

language. Also these values are reported in Table II. We use the " $Dq$ " although it has a different meaning from  $Dq$  of the point charge model, since it is familiar to the inorganic chemist.<sup>30</sup> The " $Dq$ " values for tertiary nitrogen and thioetheral sulfur are quite close to each other in substantial accord with previous findings.<sup>31</sup> The position of phosphorus in the spectrochemical series is not well settled. The present results suggest it should be on the high-field side of the amine nitrogen. The series for  $I_2$  appears to be  $Br > N > S \geq P$ .

Finally it is interesting to compare the values of  $I_2$ ,  $I_4$ , and " $Dq$ " with those straightforwardly obtainable from the general ligand field diagrams of Figure 3, where, owing to the large number of parameters,  $I_2/I_4$  is assumed equal for all the donors within a chromophore.<sup>32</sup> This restrictive condition requires an increase of the  $I_2/I_4$  ratio in going from  $CoNN_3Br$  to  $CoNP_3Br$  in order to account for the large separation between the  $F \rightarrow P$  transitions (see Figure 2). These results are in contrast with those obtained when the appropriate  $I_2/I_4$  ratio is considered for each donor atom. The comparison between the two types of calculations represents a meaningful example of the type of errors made when simple crystal field calculations ( $I_2/I_4$  constant within a chromophore) are used to fit the spectra in low-symmetry chromophores.

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**Registry No.**  $CoNS_3Br$ , 53608-74-5;  $CoNN_3Br$ , 34376-74-4;  $CoNP_3Br$ , 52225-43-1.

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## Geometrical, Optical, and Conformational Isomers of Octahedral Metal Complexes Formed with a Linear Quadridentate Amine Ligand. The 3,2,3-tet System

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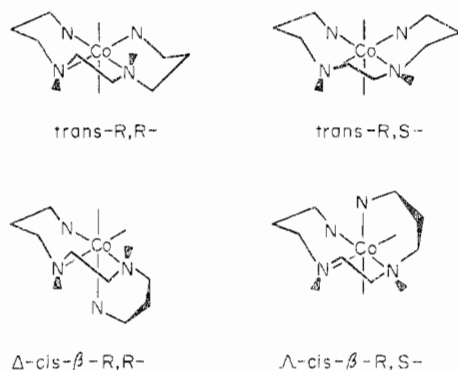
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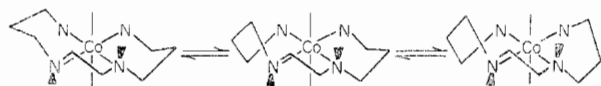
An extensive series of metal complexes of Co(III) (and one each of Rh(III) and Cr(III)) containing the linear quadridentate ligand 3,2,3-tet  $(NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2)$  have been isolated, characterized, and obtained in optical forms. Four of the five possible stable isomers have been isolated, three of which were separated into optical isomers. These four isomers represent the basic cis- $\beta$  and trans geometries which additionally display a secondary isomerism due to the meso and racemic configurations of the inner nitrogen atoms. Most of the complexes were of the type *trans-R,R',S,S'*-[Co(3,2,3-tet)XY]<sup>n+</sup>, where X and Y represent a wide variety of unidentate ligands. A number of these trans complexes have been resolved directly and most of the others have been obtained in optically active forms by chemical conversion. The absolute configurations of all the complexes have been unambiguously correlated by chemical interconversions. Various physical measurements are recorded which support the assigned stereochemistries. Equilibria data were obtained for the various geometrical and conformational isomers. It was found that the ligand preferred the racemic configuration of the inner racemic atoms in all stereochemistries, the most stable of which was the trans disposition of the ligand. These systems are relatively optically stable even when proton exchange occurs provided that the X and/or Y groups are not the aquo ligands. The presence of an aquo group leads to proton exchange and racemization even in concentrated acid solutions. The broad aspects of the racemization of the diaquo, hydroxoquo, and dihydroxo species have been studied kinetically. It was found that the hydroxoquo species in neutral water racemized faster than the dihydroxo species at pH 11.3 and that in 5 M perchloric acid the diaquo species racemized slowly but efficiently in the sense that proton exchange was only 5 times as fast as racemization.

Octahedral metal complexes formed with simple linear quadridentate amines potentially provide a diversity of possible geometrical and conformational isomers, many of which exist in resolvable species. The factors which determine the stability of these forms are subtle and complicated, and though a

number of recent attempts<sup>1-3</sup> have been made to interpret the stereochemical behavior of these systems, the interplay and the predominance of the various effects involved are poorly understood. In their thorough study of the cobalt complexes of the ligand 1,8-diamino-3,6-diazaoctane (trien), Sargeson



**Figure 1.** Four of the five possible isomers of the system  $[\text{Co}(3,2,3\text{-tet})\text{X}_2]^{n+}$ . The terminal rings are shown in chair conformations. The other isomer (*cis-α*) is not shown.



**Figure 2.** Possible conformational equilibria of the *trans-R,R*- $[\text{Co}(3,2,3\text{-tet})\text{X}_2]^+$  ion with a  $\delta$  inner ring. The structure on the left has two chair terminal rings, the one in the middle has one  $\lambda$ -skew and one chair terminal ring, and the one on the right has two  $\lambda$ -skew terminal rings.

and Searle<sup>1</sup> showed that under most circumstances the ligand had a tendency to form *cis*-octahedral complexes. The present study is concerned with the homologous ligand  $\text{NH}_2(\text{C}-\text{H}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$ , 1,10-diamino-4,7-diazadecane (3,2,3-tet), the proclivities of which, as we show, are to the production of *trans*-octahedral complexes. As in all linear quadridentate amine systems, the 3,2,3-tet ligand can display three basic stereochemistries<sup>1-5</sup> *cis-α*, *cis-β*, and *trans*, the *cis-β* and *trans* geometries having two additional isomers which are related to the configurations of the inner two nitrogen atoms (Figure 1). In addition, the terminal six-membered ring systems of the complexed 3,2,3-tet ligand can adopt at least two conformational forms (the chair and the skew) which may be of similar energy.<sup>6</sup> Thus all the six-membered rings in the complexes shown in Figure 1 are capable of conformational interconversion. Of particular interest is the potential conformational lability of these rings in the racemic *trans* geometry where the conformational equilibrium shown in Figure 2 may exist. It will be noted that, in this system, the geometrical constraints of the inner nitrogen atoms are such that the outer rings in the skew conformation will be of opposite chirality to the inner five-membered ring and that terminal chair rings are devoid of any first-order conformational dissymmetry. Thus we would expect that the circular dichroism spectra of the optically active *trans* complexes would be extremely sensitive to conformational variations. It is the purpose of this and subsequent papers in this series to investigate the geometrical and conformational isomers of the 3,2,3-tet ligand and a series of methyl-substituted analogs. This paper is concerned mainly with preparative chemistry of the cobalt complexes derived from the 3,2,3-tet ligand.

## 1. General Chemistry

Aerial oxidation of a methanolic solution of cobalt chloride and the 3,2,3-tet ligand leads to the rapid formation of the somewhat insoluble brown peroxo complex. Upon the addition of hydrochloric acid, this product is smoothly converted to the green *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]^+$  ion in 90% yield. There is also a small amount (<5%) of the green *trans-R,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]^+$  ion in the preparative mixture which is difficult to obtain pure from the side products of the reaction. No other isomers could be detected in this reaction mixture.

Starting with the *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]^+$  ion the following *trans* compounds were prepared; *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{X}_2]^{n+}$ , where  $\text{X} = \text{Br}^-$ ,  $\text{N}_3^-$ ,  $\text{NCS}^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{NO}_3^-$ . The first four involved simple reactions in water, while the ammine complex was prepared in liquid ammonia and the  $\text{CN}^-$  reaction was carried out in dimethyl sulfoxide. The  $\text{NO}_3^-$  species was usually made from the carbonato complex. In all these reactions at least 95% of the product has the inner nitrogen atoms in the racemic configuration. A series of mixed complexes of the type *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{YX}]^{n+}$ , where  $\text{Y} = \text{NO}_2^-$ ,  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{N}_3^-$ ,  $\text{NCS}^-$ ;  $\text{Y} = \text{NCS}^-$ ,  $\text{X} = \text{Cl}^-$ ,  $\text{N}_3^-$ ;  $\text{Y} = \text{N}_3^-$ ,  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , have been isolated. The nitro- $\text{X}$  species were formed by the selective removal of one  $\text{NO}_2^-$  group from the dinitro complex in perchloric acid followed by anation. The azido- $\text{X}$  species were prepared by the catalytic removal of one azido group with  $\text{NO}^+$  and the other complexes were prepared by simple anation reactions. As in the previous complexes all the reactions gave at least 95% of the *R,R,S,S-trans* isomer.

Reaction of the *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]^+$  ion with the  $\text{CO}_3^{2-}$  ion gives the red *cis-β-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{CO}_3]^+$  ion in high yield. Equilibration of this complex in the presence of base and/or charcoal followed by exhaustive crystallization did not reveal the presence of any other isomer. Reaction of the carbonato complex with concentrated perchloric acid gave the red crystalline *cis-β-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})(\text{H}_2\text{O})_2](\text{ClO}_4)_3$  complex. Addition of hydrochloric acid to either the carbonato or the diaquo complexes leads to the exclusive production of the racemic *trans*-dichloro complex. Under carefully controlled mild conditions the carbonato complex can be converted to the red (presumably *cis-β*) *cis-β-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}(\text{H}_2\text{O})]\text{Cl}$  complex which is unstable in neutral solution and even more so in basic media to produce the racemic *trans*-dichloro complex. This reaction even occurs in the solid state. Addition of 1 equiv of base to the diaquo complex causes the almost immediate precipitation of the purple *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{OH}(\text{H}_2\text{O})](\text{ClO}_4)_2$  complex. Perchloric acid immediately converts the hydroxoquo species to the greenish brown diaquo species, which slowly isomerizes to an equilibrium mixture of the *cis-β* and *trans* racemic diaquo species which can also be obtained by equilibration of the *cis-β*-diaquo complex. Addition of base to either of the diaquo complexes or the hydroxoquo species gives exclusively the pink-violet *trans*-dihydroxo complex which is stable as the *trans* complex. (The *cis*-dihydroxo is transiently formed but rapidly converts to the *trans* species.)

Acetylacetonone reacts with the *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{OH}(\text{H}_2\text{O})](\text{ClO}_4)_2$  complex to give a mixture of *cis-β-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{acac}](\text{ClO}_4)_2$  and *cis-β-R,S*- $[\text{Co}(3,2,3\text{-tet})\text{acac}](\text{ClO}_4)_2$  which can be separated as pink crystals by fractional crystallization. Addition of  $\text{NO}_2^-$  ions to a hydrochloric acid solution of the *cis-β-R,R,S,S* compound leads to the rapid removal of the acac ligand and the precipitation of the green *trans-R,R,S,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]\text{ClO}_4$  complex whereas the same reaction with the *cis-β-R,S* compound leads to the isolation of the more soluble olive green *trans-R,S*- $[\text{Co}(3,2,3\text{-tet})\text{Cl}_2]\text{ClO}_4$  complex. This last solid meso complex is morphologically distinct from its racemic analog in that the former crystallizes as splendid shiny olive green flakes whereas the racemic compound deposits as dull green blocks.

