the minimum volume of hot water by the addition of excess $NaClO_4$, finally forming as lustrous brown-orange flakes; $[\alpha]_D$ −28° (2 × 10^{-3} *M* in water); Λ_M = 82 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)(NO_2)NCS]ClO_4$: C, 31.7; H, 6.1; N, 17.1; S, 6.5. Found: C, 31.4; H, 6.3; N, 17.3; S, 5.9.

A known mass of the complex was heated on the steam bath with a 2 molar amount of $Hg(ClO_4)_2$ (0.1 *M* in 1 *M* $HClO_4$) for 5 min. Excess HCl (12 *M*) was added, heating was continued 10 min, and the solution was then made up to an exact volume with methanol. The CD of this solution was in quantitative agreement with that of the (+)-*trans*-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]$^+$ ion.

D. Co(III) Complexes of *R*,*S*,*R*,*S*-ch-3,2,3. *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4. *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl (0.50 g) was dissolved in HCl (2 *M*, 10 ml, 80°) and mixed with $HClO_4$ (12 *M*, 2 ml). Green crystals rapidly began to precipitate and after cooling for 2 hr at 0° were filtered off and washed with water, ethanol, and ether (0.54 g, 94%). Recrystallization from HCl by the addition of $HClO_4$ gave long, bright green needles; Λ_M = 84 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]ClO_4$: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.4; H, 6.7; N, 12.1; Cl, 23.4.

***trans*-*R*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl.** A solution of *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl (0.40 g) in methanol (50 ml) was refluxed for 18 hr. HCl (12 *M*, 5 ml) was added and the still green solution evaporated to dryness under vacuum. The residue of blue and green solids was extracted with acidified methanol (15 ml containing 1.5 ml of 12 *M* HCl), the blue solid (*ca.* 0.1 g) being almost completely insoluble. The extract was filtered, diluted with ether (75 ml), and allowed to stand at 0° for 3 hr to precipitate a very small amount of blue powder and a few green crystals. These solids were filtered out and more ether (125 ml) was added to the filtrate. On continued cooling, fine yellow-green needles (0.18 g, 45%) were deposited. To eradicate completely some blue starting complex the material was twice more recrystallized from acidic methanol (5 ml) by the addition of ether (25 ml); Λ_M = 74 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl$: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.2; H, 7.7; N, 13.9; Cl, 27.1.

***cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]Cl.** *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl (4.0 g) and Li_2CO_3 (1.0 g) were heated on the steam bath in a mixture of water (30 ml) and methanol (10 ml). After 30 min the deep pink-violet solution formed was filtered and diluted with acetone (200 ml) and ether (50 ml). Storage at 0° for 3 hr then gave small pink needles (3.5 g, 90%), which were washed with acetone and ether. The complex was recrystallized from water by the addition of acetone; Λ_M = 73 cm^2 ohm^{-1} mol^{-1} (in water).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)CO_3]Cl$: C, 40.6; H, 7.9; N, 14.6; Cl, 9.2. Found: C, 40.6; H, 8.1; N, 14.7; Cl, 9.4.

Resolution of *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]Cl. NH_4(+)BCS (3.0 g) was added to a hot, filtered solution of *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]Cl (3.5 g) in water (40 ml, 80°). The solution produced was allowed to cool slowly to room temperature (agitation at this stage produces an unfilterable pink slime), and then it was allowed to stand 12 hr to complete precipitation of fine, pink needles, which were washed with acetone and ether (2.3 g, 38%; [*α*]D +92°, 2 × 10^{-3} *M* in water). Recrystallization from methanol (15 ml) by the addition of acetone (60 ml) and ether (30 ml) gave fluffy pink needles (which, on standing at 0°, slowly transformed into pink-violet blocks) of identical activity.

Anal. Calcd for $[Co(C_{12}H_{30}N_4)CO_3]C_{10}H_{14}BrO_4S$: C, 41.8; H, 6.7; N, 8.5. Found: C, 41.7; H, 6.8; N, 8.4.