The meso-*trans* isomer can also be isolated by two other methods of which the first involves simply heating the racemic *trans*-dichloro complex in base. This procedure is not very satisfactory. The second procedure is more interesting and involves the formation of what we believe is a "hexol" species consisting of three *cis* (presumably  $\beta$ ) dihydroxo complexes bound by hydroxo bridges to a central six-coordinate cobalt(II) atom. It appears that one of the *cis-β*- $[\text{Co}(3,2,3\text{-tet})(\text{OH})_2]^+$

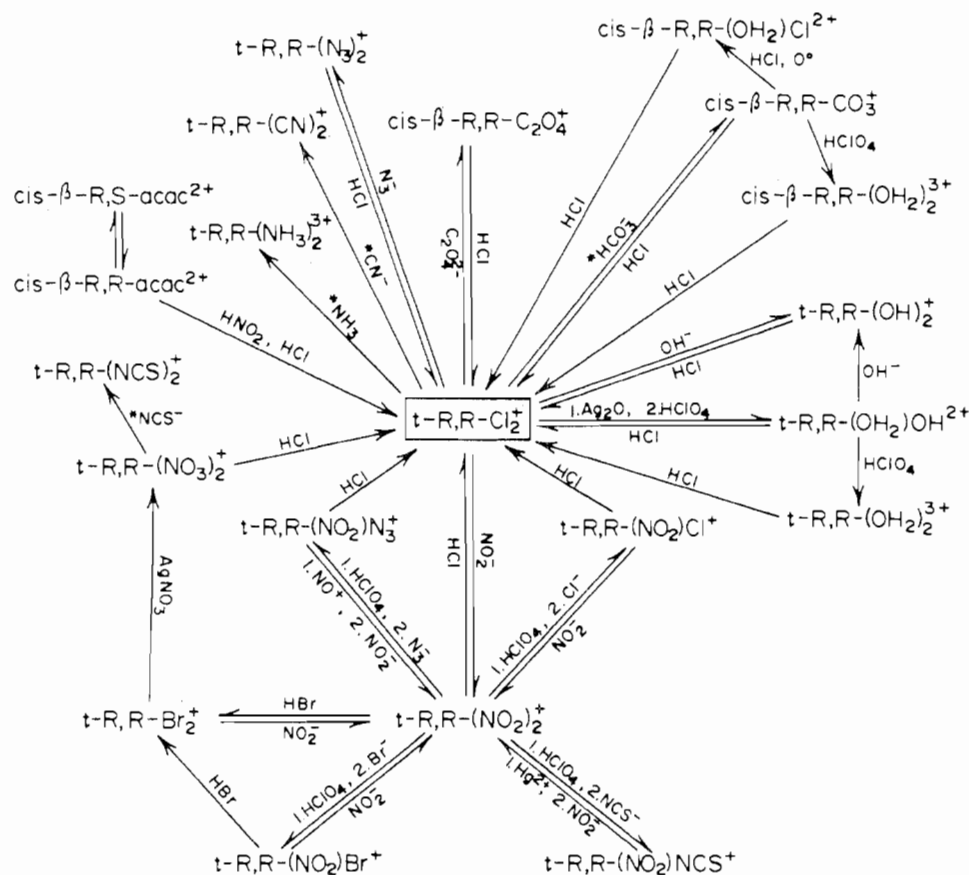


Figure 3. Chemical interconversions of the optically active complexes. Conditions have been found for all the reactions where complete retention of optical activity obtains, except the four represented by asterisks where partial racemization occurs.

ions is in the *R,S* configuration while the other two are in the racemic configuration of the inner nitrogen atoms because reaction with hydrochloric acid leads to the decomposition of the "hexol" to give the *trans-R,R,S,S*- and *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ions in the ratio of 2:1, respectively. The *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ion is stable in acid solution but in neutral or basic solution is converted to the racemic compound. If the meso compound is heated in dilute acidic aqueous solution, the solution changes from green to pink indicating the formation of the *cis-beta-R,S*-[Co(3,2,3-tet)ClH<sub>2</sub>O]<sup>2+</sup> ion. We have not isolated this ion pure but when it is anated with chloride ions it immediately reverts to the *meso-trans*-dichloro complex. The *rac-trans*-dichloro complex does not undergo stereochemical change when heated in aqueous solution; it remains green and consists of a mixture of the *trans*-dichloro and *trans*-chloroaquo species.

Oxalic acid reacts with the *trans-R,S*-dichloro complex to give mainly the red *cis-beta-R,S*-[Co(3,2,3-tet)ox]<sup>+</sup> ion whereas the reaction between disodium oxalate and either the *trans-meso*- or *trans-rac*-dichloro species gives about 90% *cis-beta-R,S*-[Co(3,2,3-tet)ox]<sup>+</sup> and 10% *cis-beta-R,S*-[Co(3,2,3-tet)ox]<sup>+</sup>.

In addition to these cobalt complexes we have prepared the corresponding *trans-R,R,S,S*-[Rh(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> and *trans-R,R,S,S*-[Cr(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ions. The first was prepared from Gillard's salt (*trans*-[Rh(py)<sub>4</sub>Cl<sub>2</sub>]Cl) and the latter by the reaction between the ligand and anhydrous CrCl<sub>3</sub> in dimethylformamide. In neither reaction did we obtain evidence for other stereochemistries.

We have resolved directly the compounds *trans-R,R,S,S*-[M(3,2,3-tet)X<sub>2</sub>]<sup>+</sup>, where M = Co, X = Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup>; M = Rh, X = Cl<sup>-</sup>; and M = Cr, X = Cl<sup>-</sup>, by means of their (+)- $\alpha$ -bromocamphor- $\pi$ -sulfonic acid salts. The *cis-beta-R,R,S,S*-[Co(3,2,3-tet)acac]<sup>+</sup> ion was resolved by its arsenyl

(-)-tartrate salt. Most of the other compounds described here have also been obtained in their optically pure forms by chemical interconversions. Despite numerous attempts, we have not been able to obtain any evidence for the *cis-alpha* geometry.

## 2. Chemical Interconversions

Apart from the *trans-R,R,S,S*-[Co(3,2,3-tet)YX]<sup>+</sup> ions, where Y = N<sub>3</sub><sup>-</sup>, X = Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup> and Y = NCS<sup>-</sup>, X = Cl<sup>-</sup>, which we have obtained partly optically active, the other complexes we describe here have been obtained in enantiomerically pure forms. An outline of the methods which we have used for the chemical interconversions of the optically active isomers is shown in Figure 3, the details of which are given in the Experimental Section. Apart from the four reactions indicated which lead to some racemization, all the others proceed with complete retention of optical activity and each step proceeds essentially quantitatively. In addition we have shown by deuteration studies that all the reactions carried out in HCl occur without amino proton exchange. The absence of proton exchange, together with the production of the same activity after each cycle of interconversion, establishes that all the compounds have been prepared to the same degree of optical purity. In addition, since the independently resolved *trans*-dinitro, *trans*-dichloro, and *cis-beta-R,R,S,S*-acac complexes are converted into one another to give the same rotation as obtained by the resolution procedure, it is suggested that all the compounds are optically pure. Indeed the optical purity can be effectively monitored by the morphology of the active crystals, which in all cases are distinctly different from the racemic materials and which only appear in their needlelike forms when maximum rotation is achieved. Although we have been unable to interconvert satisfactorily the *trans*-(NCS)<sub>2</sub>, -(NH<sub>3</sub>)<sub>2</sub>, and -(CN)<sub>2</sub> species, these complexes have been

crystallized to maximum rotations and we believe them to be optically pure.

The optically active *cis*- $\beta$ -*R,S*-[Co(3,2,3-tet)acac]<sup>+</sup> was obtained from the *cis*- $\beta$ -*R,R* isomer by amino proton exchange. The reaction between NO<sup>+</sup> and the active *cis*- $\beta$ -*R,S*-[Co(3,2,3-tet)acac]<sup>+</sup> ion leads to optically inactive *trans*-*R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ion. Molecular models indicate that the ligand in the *trans*-*R,S* geometry may exist in an asymmetric configuration (Figure 1) and the above result suggests that, under the experimental conditions used, the conformational interconversion is rapid. This is presumably because the conformation, in the *R,S* nitrogen configuration, is not fixed by chiral nitrogen centers.

### 3. Stereochemistry

The assignment of the geometrical isomerism of these complexes is based on three physical properties: (a) the nmr signals shown by the amino hydrogen nuclei, (b) the visible spectra, and (c) the circular dichroism spectra. Visible absorption and circular dichroism spectra do not satisfactorily distinguish between the *cis*- $\alpha$  and *cis*- $\beta$  geometries but these two spectra, in most cases, do distinguish either of the *cis* species from the *trans*. The complexes containing the bidentate ligands, acac, ox, and CO<sub>3</sub><sup>2-</sup> are *cis* complexes and show visible and circular dichroism spectra consistent with this geometry. The *R,S* vs. the *R,R,S,S* configurations of the inner nitrogen atoms of the *cis*- $\beta$  complexes is established by chemical conversion to the *trans*-dichloro compounds in acid solution, where it was shown that no proton exchange occurs. The acac and ox complexes having the *R,S* nitrogen atom configurations must have the *cis*- $\beta$  geometry, since an *R,S* configuration of the nitrogen atoms is not sterically compatible with the *cis*- $\alpha$  configuration. In the absence of any complicating conformational equilibria, the *cis*- $\alpha$  geometry is expected to show three sets of amino proton resonances (areas 2:2:2) whereas the *cis*- $\beta$  geometry has all of its amino protons in environmentally different positions. This is expected because of the presence of a twofold axis in the former, the latter being devoid of any elements of symmetry.<sup>3,7</sup>

The 60-MHz nmr spectra of the following *cis*- $\beta$ -*R,R,S,S* complexes have been measured: carbonato in D<sub>2</sub>O (Cl<sup>-</sup> salt) and in DMSO-*d*<sub>6</sub> (ClO<sub>4</sub><sup>-</sup> salt), oxalato in 10 *M* DCl (ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> salts) and in DMSO-*d*<sub>6</sub> (I<sup>-</sup> salt), acetylacetonato in DMSO-*d*<sub>6</sub> (ClO<sub>4</sub><sup>-</sup> salt), diaquo in D<sub>2</sub>O-DClO<sub>4</sub> (ClO<sub>4</sub><sup>-</sup> salt). In all cases the complexes were stable during the time of measurement and in all cases the amino proton resonances (checked by deuteration) showed a complicated pattern devoid of the symmetry expected for the *cis*- $\alpha$  geometry. Of particular interest is the observation that in all these cases there exists at least one clearly separated amino proton signal which integrates to an area corresponding to one proton. In the absence of fortuitous conformational equilibria of the *cis*- $\alpha$  geometry, this last fact is taken as firm evidence for the *cis*- $\beta$  assignment. Further, both the *R,R,S,S* and the *R,S* acac complexes show two methyl proton resonances. The central proton of the acac molecule has a resonance at  $\delta$  5.8 for the *R,R,S,S* species while the *R,S* species shows this proton at  $\delta$  5.7. This difference can be conveniently used to monitor the purity of the two species.

Finally we point out that the *cis*- $\beta$ -*R,S* oxalato and acetylacetonato complexes, which because of the steric constraints imposed by the inner nitrogen atoms must be *cis*- $\beta$ , show amino proton resonances which are similar to their *cis*- $\beta$ -*R,R,S,S* analogs.

Our conclusion concerning the topology of the oxalato complex having the *R,R,S,S* configuration of the inner nitrogen atoms is contrary to a previous proposal.<sup>5,8</sup> We show the nmr spectrum of the *cis*- $\beta$ -*R,R,S,S*-[Co(3,2,3-tet)ox]Br complex dissolved in 10 *M* DCl in Figure 4.

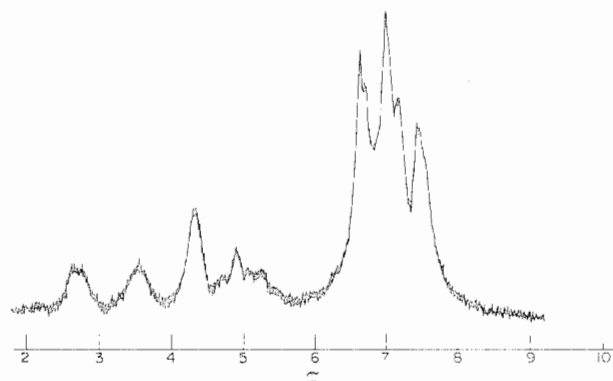


Figure 4. A 60-MHz nmr spectrum of the *cis*- $\beta$ -*R,R,S,S*-[Co(3,2,3-tet)ox]Br complex in DCl (10 *M*) (TMS external reference).

Given the known absolute configuration of the inner nitrogen atoms of the *cis*- $\beta$ -*R,R,S,S*-[Co(3,2,3-tet)ClH<sub>2</sub>O]Cl<sub>2</sub> complex, the most convincing evidence for the *cis*- $\beta$  geometry is the fact that its circular dichroism spectrum under the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> absorption of the cobalt atom is very similar to the circular dichroism spectra shown by the other *cis*- $\beta$  complexes. We have no evidence for the isomerism of the aquochloro groups though we suspect we have isolated a pure isomer because of the well-formed homogeneous crystals that were obtained.

The evidence for the geometric assignments of the *trans* complexes is, in most cases, less firmly based than that given for the *cis* complexes.

The absorption spectra due to transitions of the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> (or <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> for Cr(III)) manifold of all the *trans* complexes described here are similar to and consistent with the spectra shown by other *trans*-[CoN<sub>4</sub>XY]<sup>n+</sup> chromophores where the *trans* geometry has been established independently.<sup>9-16</sup> In some cases these absorption spectra comparisons are quite diagnostic, particularly where the Y, X ligands have weak ligand fields, but in other cases the *cis* and *trans* spectra are very similar. When Y = X = NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup> and NCS<sup>-</sup>, the nmr spectra of the amino protons of the 3,2,3-tet ligand occur as three separate signals integrating in the ratio of 2:2:2 when the spectra are measured in DMSO-*d*<sub>6</sub> or D<sub>2</sub>O at 100 MHz. This establishes that these molecules possess a twofold axis. When Y = X = NO<sub>2</sub><sup>-</sup> and CN<sup>-</sup>, two resonances appear in the ratio of 2:4 under the same conditions. Both these observations exclude the *cis*- $\beta$  geometry. When Y ≠ X, complicated patterns are observed. As an example of the nmr spectra of the *trans* complexes we show the spectra of *trans*-*R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> and *trans*-*R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> in Figure 5.

When the rotational strengths of the first magnetic dipole allowed transition of the *trans* complexes are compared with those observed for the *cis* complexes, it is found that the former are always at least 5 times weaker than the latter. If any of those assigned *trans* were in fact *cis* complexes, we would expect comparable rotational strengths. Furthermore, unlike either of the *cis* species, the *trans* complexes should show one component of the <sup>1</sup>T<sub>1g</sub> manifold occurring at the absorption energy of <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> (ca. 490 mμ).<sup>17</sup> In all cases where this component is resolved in the circular dichroism spectrum it is found to occur at around 490 mμ for the *trans* complexes. The absorption and circular dichroism spectra of these *trans* complexes are given elsewhere.

### 4. Absolute Configurations

The absolute configurations of both (-)-*trans*-*R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Br and (+)-*trans*-*R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub> have been determined by the Bijvoet method.<sup>18</sup> The structures in both cases, including the chair terminal rings, are the one shown in Figure 1. The powder X-ray diffraction patterns of the diastereomeric (+)- $\alpha$ -bromocamphor- $\pi$ -

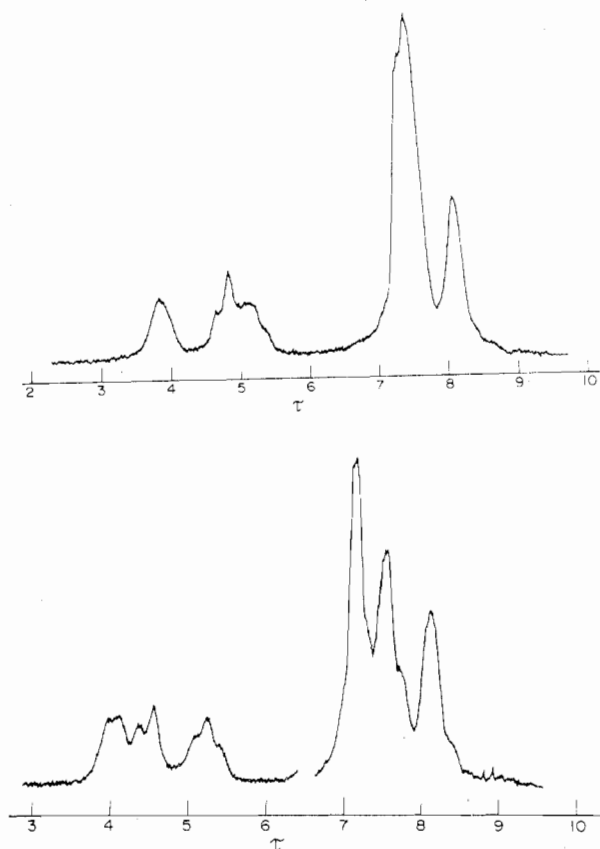


Figure 5. The nmr spectra of *trans-R,R:S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (top) in (CD<sub>3</sub>)<sub>2</sub>SO and *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (bottom) in (CD<sub>3</sub>)<sub>2</sub>SO-DCl at 60 MHz (TMS internal reference).

sulfonate (BCS) salts of the (-)-*trans*-[Cr(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> and (+)-*trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ions are identical and suggest that the Cr(III) and Co(III) complex ions have the same absolute configurations. The Rh(III) diastereomer shows a different powder pattern and the absolute configuration is based on the similarity of the circular dichroism spectrum to the spectra observed for the Cr(III) and Co(III) complexes. The assignment of the *trans*-dichloro complex is consistent with that derived from stereospecificity arguments<sup>19</sup> if it is accepted that similarities in the circular dichroism of similar compounds reflect the same absolute configuration.

From the chemical correlations shown in Figure 3 the absolute configurations of *cis-β* complexes with racemic nitrogen atoms, derived from the *R,R* configurations of these atoms, are all Δ (Figure 1). The absorption and circular dichroism spectra of the Δ-*cis-β-R,R*-[Co(3,2,3-tet)acac]<sup>2+</sup> and Δ-*cis-β-R,S*-[Co(3,2,3-tet)acac]<sup>2+</sup> species are shown in Figure 6; we also show the absorption and circular dichroism spectra of the Δ-*cis-β-R,R* oxalato and Δ-*cis-β-R,R* carbonato ions and the absorption spectrum of the *cis-β-R,S* oxalato species in Figure 7.

It is interesting to consider the circular dichroism spectra associated with the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> transition which are observed for the following series of complexes:<sup>8</sup> Δ-*cis-β-R,R*-[Co(trien)ox]<sup>+</sup>, Δ-*cis-β-S,S*-[Co(2,3,2-tet)ox]<sup>+</sup>, and Δ-*cis-β-R,R*-[Co(3,2,3-tet)ox]<sup>+</sup>. From this and previous work<sup>1,20</sup> these absolute configurations are known with certainty. The first and last complexes show a positive circular dichroism band at lower energies and a stronger negative band at higher energies, whereas the second complex shows a negative band at lower energies and a (weaker) positive band at higher energies. Thus it appears that the equivalent spectroscopic components of the second compound compared to the other two are reversed in sign. We are uncertain as to the reasons

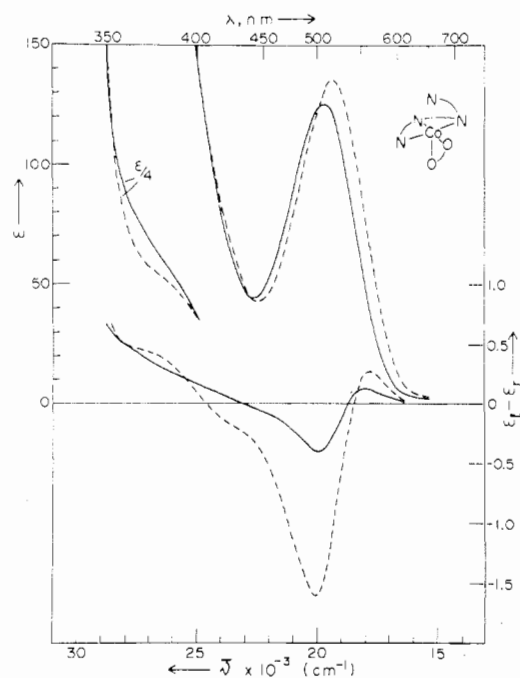


Figure 6. The absorption and circular dichroism spectra of (+)-Δ-*cis-β-R,R*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> (-----) and (+)-Δ-*cis-β-R,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> (—) in water.

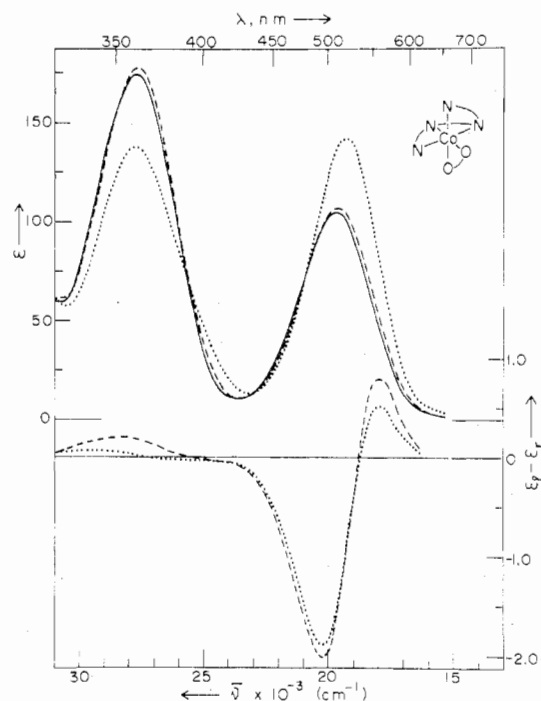


Figure 7. The absorption spectrum of *cis-β-R,S*-[Co(3,2,3-tet)ox]ClO<sub>4</sub> (—) in 1 M HCl and the absorption and circular dichroism spectra of Δ-*cis-β-R,R*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub> (·····) and Δ-*cis-β-R,R*-[Co(3,2,3-tet)ox]ClO<sub>4</sub> (-----) in water.

for this behavior but it does elicit caution in any attempts at empirical correlations.

### 5. Geometrical and Optical Stability

The *cis-β-R,R:S,S*-[Co(3,2,3-tet)ClH<sub>2</sub>O]Cl complex is rapidly converted to the *trans-R,R:S,S*-dichloro complex in both aqueous and methanolic solutions. The *cis-β-R,R:S,S*-[Co(3,2,3-tet)ox]<sup>+</sup> and *cis-β-R,R:S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]<sup>+</sup> ions are quite stable as their *cis* isomers. Aqueous solutions, in the presence of excess sodium oxalate and sodium carbonate, respectively, of these ions lead to the rapid exchange of the



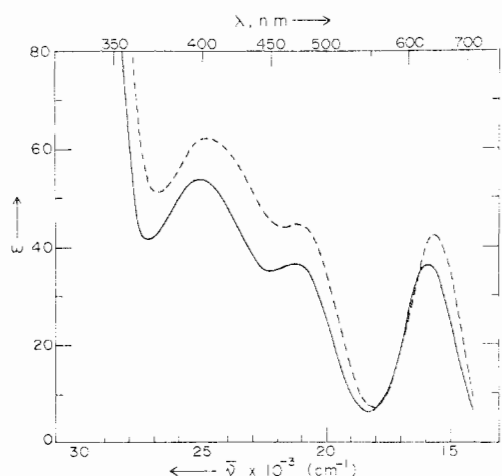


Figure 8. The visible absorption spectra of *trans-R,R:S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (—) and *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (---) in methanol.

amino protons. Allowing solutions of the carbonato complex to equilibrate over a period of 1 hr at 80° causes no change in the absorption spectrum but rapid racemization occurs. Slow racemization occurs even at room temperature in neutral water and there is no evidence of mutarotation as shown by the zero isodichroic points. The resultant solutions can then be converted to the *trans-R,R:S,S*-dichloro salt in about 97% yield. We have thus been unable to detect the presence of the *cis-β-R,S* carbonato complex. The analogous reaction with the oxalato complex leads to a slow (very small) increase in the magnitude in the circular dichroism spectrum which is consistent with a mutarotation. Conversion of the equilibrated oxalato complex to the *trans*-dichloro complex leads to the isolation of about 85% of the *trans-R,R:S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ion; the supernatant solution consists of the *trans-R,S* isomer. Monitoring the equilibration of the oxalato complex by physical methods is difficult since very small changes are involved; we have not pursued the problem.