Gradual addition of a filtered solution of sodium tetraphenylborate to an aqueous solution of the diastereoisomer caused essentially quantitative precipitation of small pink needles of (+)-Λ-*cis*-*β*-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]BPh_4, [*α*]D +63° (10^{-3} *M* in methanol). (No other insoluble salt of the optically active complex was discovered.)

Anal. Calcd for $[Co(C_{12}H_{30}N_4)CO_3]B(C_6H_5)_4\cdot 3H_2O$: C, 61.6; H, 7.8; N, 7.8. Found: C, 61.7; H, 7.5; N, 8.1.

The filtrate from the initial diastereoisomer precipitate was evaporated to dryness under vacuum and the residue redissolved in water (20 ml). A large excess of $NaClO_4$ (5 g) was added and the solution was allowed to stand at 0° for 12 hr to precipitate pink-violet needles of inactive *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]ClO_4 (0.9 g). This was filtered off and HCl (12 *M*, 5 ml) was added to the filtrate. After being heated on the steam bath for 15 min the then dull violet solution was allowed to stand at 0° for 12 hr to deposit green needles (0.9 g, 22%, [*α*]$_{546nm}$ −56°) of (−)$_{546nm}$-*trans*-*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4, which were washed with water, ethanol, and ether. Recrystallization from HCl (2 *M*, 25 ml, 80°) by addition of $HClO_4$ (12 *M*, 5 ml) did not produce an appreciable increase in activity.

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]ClO_4$: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.4; H, 6.6; N, 12.3; Cl, 23.3.

On reaction with a large excess of $NaHCO_3$ in aqueous solution over a period of 2 hr, this *trans*-dichloro complex gave a CD spectrum enantiomorphic in form, of 94% of the magnitude of that of the insoluble carbonato complex diastereoisomer. Slow racemization of the carbonato complex occurring under these conditions accounts for this diminished activity.

***R*,*S*,*R*,*S*-ch-3,2,3·4HCl.** To demonstrate the nonresolvable nature of the ligand present in the above active complexes, the ligand hydrochloride was isolated from the active *trans*-dichloro complex. (−)$_{546nm}$-*trans*-*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4 (0.50 g) and $SnCl_2\cdot 2H_2O$ (0.15 g) were heated in boiling ethanol (50 ml) containing HCl (12 *M*, 5 ml) for 30 min. White crystals began to form after a few minutes and a quite copious precipitate was formed in the full reaction period. The mixture was allowed to stand for 2 hr at 0° and the fine white needles (0.40 g, 98%) were then filtered off and washed with ethanol and ether. Recrystallization from HCl (1 *M*, 5 ml) by the addition of ethanol (5 ml) and acetone (40 ml) gave very long, white needles, [*α*]D 0°.

Anal. Calcd for $C_{12}H_{30}N_4\cdot 4HCl$: C, 38.3; H, 9.1; N, 14.9; Cl, 37.7. Found: C, 38.3; H, 9.1; N, 14.9; Cl, 37.4.

On conversion back to Co(III) complex, inactive material was obtained.

(−)-Λ-*cis*-*β*-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl. (+)-Λ-*cis*-*β*-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)CO_3]BCS (1.0 g) was dissolved in HCl (12 *M*, 5 ml) and heated on the steam bath for 5 min, evolving CO_2 and forming a blue-violet solution. This was mixed with ethanol (50 ml) and ether (500 ml) and allowed to stand at 0° for 12 hr to deposit a blue-violet powder (0.4 g, 67%), which was washed with ether. The complex was recrystallized from methanol (25 ml) containing HCl (12 *M*, 0.1 ml) by the addition of ether (75 ml), forming as lustrous blue-violet flakes, [*α*]D −1080° (2 × 10^{-3} *M* in DMSO–HCl (100:1)).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)Cl_2]Cl$: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.6; H, 7.7; N, 14.2; Cl, 27.1.