The measurement of the mutarotation of the *cis-β-R,R*-[Co(3,2,3-tet)acac]<sup>2+</sup> ion is simple and accurate. In the presence of CO<sub>3</sub><sup>2-</sup> ions the *cis-β-R,R:S,S*-[Co(3,2,3-tet)acac]<sup>2+</sup> ion in water equilibrates at a convenient rate at 30° and we have monitored the reaction by nmr, by the visible absorption spectrum, by the circular dichroism spectrum, and by changes in optical rotation. It was found at 30° that an equilibrium was established consisting of 38 ± 2% of the *cis-β-R,R:S,S*-[Co(3,2,3-tet)acac]<sup>2+</sup> ion and 62 ± 2% of the *cis-R,R:S,S*-[Co(3,2,3-tet)acac]<sup>2+</sup> ion. It is interesting to note that in basic media the amino protons rapidly exchange while the central proton of the acac molecule does not, whereas in acid solution, the amino protons do not exchange but the central proton of the acac molecule is exchanged without loss of the acac molecule.

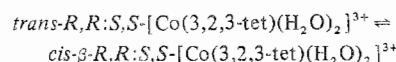
It thus appears that the amount of the *cis-β-R,S* complex at equilibrium increases from the carbonato complex to the acac complex. We are uncertain of the particular significance of this correlation between chelate ring size and the amount of *cis-β-R,S* complex at equilibrium.

All the *trans* complexes are quite optically stable in acidic solutions provided there is not a coordinated aquo group on the complex. Thus, for example, both the *rac*- and *meso-trans*-dichloro complexes can be boiled in hydrochloric acid without change in the configuration of the nitrogen atoms. In neutral methanol solutions the *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ion slowly exchanges its amino hydrogen protons and reverts to the *trans-R,R:S,S* complex which, at equilibrium, predominates to the extent of 99% of the equilibrium mixture. The physical properties (Figure 8) of the *trans-rac*- and

*trans-meso*-dichloro complexes are very similar and we have not been able to find any convenient accurate technique for monitoring the conversion. The value given for the equilibrium constant was obtained by isolation of the complex which can be achieved with accuracy. No detectable amounts of the *trans-R,S*-dichloro complex were present at equilibrium in methanol.

When an aquo group is coordinated to the metal, proton exchange and racemization occur even in acid solution. Thus, for example, the *trans-R,R*-[Co(3,2,3-tet)NO<sub>2</sub>H<sub>2</sub>O]<sup>2+</sup> ion slowly racemizes in perchloric acid solutions. This is a common feature of these complexes and we have looked at the problem more closely by measuring the properties of the *cis-β-R,R*- and *trans-R,R*-[Co(3,2,3-tet)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> ions at various acid concentrations. Because of the complicating *cis-β* ⇌ *trans* equilibrium that exists for these diaquo species, we have been unable to analyze the kinetic data in a closed form but, in spite of this, we are able to record the gross kinetic features of the reactions.

In acid aqueous solutions the *R,R:S,S* diaquo species attain the equilibrium



At 39° and at (sodium perchlorate) ionic strength of 5.0 *M* the equilibrium constant is  $[\textit{cis-}\beta]/[\textit{trans}] = 3/7$ . We have studied the kinetics of the approach to equilibrium of this reaction at acidities in the range 1–5 *M* HClO<sub>4</sub> at a constant ionic strength of 5.0 *M*. The rate of approach to equilibrium in either direction was found to be the same and is slightly (though detectably) acid dependent, and in the range studied, the observed rate constants (*k*) follow the equation  $10^4 k \text{ (sec}^{-1}\text{)} = 18.3 + 2.1[\text{H}^+]$  at 39°. The value of the equilibrium constant, however, is the same throughout this range of acidities. The rate is strongly dependent on ionic strength. Thus when the ionic strength is reduced from 5 to 1 *M* at 1 *M* HClO<sub>4</sub>, the rate constant changes from  $2.0 \times 10^{-3}$  to  $7.6 \times 10^{-4} \text{ sec}^{-1}$  which is greater than the total variation of the acid dependence in the range studied. Since the mechanism of isomerism is almost certainly governed by aquo exchange, the acid dependence of the isomerization does have a precedent in the system<sup>21</sup> [Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> and may be explained in terms of a preequilibrium protonation of the aquo groups. In order to detect any change in the configuration of the inner nitrogen atoms the reaction was quenched at various stages and at equilibrium with concentrated hydrochloric acid and we have always obtained the *trans-R,R:S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup> ion in quantitative yield. (We have checked that no proton exchange occurs during the quenching process by deuteration both the *cis*- and *trans*-diaquo species.) However, the [Co(3,2,3-tet)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> system does racemize even in 5 *M* HClO<sub>4</sub>. This racemization is inhibited by acid and is considerably slower than the attainment of *cis* ⇌ *trans* equilibrium but still proceeds, after geometrical equilibrium has been attained, with a half-life of 56 hr in 1 *M* HClO<sub>4</sub> and 200 hr in 5 *M* HClO<sub>4</sub> at 39°, the ionic strength in both cases being 5 *M*. We have measured the rates of amino proton exchange by the nmr spectrum of the isolated *trans-R,R:S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> complex. The 60-MHz signals of the amino protons of this complex occur in essentially two sets corresponding to areas of 2:4 occurring at lower and higher fields, respectively (Figure 5). The two lower field protons exchange at about 10 times the rate of the four higher field protons when measured after *cis* ⇌ *trans* equilibrium has been attained. It is remarkable<sup>22</sup> that the rate of exchange of the lower field protons is roughly 5 times that of racemization while the higher field protons exchange at about the same rate as racemization occurs. These ratios remain approximately constant in the 1–5 *M* acid range. Although we suspect that the lower field signal

corresponds to the inner two protons of the complex, we have no unambiguous proof of the assignment but, whatever the assignment, racemization is an exceptionally efficient process once a proton has been removed. We prefer not to speculate on the reason for this except to note that racemization must occur through the *R,S* configuration of the nitrogen atoms. We have no evidence as to whether the racemization proceeds *via* the *cis* and/or the *trans* complex.

Properties remarkable as those of the diaquo species are shown by the hydroxoquo complex. Isomerization of the *cis-β-R,R,S,S*-[Co(3,2,3-tet)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> ion in the presence of 1 equiv of base is immeasurably fast, the spectrum upon dissolution being that of the *trans-R,R,S,S*-[Co(3,2,3-tet)-OHOH<sub>2</sub>]<sup>2+</sup> ion. In addition, amino proton exchange of the hydroxoquo complex is complete within the time of dissolution in neutral D<sub>2</sub>O. The rate of racemization of the *trans-R,R*-[Co(3,2,3-tet)OHOH<sub>2</sub>]<sup>2+</sup> ion is far greater than that of any other complex we have made, and in water solution at 39°, the racemization rate constant is  $8 \times 10^{-3} \text{ sec}^{-1}$  ( $t_{1/2} = 1.4$  min). In comparison, although the *trans-R,R*-[Co(3,2,3-tet)(OH)<sub>2</sub>]<sup>+</sup> ion exchanges its amino hydrogen protons "instantaneously" at pH 11.3, its racemization rate constant at this pH at 39° is  $3.7 \times 10^{-5} \text{ sec}^{-1}$  ( $t_{1/2} = 5.2$  hr).

It thus appears that a crucial factor in these racemizations is not so much the rate of proton exchange but rather the presence of an aquo group in the complex. In view of the general lability of aquo complexes, particularly the hydroxoquo ion, it may be that racemization occurs *via* a five-coordinate intermediate rather than the six-coordinate complex. Whether amino proton exchange precedes the formation of the intermediate or occurs at the intermediate<sup>23</sup> is a matter that is not resolved in the present experiments.

Though we have not carried out any kinetic measurements on the racemization of the other *trans-R,R*-[Co(3,2,3-tet)-XY]<sup>n+</sup> ions, the rate observed for the dihydroxo complex seems comparable with these systems in that, in general, the *trans-R,R*-XY species racemize to the extent of about 10% over a period of several days in neutral room-temperature water.

## Experimental Section

**Instrumentation.** Ultraviolet and visible absorption spectra were recorded on Unicam SP 800 and Bausch and Lomb Spectronic 505 spectrophotometers. Circular dichroism spectra were obtained with a Roussel-Jouan Dichrographe, Model II, and rotations were measured on a Perkin-Elmer Model 141 digital polarimeter focused on the sodium D line. Conductivities were obtained at a single concentration of 10<sup>-3</sup> M on a Sargent-Welch Model MS-1 conductivity bridge. Routine nmr spectra were recorded at 60 MHz on a Varian T60 instrument. The temperature was 29°. All elemental analyses were obtained by automated microanalytical techniques.

**Kinetics. Isomerization.** The rate of approach to isomerization equilibrium was measured at 38.8° at 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 M HClO<sub>4</sub> acid concentrations where in each case, except the last, the solutions were made up to 5 M ionic strength with NaClO<sub>4</sub>. The starting material for the *trans*-diaquo → *cis*-diaquo isomerization was the *trans-R,R,S,S*-[Co(3,2,3-tet)OHOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex which was instantly protonated to give a green-brown solution of the *trans*-diaquo complex which slowly turned to the pink color of the *cis*-diaquo complex. For the isomerization *cis* → *trans* it was found that either the *cis*-diaquo or the *cis* carbonate perchlorate complexes could be used; both gave the same rate constants and, for convenience, the carbonate species was generally used. Isosbestic points were observed at 567, 472, and 390 mμ and remained throughout the reaction and at equilibrium. The greatest change in optical density was observed at 515 mμ and this wavelength was used to monitor the reaction continuously using a Perkin-Elmer 402 spectrophotometer set at that wavelength. The reaction was followed to essential equilibrium. It was found that either a Guggenheim plot or a standard plot using the equilibrium optical density gave linear curves over 5 half-lives and identical values of the rate constants were obtained; this was observed for both the *cis* and *trans* isomers as starting materials. The

initial spectra of the *trans*- and *cis*-diaquo species were found for each acid concentration by extrapolating the visible spectra to zero time. This procedure was probably sufficiently accurate in the desired spectrophotometric region that an error of not more than ±5% would be computed in the equilibrium proportions of the isomers.

**Racemization.** The rates of racemization at 38.8° of the diaquo complexes were measured in 1.0, 3.0 and 5.0 M HClO<sub>4</sub> made up to an ionic strength of 5 M with NaClO<sub>4</sub>. No detectable racemization had occurred in all cases before the isomerization equilibrium was attained. The addition of concentrated HCl to the solution just after the isomer equilibrium was established gave a quantitative yield of the *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>](ClO<sub>4</sub>) which was fully optically active. The racemization was followed by the visible circular dichroism spectra changes of the equilibrium species. Isodichroic points corresponding to zero circular dichroism were observed at 422 and 542 mμ throughout the racemization process. Samples of the active *trans-R,R*-[Co(3,2,3-tet)OHOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex were usually used but starting with active carbonate or *cis*-diaquo complexes gave the same racemization rates.

The rate of racemization of *trans-R,R*-[Co(3,2,3-tet)OHOH<sub>2</sub>]<sup>2+</sup> was carried out in degassed water at 38.8°. (Addition of NaClO<sub>4</sub> to the solution led to precipitation, and in strong ClO<sub>4</sub><sup>-</sup> solutions a pink complex, probably the *cis*-hydroxoquo species, was observed to form in the solution.) The extent of racemization was monitored by the circular dichroism spectrum of the *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>](ClO<sub>4</sub>) complex at 370 mμ (in DMF). The reaction was quenched at various times by the addition of an equal volume of concentrated HCl. This solution quantitatively precipitates the *trans*-dichloro complex as the ClO<sub>4</sub><sup>-</sup> salt. This was collected and the circular dichroism measured. The reaction was followed for 5 half-lives over which straight lines were obtained by plotting the log of the circular dichroism *vs.* time.