On reaction with HCO_3^- under the same conditions as for the *trans*-dichloro complex, a carbonato complex of similar optical purity was generated.

(+)-Λ-*cis*-*β*-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)$(N_3)_2$]$NO_3\cdot H_2O$. NaN_3 (0.10 g) was added to a filtered solution of (−)-Λ-*cis*-*β*-*R*,*R*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl (0.16 g) in water (5 ml), causing a rapid color change to deep brown-violet. $LiNO_3$ (1.0 g) was added and the solution stirred as brown crystals rapidly precipitated. After standing 30 min at 0° (prolonged standing leads to contamination with the blue *trans*-(*R*,*S*)-diazido complex), the solid was washed with water (3 ml), ethanol–ether (1:10), and ether, being obtained as a brown powder (0.10 g, 55%). The complex recrystallized from methanol on the addition of ether as brown-violet needles; [*α*]D +3700° (5 × 10^{-4} *M* in methanol); Λ_M = 79 cm^2 ohm^{-1} mol^{-1} (in methanol).

Anal. Calcd for $[Co(C_{12}H_{30}N_4)(N_3)_2]NO_3\cdot H_2O$: C, 31.8; H, 7.2; N, 34.0. Found: C, 31.6; H, 6.9; N, 34.1.

On heating the complex in HCl (12 *M*) for 5 min and then making the blue solution formed up to an exact volume with methanol, a CD spectrum identical with that of the (−)-*cis*-dichloro complex in the same solvent was obtained.

Acknowledgment. We thank the National Research Council of Canada and the Department of Chemistry for financial support.

Registry No. *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]Cl, 53834-09-6; *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4, 53834-11-0; *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*R*,*S*-ch-3,2,3)Cl_2]Cl, 53834-12-1; *cis*-*β*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)CO_3]ClO_4, 53860-96-1; *cis*-*α*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]Cl, 53834-13-2; *cis*-*β*-*R*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4, 53834-15-4; *trans*-*R*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4, 53834-17-6; *trans*-*R*,*R*:*S*,*S*-[Co(*R*,*S*,*S*,*R*:*S*,*R*,*R*,*S*-ch-3,2,3)$(NO_2)_2$]I, 53834-18-7; (+)-*trans*-*R*,*R*-[Co(*R*,*S*,*S*,*R*-ch-3,2,3)$(NO_2)_2$]BCS, 53834-20-1; (−)-*trans*-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)$(NO_2)_2$]BCS, 53834-22-3; (+)-*trans*-*R*,*R*-[Co(*R*,*S*,*S*,*R*-ch-3,2,3)$(NO_2)_2$]ClO_4, 53860-83-6; (−)-*trans*-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)$(NO_2)_2$]ClO_4, 53860-84-7; (+)-*trans*-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]Cl, 53834-23-4; (+)-*trans*-*S*,*S*-[Co(*S*,*R*,*R*,*S*-ch-3,2,3)Cl_2]ClO_4, 53860-86-9; (−)-Δ-

cis-β-S,S-[Co(*S,R,R,S*-ch-3,2,3)CO$_3$]ClO$_4$, 53834-25-6; (−)-Δ-*cis-α-R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]Cl, 53834-26-7; Λ-*cis-β-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$, 53834-28-9; *trans-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$, 53834-30-3; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(N$_3$)$_2$]ClO$_4$, 36464-25-2; (−)$_{436}$-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NCS)$_2$]ClO$_4$, 53860-91-6; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_3$)$_2$]NO$_3$, 53783-42-9; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(CN)$_2$]ClO$_4$, 53834-34-7; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NH$_3$)$_2$]Cl$_3$, 53834-35-8; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_2$)Cl]ClO$_4$, 53834-39-2; (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_2$)N$_3$]ClO$_4$, 53834-37-0; (−)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO$_2$)(NCS)]ClO$_4$, 53860-93-8; *trans-R,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl$_2$]Cl, 53834-40-5; *cis-β-R,R:S,S*-[Co(*R,S,R,S*-ch-3,2,3)CO$_3$]Cl, 53834-46-1; (+)-Λ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)CO$_3$]BCS, 53834-48-3; (+)-Λ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)CO$_3$]BPh$_4$, 53860-87-0; (−)$_{546}$-*trans-S,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl$_2$]ClO$_4$, 53834-42-7; (−)-Λ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)Cl$_2$]Cl, 53834-43-8; (+)-Λ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)(N$_3$)$_2$]NO$_3$, 53834-45-0; ch-3,2,3·4HCl, 53834-32-5.