The racemization at 38.8° of *trans-R,R*-[Co(3,2,3-tet)(OH)<sub>2</sub>]<sup>+</sup> was measured at pH 11.3 and at an ionic strength of 5.0 M made up with NaClO<sub>4</sub>. The pH was adjusted by adding a solution of NaOH to the *trans-R,R*-[Co(3,2,3-tet)OHOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> in water with the aid of a pH meter. Samples were taken at intervals and cooled in an ice bath and the visible circular dichroism was taken. Isodichroic points were observed at 438 and 558 mμ which corresponded to zero circular dichroism. These points were retained throughout the racemization process and, furthermore, the normal absorption spectrum was constant over the same period. The reaction was followed over 6 half-lives and gave good first-order plots. All the solutions were degassed and CO<sub>2</sub> was excluded during all the manipulations. The pH was the same at the end of the experiment as it was in the beginning.

**Proton Exchange.** Amino proton exchange studies at 38.8° were carried out on the deuterated *cis*-diaquo and *trans*-diaquo species at 1.0, 3.0, and 5.0 M HClO<sub>4</sub> at an ionic strength of 5.0 M adjusted with NaClO<sub>4</sub>. The *trans*-[Co(3,2,3-tet)OHOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex was deuterated by recrystallizing it twice from D<sub>2</sub>O at 80° by the addition of NaClO<sub>4</sub>; the *cis-β-R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, by recrystallizing the complex twice from D<sub>2</sub>O containing a small amount of Li<sub>2</sub>CO<sub>3</sub> by the addition of methanol. The deuterated carbonate complex was converted to the deuterated *cis-β-R,R,S,S*-[Co(3,2,3-tet)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> by the addition of (protic) HClO<sub>4</sub> in the way described later. Addition of concentrated HCl to D<sub>2</sub>O solutions of any one of the above deuterated complexes gave a quantitative precipitation of the *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>](ClO<sub>4</sub>) complex which was shown by nmr to be fully deuterated. This observation formed the basis of our analysis of the proton-exchange reactions.

It was found that no detectable proton exchange occurs before isomerization equilibrium is attained. (This was shown by quenching the reaction with HCl just after isomeric equilibrium was achieved.) The isolated *trans*-dichloro complex was fully deuterated at this stage and was so whether the *cis*-diaquo or the *trans*-diaquo species was used as starting material. The proton-exchange reaction was carried out using in most cases the deuterated *trans*-hydroxoquo complex in the protic media. The reaction was quenched with an equal volume of concentrated HCl at various times and the nmr spectrum (at 60 MHz) of the isolated *trans*-dichloro complex in DMSO-*d*<sub>6</sub> was measured. By integrating the amino proton areas against the isolated methylene peak at τ 8.10 the extent of proton uptake of both the high- and low-field amino protons was monitored (Figure 5). Such a procedure gave satisfactory first-order plots over 5 half-lives but is not very accurate. Errors of up to ±20% in the rate constants are

probable. Proton exchange of the *trans*-*R,R,S,S*-[Co(3,2,3-tet)-OH(OH)]<sup>2+</sup> in water and *trans*-*R,R,S,S*-[Co(3,2,3-tet)(OH)]<sup>+</sup> in water at pH 11.3 was complete in the time of dissolution.

In all the above reactions light was routinely excluded and all runs were repeated at least twice.

**Preparations.** **1,10-Diamino-4,7-diazadecane (3,2,3-tet).** 1,2-Dibromoethane (30 ml) was added dropwise over a period of 30 min to 1,3-diaminopropane (250 ml) which was ice-cooled and stirred. After the addition was complete, the mixture was refluxed for 60 min. The excess 1,3-diaminopropane was removed by distillation under water-pump vacuum and the remaining pale yellow, syrupy liquid was cooled to room temperature before the addition of a solution of KOH (39 g) in methanol (150 ml). After standing 60 min the precipitated KBr was filtered off and the filtrate was fractionally distilled under water-pump vacuum. The crude product was collected as a well-isolated fraction between 160 and 180°; yield 33 g (59%). Redistillation under high vacuum gave 24 g of colorless liquid, bp 127–128° (0.6 mm).

*Anal.* Calcd for C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>: C, 55.1; H, 12.7; N, 32.1. Found: C, 55.1; H, 12.3; N, 32.3.

The addition of 2 mol of water to 3,2,3-tet produces a solid white mass, which can be recrystallized from dioxane by the addition of ether to deposit long colorless needles of the amine dihydrate. This compound is readily dehydrated by vacuum desiccation and rapidly absorbs atmospheric CO<sub>2</sub> to form a stable crystalline solid.

**Optically Inactive Complexes.** **1. *trans*-*R,R,S,S*-[Co(3,2,3-tet)-Cl<sub>2</sub>Cl·H<sub>2</sub>O].** CoCl<sub>2</sub>·6H<sub>2</sub>O (24 g) in methanol (300 ml) and glacial acetic acid (3 ml) was mixed with 3,2,3-tet (18 g) in methanol (50 ml). The resultant brown-violet solution was oxidized by a vigorous passage of air for 4 hr. Concentrated HCl (25 ml) was added and the solution was heated for 10 min on the steam bath. On standing at 0° for 1 hr, the resultant solution precipitated feathery, pale green needles, which were collected and washed with ethanol and ether; yield 28 g (78%). The complex was recrystallized from a minimum volume of hot 4 M HCl by the addition of 10 volumes of methanol; Δ<sub>M</sub> = 86 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup> (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]Cl·H<sub>2</sub>O: C, 26.9; H, 6.8; N, 15.7; Cl, 29.8. Found: C, 27.1; H, 7.0; N, 15.5; Cl, 29.3.

If this same preparation is carried out in aqueous solution, the chloride salt is obtained as a flocculent precipitate which is extremely difficult to filter and dry. The rather insoluble perchlorate salt is then more conveniently handled, being obtained in 90% yield when HClO<sub>4</sub> is added with HCl to the oxidized Co(II)-amine mixture. It may be recrystallized from boiling 4 M HCl (c 70 ml/g) as small, dark green needles.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 23.8; H, 5.5; N, 13.9; Cl, 26.4. Found: C, 23.9; H, 5.5; N, 14.0; Cl, 26.1.

**2. *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]Cl·3H<sub>2</sub>O.** A mixture of *trans*-*R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.7 g) and Li<sub>2</sub>CO<sub>3</sub> (0.6 g) in water (10 ml) was heated on the steam bath for 15 min. The deep violet solution formed was filtered hot and then was diluted with ethanol (15 ml) followed by a large volume of acetone rapidly to precipitate a pink powder, which was washed thoroughly with acetone and ether; yield 2.5 g (87%). This material was recrystallized from water (8 ml) by the addition of ethanol (20 ml) followed by acetone (30 ml). On standing at 0° for 30 min the solution deposited the complex as glistening pink-violet flakes, which were washed with ethanol, acetone, and ether; Δ<sub>M</sub> = 97 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup> (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)CO<sub>3</sub>]Cl·3H<sub>2</sub>O: C, 28.2; H, 7.4; N, 14.6. Found: C, 28.5; H, 7.2; N, 14.7.

Addition of a concentrated methanol solution of NaClO<sub>4</sub> to a saturated solution of the chloride salt in methanol-water (10:1) gave a quantitative precipitation of the perchlorate. This salt was recrystallized from a minimum amount of water by the slow addition of methanol to give long, red-violet needles of the methanolate, which was not desolvated by extensive vacuum desiccation (over P<sub>2</sub>O<sub>5</sub>). The methanol solvate was detected by nmr.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)CO<sub>3</sub>]ClO<sub>4</sub>·CH<sub>3</sub>OH: C, 28.2; H, 6.2; N, 13.2. Found: C, 28.3; H, 5.9; N, 13.4.

**3. *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)Cl]Cl<sub>2</sub>.** Solid *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]Cl·3H<sub>2</sub>O (5.0 g) was added to an ice-cold mixture of HCl (10 ml, 12 M) and acetone (40 ml). The violet solution was maintained between 0 and 5° and stirred continuously. A pink-violet precipitate commenced to form after 5 min. After 15 min this was filtered off and washed with acetone; yield 2.5 g (48%). The complex continued to precipitate beyond this time but became

increasingly contaminated with *trans*-*R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O. The initial precipitate was recrystallized from dilute HCl (2 M at 0°) by the addition of a fourfold volume of acetone. Fine, deep pink needles were formed.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(OH<sub>2</sub>)Cl]Cl<sub>2</sub>·2.5H<sub>2</sub>O: C, 23.9; H, 7.3; N, 13.9; Cl, 26.4. Found: C, 24.0; H, 7.1; N, 13.8; Cl, 26.6.

**4. *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.** *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>·CH<sub>3</sub>OH (5.0 g) was dissolved, with stirring, in HClO<sub>4</sub> (12 M, 9 ml at 0°). After the CO<sub>2</sub> effervescence had ceased, the violet-brown solution was stored at 0° for 24 hr to give large, dark purple-brown blocks. These were filtered and washed with ethanol-ether (1:10) and then ether. It was recrystallized from cold water (1 ml/g) to which was added cold HClO<sub>4</sub> (c 3 ml/g). On standing at 0° for 12 hr, the red crystals were filtered; Δ<sub>M</sub> = 400 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup> (in water, extrapolated).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>: C, 17.0; H, 4.6; N, 9.9; Cl, 18.8. Found: C, 17.2; H, 4.6; N, 10.0; Cl, 18.5.

**5. *trans*-*R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>.** *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>·CH<sub>3</sub>OH (7.0 g) was dissolved in HClO<sub>4</sub> (12 M, 2.8 ml) and water (5 ml) and heated on the steam bath until the CO<sub>2</sub> evolution had ceased. The red-violet solution was cooled and then mixed with aqueous NaOH (1.00 M, 17 ml), whereupon a rapid precipitation of brown-violet crystals occurred. After standing for 2 hr at 0°, these were collected and washed with methanol (20 ml), ethanol, and ether; yield 5.8 g (75%). The complex was recrystallized from water (80°) by the addition of excess NaClO<sub>4</sub>, giving large violet blocks; Δ<sub>M</sub> = 166 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup> (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>: C, 20.6; H, 5.4; N, 12.0; Cl, 15.2. Found: C, 20.8; H, 5.4; N, 11.9; Cl, 15.4.

**6 and 7. *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> and *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>.** *trans*-*R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub> (4.7 g) was heated on the steam bath with a solution of 2,4-pentanedione (1.1 g) in methanol (100 ml) for 10 min. The rapidly formed deep red solution was taken to dryness under vacuum and the rose pink residue redissolved in dilute HClO<sub>4</sub> (0.1 M, 40 ml, 80°). The solution was filtered and after 12 hr at room temperature gave small orange-red crystals which were collected and washed with ethanol-ether (1:2) and then ether; yield 1.6 g (ca. 95% isomeric purity). One recrystallization from dilute HClO<sub>4</sub> (0.1 M, 20 ml, 80°) gave pure *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> (0.9 g) as large orange-red blocks; Δ<sub>M</sub> = 165 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup> (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>: C, 29.4; H, 5.5; N, 10.5; Cl, 13.4. Found: C, 29.2; H, 5.8; N, 10.4; Cl, 13.4.

Addition of HClO<sub>4</sub> (12 M, 10 ml) to the filtrate from the first fraction and storage at 0° for 3 hr gave a mixture of orange-red blocks (*cis*-*β*-*R,R,S*) and rose red plates (*cis*-*β*-*R,R,S,S*) (2.6 g), the latter being the major (ca. 80%) constituent. Two recrystallizations from dilute HClO<sub>4</sub> (0.1 M, 20 ml, 80°) followed by the addition of HClO<sub>4</sub> (12 M, 1 ml) gave pure *cis*-*β*-*R,R,S,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> (0.8 g) as clusters of very large, rose red plates; Δ<sub>M</sub> = 182 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>.