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Conformational Dissymmetry. Circular Dichroism Spectra of a Series of Complexes Containing a Quadridentate Amine Ligand with Chair Six-Membered Chelate Rings

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Received July 5, 1974 AIC40438M

The circular dichroism spectra of a series of complexes of the type *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]$^{n+}$ where *S,R,R,S*-ch-3,2,3 is a stereospecific quadridentate ligand, the substitutents of which fix the terminal six-membered chelate rings in chair conformations, are recorded. The X and Y ligands span the spectrochemical series. Despite the fixed conformations of the rings, large solvent variations are observed in the circular dichroism patterns of these complexes. These variations are very similar to those found for the corresponding *trans-R,R*-[Co(3,2,3-tet)XY]$^{n+}$ complexes where it might have been assumed that the circular dichroism changes were due to conformational instability. The results described for the *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]$^{n+}$ system strongly suggest that this is not the case and that the variations are due to other effects engendered by the medium.

In a previous paper[1] we showed that complexes of the type *trans-R,R*-[Co(3,2,3-tet)XY]$^{n+}$ gave circular dichroism spectra which were extremely sensitive to the environment. So gross and spectacular were some of these effects, that a genuine case could be made which inferred changes in the conformations from one environment to another. More particularly, some of the observations could be construed as being a result of chair–skew conformational changes of the terminal six-membered chelate rings. We have sought to resolve this inference by preparing complexes of the 3,2,3-tet type where, by methyl substitution of the terminal rings, the conformations would be fixed in either the chair[2] or skew geometries. This paper presents the circular dichroism spectra of an analogous series of complexes where the terminal rings are fixed in chair conformations; a subsequent paper deals with fixed skew terminal rings.

Except for two dichloro complexes, all the complexes derived from the active *S,R,R,S*-ch-3,2,3 ligand have the structure and absolute configuration *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]$^{n+}$ (Figure 1). With this absolute configuration, the inner five-membered ring is δ and with the given sequence of chiral centers, both terminal rings are in chair conformations. Apart from the methyl groups, the complexes are superimposable on the *trans-R,R*-[Co(3,2,3-tet)XY]$^{n+}$ complexes discussed previously.[1] The analogy is therefore complete except for a presumably small vicinal effect due to the asymmetric carbon atoms and that which distinguishes this system from the unsubstituted analog, a certainty about the chair conformations of the terminal chelate rings. The absolute configurations of these complexes of the racemic ligand are derived on fairly convincing empirical grounds[2] and are almost certainly correct but are not proven beyond doubt. What is certain, however, is that they all have the same absolute configurations;[2] and since the primary object of this paper is to begin to resolve the issue of conformational lability in inducing the circular dichroism changes in the 3,2,3-tet complexes, the argument does not hinge on a certain knowledge of the absolute configuration.

In a preceding paper,[1] we gave a fairly comprehensive introduction to and analysis of the circular dichroism spectra of these types of complexes. We will not repeat these here. The material and methodology of the preceding paper are assumed to serve as an introduction to this and the subsequent paper on systems with skew rings. We begin slightly obliquely by describing the spectra of three *trans*-dichloro complexes which have various conformations of the terminal rings because