*Anal.* Found: C, 29.3; H, 5.7; N, 10.4; Cl, 13.2.

**8. [Co<sup>III</sup>(3,2,3-tet)(OH)<sub>2</sub>]<sub>3</sub>Co<sup>II</sup>(ClO<sub>4</sub>)<sub>5</sub>, "Hexol."** A filtered solution of *trans*-*R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub> (8.0 g) in NaOH (1.00 M, 17.1 ml) was heated on the steam bath as a solution of [Co(OH<sub>2</sub>)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (3.1 g) in water (10 ml) was slowly stirred in. Initially, some precipitation of the hydroxyquo complex (and Co(OH)<sub>2</sub>) occurred, but on continued heating and stirring this violet precipitate was transformed into rust red crystals. After 5 min of heating, the mixture was cooled at 0° for 12 hr and the precipitate was collected and washed with methanol and ether; yield 7.0 g (90%); μ<sub>eff</sub> = 4.8 BM (calculated by assuming a (temperature-independent) paramagnetism of 0.5 BM for each Co(III) atom).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(OH)<sub>2</sub>]<sub>3</sub>Co(ClO<sub>4</sub>)<sub>5</sub>: C, 21.2; H, 5.1; N, 12.4; Cl, 13.1. Found: C, 21.2; H, 5.2; N, 12.3; Cl, 12.9.

**9. *trans*-*R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>.** (i) NaNO<sub>2</sub> (0.5 g) was added to an ice-cold solution of *cis*-*β*-*R,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub> (1.0 g) in HCl (5 M, 10 ml). An immediate color change from red to yellow-brown occurred. HClO<sub>4</sub> (12 M, 2 ml) was added and the solution was heated on the steam bath for 30 min. It became green-yellow. On standing of the mixture at room temperature for 12 hr, large, very thin, yellow-green plates deposited. These were washed with water (10 ml), ethanol, and ether; yield 0.45 g (60%). The complex was recrystallized from HCl (5 M, 10 ml, 100°) by the addition of HClO<sub>4</sub> (12 M, 2 ml).

(ii) A solution of [Co(3,2,3-tet)(OH)<sub>2</sub>]<sub>3</sub>Co(ClO<sub>4</sub>)<sub>5</sub> (3.6 g) in HCl



(2 M, 100 ml) was heated on the steam bath for 30 min.  $\text{HClO}_4$  (12 M, 2 ml) was added and the solution was allowed to stand at 0° for 12 hr. The precipitate of pure *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (2.0 g) was filtered off and the filtrate was taken to dryness under vacuum. The residue, which often contained some pink crystals, presumably *cis-β-R,R,S,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)Cl]Cl<sub>2</sub>, was dissolved in HCl (5 M, 20 ml, 80°), filtered, and mixed with  $\text{HClO}_4$  (12 M, 5 ml). On standing of the mixture for 24 hr at 0°, 0.8 g (75% of possible *R,S*) of the *trans-R,S*-dichloro complex was obtained as yellow-green plates. A variation of this preparation was to heat the "hexol" in a mixture of HCl-HClO<sub>4</sub> (each 5 M), thus precipitating both of the complexes together. The *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> may then be preferentially extracted into acetone, in which it is readily soluble in the cold.

(iii) A solution of *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (40 g) and NaOH (10 g) in water (500 ml) was heated on the steam bath for 30 min. HCl (12 M, 50 ml) and  $\text{HClO}_4$  (12 M, 5 ml) were added; the solution was heated a further 10 min and then allowed to stand at 0° for 12 hr. The precipitated *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (38 g) was filtered off and the filtrate taken to dryness under vacuum. The residue was extracted with boiling HCl (2 M, 20 ml) and the extract filtered and mixed with  $\text{HClO}_4$  (12 M, 5 ml) to precipitate (on cooling) 1.0 g (2.5%) of *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>;  $\Delta\mu = 80 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in methanol).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 23.8; H, 5.5; N, 13.9; Cl, 26.4. Found: C, 23.7; H, 5.6; N, 14.0; Cl, 26.2.

**10. *cis-β-R,R,S,S*-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>]ClO<sub>4</sub>.** *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (0.55 g) and oxalic acid dihydrate (0.55 g) in water (10 ml) were heated on the steam bath for 15 min, giving a pink-violet solution. This was cooled, filtered, mixed with  $\text{HClO}_4$  (12 M, 1 ml) and ethanol (100 ml), and allowed to stand at 0° for 12 hr to deposit small red-violet crystals. These were recrystallized from  $\text{HClO}_4$  (1 M, 30 ml, 80°) to give shiny, pink flakes; yield 0.20 g (35%). (When heated with HCl-HClO<sub>4</sub> for 2 hr these were converted back to *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>;  $\Delta\mu = 79 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ .)

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)C<sub>2</sub>O<sub>4</sub>]ClO<sub>4</sub>: C, 28.5; H, 5.3; N, 13.3. Found: C, 28.5; H, 5.5; N, 13.4.

**11. *cis-β-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O.** *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (4.5 g) was dissolved in a hot, filtered solution of oxalic acid dihydrate (1.6 g) and Li<sub>2</sub>CO<sub>3</sub> (0.95 g) in water (40 ml) and heated on the steam bath for 30 min. The deep pink-violet solution that formed was cooled, diluted with acetone (80 ml), and allowed to stand at 0° for 12 hr to precipitate pink needles, which were washed with acetone; yield 4.2 g (89%). Recrystallization from hot water by the addition of a fourfold volume of ethanol gave large, shiny, red-violet flakes of the oxalato complex;  $\Delta\mu = 83 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)C<sub>2</sub>O<sub>4</sub>]Cl·H<sub>2</sub>O: C, 32.0; H, 6.5; N, 14.9. Found: C, 32.2; H, 6.5; N, 15.1.

The sparingly soluble bromide salt is slowly formed as large needles by addition of LiBr to a concentrated aqueous solution of the chloride.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)C<sub>2</sub>O<sub>4</sub>]Br·4H<sub>2</sub>O: C, 25.4; H, 6.4; N, 11.8. Found: C, 25.3; H, 6.5; N, 11.8.

**12. *trans-R,R,S,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>.** *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (18 g) and NaNO<sub>2</sub> (10 g) were dissolved in water (100 ml) and heated on the steam bath for 30 min to produce a clear, deep yellow solution. Addition of NaClO<sub>4</sub> (10 g) gave a yellow precipitate, which, after cooling 60 min at room temperature, was collected and washed with water, ethanol, and ether; yield 20 g (94%). The complex was recrystallized from boiling water (c 40 ml/g) to give chunky yellow-orange crystals;  $\Delta\mu = 81 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>: C, 22.6; H, 5.2; N, 19.8. Found: C, 22.8; H, 5.4; N, 19.4.

**Iodide.** Substitution of the NaClO<sub>4</sub> with NaI (10 g) provided the iodide salt of the complex in similar yield. It also was recrystallized from boiling water.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)<sub>2</sub>]I: C, 21.2; H, 4.9; N, 18.6. Found: C, 21.4; H, 4.9; N, 18.5.

**Chloride.** The chloride salt could be conveniently prepared from the perchlorate. *trans-R,R,S,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> (80 g) in dimethylformamide (600 ml) was mixed with LiCl (15 g) in water (20 ml) and allowed to stand at 0° for 30 min. The yellow precipitate was washed with dimethylformamide (50 ml), acetone, and ether; yield 70 g (98%). By slow addition of acetone to its saturated aqueous solution, the complex was recrystallized as lustrous, golden flakes.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)<sub>2</sub>]Cl·H<sub>2</sub>O: C, 25.4; H, 6.4; N, 22.2. Found: C, 25.4; H, 6.5; N, 22.0.

**13. *trans-R,R,S,S*-[Co(3,2,3-tet)Br<sub>2</sub>]ClO<sub>4</sub>.** *cis-β-R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>·CH<sub>3</sub>OH (0.5 g) was dissolved in HBr (5 M, 5 ml) and heated for 5 min on the steam bath. On standing of the mixture at 0° for 12 hr, large yellow-green needles deposited, which were collected and washed with water, ethanol, and ether; yield 0.58 g (100%). The complex was recrystallized from boiling HBr (5 M);  $\Delta\mu = 90 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water, extrapolated; dissociation).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Br<sub>2</sub>]ClO<sub>4</sub>: C, 19.5; H, 4.5; N, 11.4; Br, 32.5; Cl, 7.2. Found: C, 19.4; H, 4.6; N, 11.2; Br, 32.3; Cl, 7.2.

**14. *trans-R,R,S,S*-[Co(3,2,3-tet)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>.** *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.0 g) and NaN<sub>3</sub> (1.5 g) in water (20 ml, 80°) were heated on the steam bath for 30 min, to give an intensely deep blue solution. The hot solution was filtered and NaClO<sub>4</sub> (2.0 g) was added. The solution was allowed to cool and stand at room temperature for 30 min. The small, green-blue crystals thus formed were collected and washed with water (10 ml), ethanol, and ether; yield 2.2 g (94%). Recrystallization from water (80 ml, 100°) gave large, shiny, almost black plates;  $\Delta\mu = 85 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>: C, 23.0; H, 5.3; N, 33.6. Found: C, 23.0; H, 5.4; N, 33.6.

**15. *trans-R,R,S,S*-[Co(3,2,3-tet)(NCS)<sub>2</sub>]ClO<sub>4</sub>.** *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.0 g) and NaNCS (1.8 g) in water (20 ml, 80°) were heated on the steam bath. *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]NCS precipitated initially but dissolved in 2-3 min to give a violet solution, which, in 15 min, became deep red. After 30 min the solution was filtered hot and NaClO<sub>4</sub> (2.0 g) added to precipitate rose red crystals. On cooling for 60 min at room temperature these were washed with ethanol-water (1:1, 10 ml), ethanol, and ether; yield 2.0 g (80%). Recrystallization from water (30 ml, 100°) gave large, thin, rose red flakes;  $\Delta\mu = 81 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NCS)<sub>2</sub>]ClO<sub>4</sub>: C, 26.7; H, 4.9; N, 18.7. Found: C, 26.7; H, 5.1; N, 18.4.

**16. *trans-R,R,S,S*-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>.** Finely ground NaCN (0.50 g) was added to a magnetically stirred solution of *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (2.0 g) in DMSO (30 ml). The green solution rapidly turned brown and then yellow, and after 5 min no further color change could be discerned. After 15 min an appreciable amount of a yellow precipitate was present, presumably *trans-R,R,S,S*-[Co(3,2,3-tet)(CN)<sub>2</sub>]Cl. Precipitation was completed by the addition of ethanol (50 ml) and ether (250 ml). After the yellow powder had settled, it was filtered off, dissolved in water (80 ml, 80°), and filtered. NaClO<sub>4</sub> (5.0 g) was added and the solution was allowed to stand for 60 min to give bright yellow crystals, which were collected and washed with water (10 ml), ethanol, and ether; yield 1.5 g (78%). Recrystallization from boiling water gave small yellow needles;  $\Delta\mu = 77 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(CN)<sub>2</sub>]ClO<sub>4</sub>: C, 31.2; H, 5.8; N, 21.9. Found: C, 31.1; H, 5.9; N, 21.8.

**17. *trans-R,R,S,S*-[Co(3,2,3-tet)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·HNO<sub>3</sub>.** *cis-β-R,R,S,S*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>·CH<sub>3</sub>OH (0.50 g) was dissolved in HNO<sub>3</sub> (8 M, 5 ml) and the solution was allowed to stand at 0° for 12 hr. Large, red-green dichroic needles were deposited, which on washing with ethanol and ether powdered slightly and turned dull green; yield 0.45 g (79%). The complex was recrystallized by the addition of an equal volume of HNO<sub>3</sub> (14 M) to its concentrated (aqueous) solution in water. After 12 hr at 0° the crystals were collected;  $\Delta\mu = 80 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (for the simple nitrate, see preparation described for the optically active complex, in methanol). The complex rapidly aquates in water but does not solvolyze in methanol.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·HNO<sub>3</sub>: C, 19.9; H, 4.8; N, 23.2. Found: C, 20.1; H, 5.0; N, 23.2.

**18. *trans-R,R,S,S*-[Co(3,2,3-tet)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>·H<sub>2</sub>O.** *trans-R,R,S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (1.0 g) was dissolved in aqueous ammonia (15 M, 10 ml), giving a deep pink solution. Absolute ethanol (100 ml) was added and the still clear solution was allowed to stand at 0° for 24 hr, after which the dull orange powder was collected and washed with ethanol and ether; yield 0.40 g (37%). To free it of a small amount of a pink contaminant, the complex was twice recrystallized from HCl (0.1 M) by the addition of ethanol (five volumes), thus forming as deep orange needles;  $\Delta\mu = 316 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NH}_3)_2]\text{Cl}\cdot\text{H}_2\text{O}$ : C, 24.5; H, 7.7; N, 21.5. Found: C, 24.7; H, 8.0; N, 21.5.

**19–22.** *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)X]ClO<sub>4</sub>* (X = Cl, Br, NCS, N<sub>3</sub>). Finely ground *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>* (0.50 g) was dissolved in boiling HClO<sub>4</sub> (1 M, 20 ml) to give a clear, deep orange solution. This was cooled at 0° for 1 hr and filtered if any *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>* had precipitated. Addition of LiCl (0.20 g), LiBr (0.40 g), NaNCS (0.40 g) or NaN<sub>3</sub> (1.0 g) followed by warming to 50° for 2 min caused ready precipitation of bright red *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)Cl]ClO<sub>4</sub>* (0.45 g, 92%), deep red *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)Br]ClO<sub>4</sub>* (0.49 g, 91%), orange *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)NCS]ClO<sub>4</sub>* (0.30 g, 58%) or dark red-brown *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)N<sub>3</sub>]ClO<sub>4</sub>* (0.35 g, 71%), respectively. All these products were collected and washed with water (5 ml), ethanol, and ether. The chloro- and bromonitro complexes were recrystallized from the respective dilute hydrohalic acid (0.01 M); the azido and isothiocyanato species were crystallized from water. All formed as clusters of very small needles.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)\text{Cl}]ClO_4$ : C, 23.2; H, 5.4; N, 16.9; Cl, 17.1. Found: C, 23.3; H, 5.6; N, 16.4; Cl, 16.9.  $\Delta_M = 86 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ .

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)\text{Br}]ClO_4$ : C, 20.9; H, 4.8; N, 15.3; Cl, 7.7; Br, 17.4. Found: C, 21.1; H, 4.8; N, 15.5; Cl, 8.0; Br, 17.9.  $\Delta_M = 75 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water, extrapolated).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)\text{NCS}]ClO_4$ : C, 24.7; H, 5.1; N, 19.2; S, 7.3. Found: C, 24.6; H, 5.0; N, 19.2; S, 7.2.  $\Delta_M = 79 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)\text{N}_3]ClO_4$ : C, 22.8; H, 5.3; N, 26.6. Found: C, 22.7; H, 5.0; N, 26.4.  $\Delta_M = 85 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

**Resolutions.** **1.** *trans-R,R,S,S-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O*. A filtered aqueous solution of *trans-R,R,S,S-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O* (18.0 g in 125 ml, 80°) was mixed with NH<sub>4</sub>(+)BCS (8.5 g in 25 ml, 80°), cooled to room temperature, and then allowed to stand at 0° for 3 hr. The large green needles that deposited were collected and washed with ethanol (200 ml) and ether; yield 12.5 g (74% optical yield). Recrystallization from methanol (150 ml, 66°) again gave large needles;  $[\alpha]_D +67 \pm 2^\circ$  (10<sup>-2</sup> M in 0.1 M HCl). Repeated recrystallization from methanol (or water) caused no change in this rotation.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{Cl}_2](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})\cdot 3\text{H}_2\text{O}$ : C, 32.4; H, 6.4; N, 8.4. Found: C, 32.3; H, 6.3; N, 8.3.

**(+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O***. The recrystallized **(+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>]BCS*** (8.7 g) was dissolved in HCl (6 M, 40 ml, 50°) and mixed with methanol (200 ml). After standing at 0° for 2 hr the solution deposited feathery, fine, green needles of **(+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O*** which were collected and washed with ethanol and ether; yield 4.8 g,  $[\alpha]_D +30 \pm 1^\circ$  (2 × 10<sup>-2</sup> M in 0.1 M HCl). Recrystallization from HCl-methanol did not change this rotation.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{Cl}_2]Cl\cdot\text{H}_2\text{O}$ : C, 26.9; H, 6.8; N, 15.7. Found: C, 27.4; H, 6.8; N, 15.4.

Addition of HClO<sub>4</sub> to a warm aqueous solution of either the BCS<sup>-</sup> or Cl<sup>-</sup> salts gave essentially quantitative precipitation of **(+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>***;  $[\alpha]_D +92 \pm 3^\circ$  (10<sup>-2</sup> M in DMF). Recrystallization from HCl (as below for the (-) isomer) did not change the rotation.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{Cl}_2]ClO_4$ : C, 23.8; H, 5.5; N, 13.9; Cl, 26.4. Found: C, 23.8; H, 5.5; N, 13.9; Cl, 26.1.

**(-)-*trans-S,S-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O***. The filtrate and the first 20 ml of ethanol wash from the initial diastereoisomer precipitate were combined and HClO<sub>4</sub> (12 M, 3 ml) was added, giving an immediate pale green precipitate. After standing of the mixture 30 min, the solid was filtered off and washed with water, ethanol, and ether; yield 8.0 g (39%). Recrystallization was effected from HCl (4 M, 800 ml, 100°). After 12 hr at room temperature dark green needles were formed;  $[\alpha]_D -84 \pm 3^\circ$  (10<sup>-2</sup> M in DMF). Another recrystallization gave material for which the rotation did not change on further recrystallization; yield 4.0 g (39% optical yield),  $[\alpha]_D -92 \pm 3^\circ$ .

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{Cl}_2]ClO_4$ : C, 23.8; H, 5.5; N, 13.9; Cl, 26.4. Found: C, 23.9; H, 5.5; N, 13.8; Cl, 26.7.

**2.** *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Cl·H<sub>2</sub>O*. Solid Ag(+)BCS (22.1 g) was added to a solution of *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Cl·H<sub>2</sub>O* (20 g) in water (100 ml, 80°) and the mixture was

kept hot while being vigorously shaken for 10 min. The AgCl was filtered off and washed with water (eight 25-ml portions, 80°), and the filtrate and washings were taken to dryness under vacuum. The residue was taken up in water (100 ml, 80°), filtered, cooled slowly to room temperature, and stored at 0° for 12 hr. The golden needles thus deposited were washed with acetone-water (1:1, 20 ml), acetone, and ether; yield 13.0 g (82% optical yield),  $[\alpha]_D +30 \pm 1^\circ$  (2 × 10<sup>-2</sup> M in water). The filtrate and acetone-water wash were set aside. Recrystallization from water (10 ml/g, 80°) gave large golden-brown needles of identical rotation.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)_2](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})\cdot 2\text{H}_2\text{O}$ : C, 32.2; H, 6.0; N, 12.5. Found: C, 32.1; H, 6.0; N, 12.4.

**(-)-*trans-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>***. Dissolution of the recrystallized diastereoisomer (6.5 g) in water (75 ml, 80°) and addition of aqueous NaClO<sub>4</sub> (2.5 g in 10 ml) produced fine yellow needles of *trans-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>* (3.8 g);  $[\alpha]_D -19 \pm 1^\circ$  (10<sup>-2</sup> M in water) or  $+11 \pm 1^\circ$  (2 × 10<sup>-2</sup> M in DMF), these rotations being unchanged by recrystallization.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)_2]ClO_4$ : C, 22.6; H, 5.2; N, 19.8. Found: C, 22.6; H, 5.2; N, 19.7.

**(+)-*trans-S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>***. Reduction of the volume of the filtrate (plus acetone-water wash) from the initial diastereoisomer precipitate to 75 ml gave an additional 2.3 g of precipitate;  $[\alpha]_D +50 \pm 2^\circ$  (2 × 10<sup>-2</sup> M in water). This was far more soluble in water than the first fraction and on conversion to the perchlorate gave almost racemic (weakly dextrorotatory) material, which was discarded. Addition of NaClO<sub>4</sub> (5.0 g) to the filtrate from this second fraction gave optically impure **(+)-*trans-S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>*** (10.5 g);  $[\alpha]_D +13 \pm 1^\circ$  (10<sup>-2</sup> M in water). Three recrystallizations from water (30 ml/g, 100°) gave material of constant rotation, *trans-S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>* (2.5 g);  $[\alpha]_D +19 \pm 1^\circ$  (10<sup>-2</sup> M in water).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{NO}_2)_2]ClO_4$ : C, 22.6; H, 5.2; N, 19.8. Found: C, 22.7; H, 5.5; N, 19.9.

Some racemization may occur during recrystallization of this dinitro complex if the heating during dissolution is prolonged. Hence, it is advantageous to grind the solid finely beforehand.

**3.** *trans-R,R,S,S-[Co(3,2,3-tet)(CN)<sub>2</sub>]Cl·trans-R,R,S,S-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>* (1.75 g) was quantitatively converted to the chloride by shaking a hot methanolic slurry of the solid with a large excess of Dowex 2-X8 Cl<sup>-</sup> form anion-exchange resin until a clear yellow solution had formed. This solution was taken to dryness under vacuum, and the residue was dissolved in water (50 ml) and then mixed with Ag(+)BCS (1.90 g) in methanol (50 ml). The mixture was heated and stirred on the steam bath for 10 min before filtering off the AgCl, which was washed with boiling water (20 ml). The filtrate-wash was taken to dryness under vacuum and the residue was dissolved in boiling methanol (110 ml), filtered, and allowed to stand at 0° for 12 hr to precipitate fluffy, pale yellow needles, which were collected and washed with methanol (5 ml), methanol-ether (1:1), and ether; yield 0.9 g,  $(\epsilon_l - \epsilon_r) = -0.74$  (417 nm). (The small D line rotation of the diastereoisomer made CD measurement a much more precise check of activity.) Recrystallization from boiling methanol (90 ml) gave yellow needles of slightly increased activity  $[(\epsilon_l - \epsilon_r) = -0.83$  (417 nm),  $[\alpha]_D -7 \pm 2^\circ$  (2 × 10<sup>-3</sup> M in water)], which was unaffected by further recrystallization.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{CN})_2](\text{C}_{10}\text{H}_{14}\text{O}_4\text{SBr})\cdot 1/2\text{H}_2\text{O}$ : C, 39.7; H, 6.2; N, 13.9. Found: C, 39.6; H, 6.6; N, 14.0.

**(-)-*trans-R,R-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>***. The pure diastereoisomer (0.40 g) was dissolved in water (20 ml, 80°) and mixed with HClO<sub>4</sub> (12 M, 2 ml) to precipitate fine, bright yellow needles of *trans-R,R-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>*; 0.25 g,  $[\alpha]_D -86^\circ$  (2 × 10<sup>-3</sup> M in water). Recrystallization from dilute HClO<sub>4</sub> (0.05 M, c 30 ml/g) did not improve the activity of this material.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{CN})_2]ClO_4$ : C, 31.2; H, 5.8; N, 21.9. Found: C, 31.2; H, 5.8; N, 21.8.

**(+)-*trans-S,S-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>***. The filtrate from the initial diastereoisomer precipitate was reduced in volume to 40 ml, and after 12 hr at 0° the precipitated flocculent yellow material, 0.3 g, was shown by its CD to be nearly racemic with respect to the complex. (Recrystallization from methanol (10 ml) gave a small amount (ca. 0.05 g) of pure less soluble diastereoisomer.) The filtrate from the flocculent precipitate was taken to dryness; the residue was dissolved in water (10 ml, 80°) and mixed with HClO<sub>4</sub> (12 M, 2 ml), and the mixture was allowed to stand at 0° for 30 min to give yellow needles; 0.7 g,  $[\alpha]_D +49^\circ$  (2 × 10<sup>-3</sup> M in water). Three recrystallizations from water (10 ml/g, 80°) gave large golden-brown needles of identical rotation.

tallizations from dilute  $\text{HClO}_4$  (0.05  $M$ ,  $100^\circ$ ,  $c$  30 ml/g) gave fine yellow needles of activity which was not increased by further recrystallizations; 0.20 g,  $[\alpha]_D^{+86^\circ}$  ( $2 \times 10^{-3} M$  in water). Once again, the attainment of constant activity was marked by a readily discernible uniformity in the size and shape of crystals precipitated.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{CN})_2]\text{ClO}_4$ : C, 31.2; H, 5.8; N, 21.9. Found: C, 31.3; H, 5.8; N, 21.9.

4. *cis-β-R,R,S,S-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>*. Hot filtered solutions of *cis-β-R,R,S,S-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* (10.0 g) in methanol (100 ml) and sodium arsenyl (+)-tartrate (10.5 g) in water (100 ml) were quickly mixed and then allowed to cool slowly. Clusters of small, pink needles began to form within 1 min, and, after storage at  $0^\circ$  for 2 hr, these were filtered off and washed with methanol and ether; yield 7.2 g (94% optical yield),  $(\epsilon_1 - \epsilon_r)_{497\text{nm}} = +1.47$ . Recrystallization from water (150 ml,  $100^\circ$ ) by the addition of methanol (150 ml) gave broad, flesh pink needles (6.1 g) of marginally greater activity;  $(\epsilon_1 - \epsilon_r)_{497\text{nm}} = +1.54$ ,  $[\alpha]_D^{-13^\circ}$  ( $10^{-3} M$  in water). Further recrystallization caused no change in activity.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{C}_5\text{H}_7\text{O}_2)](\text{AsOC}_4\text{H}_4\text{O}_6)_2$ : C, 31.1; H, 4.6; N, 6.8. Found: C, 31.4; H, 4.3; N, 7.2.

(-)- $\Delta$ -*cis-β-S,S-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>*. The pure diastereoisomer (5.0 g) was ground with a solution of  $\text{NaClO}_4$  (10 g) in water (20 ml). An almost immediate transformation to small dark red crystals occurred. After 5 min, (-)- $\Delta$ -*cis-β-S,S-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* was filtered off and washed with  $\text{HClO}_4$  (5  $M$ , 5 ml,  $0^\circ$ ), ethanol-ether (1:2), and ether; yield 2.9 g. Recrystallization from methanol (50 ml,  $66^\circ$ ) by the gradual addition of ether (50 ml) gave large, blood red blocks (2.5 g);  $[\alpha]_D^{-39^\circ}$  ( $2 \times 10^{-3} M$  in water), the activity being unaffected by further recrystallization.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{C}_5\text{H}_7\text{O}_2)](\text{ClO}_4)_2$ : C, 29.4; H, 5.5; N, 10.5. Found: C, 29.3; H, 5.7; N, 10.5.

(+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>*. The filtrate from the initial diastereoisomer precipitate was evaporated to dryness under vacuum and the residue dissolved in water (50 ml,  $80^\circ$ ). Addition of  $\text{NaClO}_4$  (10 g) caused immediate precipitation of small, blood red crystals, which, after cooling for 2 hr at  $0^\circ$ , were collected as described for the (-) isomer; yield 3.9 g (78% optical yield),  $[\alpha]_D^{+39^\circ}$  ( $2 \times 10^{-3} M$  in water). Recrystallization from methanol by the addition of ether gave (+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* as large, blood red blocks, without change in activity.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{C}_5\text{H}_7\text{O}_2)](\text{ClO}_4)_2$ : C, 29.4; H, 5.5; N, 10.5. Found: C, 29.6; H, 5.6; N, 10.6.

**Preparations of Optically Active Complexes by Chemical Interconversions.** In many cases the methods described for conversions of *trans-R,R,S,S-[Co(3,2,3-tet)Cl<sub>2</sub>]<sup>+</sup>* and *trans-R,R,S,S-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>* ions to other complexes gave racemic complexes when optically active starting materials were used. Thus, alternative or modified preparations were developed to provide the active complexes in these instances. To check on the retentivity of all preparations the products were converted back, where possible, to either the dichloro or dinitro complex and their activities were thereby compared with those of the directly resolved species. These were first chemically interrelated as follows.

(i)  $\text{Cl}_2 \rightarrow (\text{NO}_2)_2$ . *trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>Cl·H<sub>2</sub>O* (0.0300 g,  $[\alpha]_D^{+30^\circ}$  in 0.1  $M$   $\text{HCl}$ ) and  $\text{NaNO}_2$  (0.10 g) were dissolved in water (10 ml) and allowed to react for 5 hr at room temperature. The visible absorption spectrum and rotation of this solution were then identical with those of an equimolar solution of *trans-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>ClO<sub>4</sub>]* ( $[\alpha]_D^{-19^\circ}$  in water).

(ii)  $(\text{NO}_2)_2 \rightarrow \text{Cl}_2$ . Finely ground *trans-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>ClO<sub>4</sub>]* (0.502 g) was added in portions to  $\text{HCl}$  (12  $M$ , 10 ml,  $80^\circ$ ) over a period of 10 min. The red-brown solution formed was heated for 2 hr on the steam bath, cooled, and mixed with  $\text{HClO}_4$  (12  $M$ , 2 ml); the mixture was allowed to stand at  $0^\circ$  for 5 hr. The long, dark green needles of the dichloro salt then precipitated were collected, washed well with ethanol and ether, and dried to constant weight; yield 0.473 g (99%),  $[\alpha]_D^{+92^\circ}$  ( $10^{-2} M$  in DMF).

(iii)  $\text{acac} \rightarrow \text{Cl}_2$ .  $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* (0.408 g,  $[\alpha]_D^{+33^\circ}$  in water) was dissolved in  $\text{HCl}$  (5  $M$ , 20 ml) and cooled to  $0^\circ$ .  $\text{NaNO}_2$  (0.4 g) was added. A rapid reaction occurred to give a brown-orange solution. Addition of  $\text{HClO}_4$  (12  $M$ , 4 ml) and heating on the steam bath for 15 min led to rapid precipitation of green needles, leaving a pale brown supernatant. After standing of the mixture for 12 hr at  $0^\circ$ , the solid was collected and washed with  $\text{HClO}_4$  (5  $M$ ), ethanol, and ether; yield 0.2412 g (78%). A CD spectrum showed this material to be identical with pure *trans-R,R-*

*R-[Co(3,2,3-tet)Cl<sub>2</sub>ClO<sub>4</sub>]*. The nonquantitative conversion is apparently due to some side reaction leading to complete decomposition of the starting complex.

(iv)  $\text{Cl}_2 \rightarrow (\text{CN})_2$ . When (+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>ClO<sub>4</sub>]* was allowed to react with  $\text{NaCN}$  according to the procedure described for the preparation of *trans-R,R,S,S-[Co(3,2,3-tet)(CN)<sub>2</sub>ClO<sub>4</sub>]*, a product of weak and variable, though always negative, rotation was obtained, the magnitude of the rotation being greater when lumpy  $\text{NaCN}$  was used so as to cause a slower reaction. With relatively large-scale preparations, pure *trans-R,R-[Co(3,2,3-tet)(CN)<sub>2</sub>ClO<sub>4</sub>]* could be isolated by repeated fractional crystallization of the reaction product.

1. (+)- $\Delta$ -*cis-β-R,R,S-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>*. (+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* (2.0 g,  $[\alpha]_D^{+39^\circ}$ ) and  $\text{Na}_2\text{CO}_3$  (0.075 g) were dissolved in water (30 ml) and the mixture was allowed to stand at room temperature for 2 hr.  $\text{HClO}_4$  (12  $M$ , 5 ml) was then added, and the solution was allowed to stand at  $0^\circ$  for 48 hr to reprecipitate (+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>* (1.1 g) as deep red blocks. These were filtered off and the filtrate volume was reduced to ca. 10 ml under vacuum. Addition of ethanol (50 ml) followed by ether (400 ml) precipitated a red-orange powder, which was taken up in dilute  $\text{HClO}_4$  (0.1  $M$ , 5 ml,  $80^\circ$ ). Addition of  $\text{NaClO}_4$  (2.0 g) and storage at  $0^\circ$  for 1 hr gave small orange needles (0.4 g,  $[\alpha]_D^{+138 \pm 5^\circ}$  in water), which were collected and washed with ice-cold ethanol (2 ml) and ether. To remove a small amount of *cis-β-R,R* complex contaminant ( $\leq 5\%$ , as detected by nmr) this material was recrystallized from dilute  $\text{HClO}_4$  (0.1  $M$ , 3 ml) by the addition of  $\text{NaClO}_4$  (1.0 g); yield 0.25 g (13%),  $[\alpha]_D^{+144 \pm 5^\circ}$  ( $2 \times 10^{-3} M$  in water).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{C}_5\text{H}_7\text{O}_2)](\text{ClO}_4)_2$ : C, 29.4; H, 5.5; N, 10.5. Found: C, 29.4; H, 5.6; N, 10.3.

2. (+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)CO<sub>3</sub>ClO<sub>4</sub>·CH<sub>3</sub>OH]*. (+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>Cl·H<sub>2</sub>O* (1.0 g,  $[\alpha]_D^{+30^\circ}$ ) and  $\text{NaHCO}_3$  (0.5 g) in water (10 ml) were heated on the steam bath for exactly 2 min. The mixture initially effervesced and then rapidly formed a deep pink-violet solution. Dissolution of  $\text{NaClO}_4$  (2.0 g), dilution with methanol (100 ml), and storage at  $0^\circ$  for 2 hr caused precipitation of fine pink needles, which were washed thoroughly with methanol; yield 0.60 g,  $[\alpha]_D^{+19 \pm 1^\circ}$  ( $2 \times 10^{-2} M$  in water). This material was fractionally crystallized from water (4 ml) by addition of successive equal volumes of methanol, optically pure complex coming down in the latter, more soluble fractions,  $[\alpha]_D^{+21^\circ}$  being the maximum rotation achieved.

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{CO}_3]\text{ClO}_4\cdot\text{CH}_3\text{OH}$ : C, 28.2; H, 6.2; N, 13.2. Found: C, 28.5; H, 6.5; N, 13.4.

$\text{CO}_3 \rightarrow \text{Cl}_2$ . Treatment of the active carbonate complex with excess  $\text{HCl}$  and  $\text{HClO}_4$  gave quantitative conversion to (+)-*trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>ClO<sub>4</sub>]* ( $[\alpha]_D^{+92^\circ}$  in DMF).

3. (-)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)(OH<sub>2</sub>)Cl]Cl<sub>2</sub>·2H<sub>2</sub>O*. (-)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)CO<sub>3</sub>ClO<sub>4</sub>·CH<sub>3</sub>OH* (0.40 g) was dissolved in an ice-cold mixture of  $\text{HCl}$  (12  $M$ , 1 ml) and acetone (4 ml) and stirred for 5 min, the temperature being held at  $0^\circ$ . More acetone (25 ml) and ether (20 ml) were added and stirring and cooling were continued until precipitation of a pink-violet powder was complete. After being washed with ether, the powder was dissolved in  $\text{HCl-HClO}_4$  (each 12  $M$ , 10:1, 5 ml,  $0^\circ$ ); the mixture was filtered to remove some green *trans*-dichloro complex, mixed with acetone (60 ml) and ether (40 ml), and stored at  $0^\circ$  for 12 hr. The complex then precipitated as fine, pink-violet, glittering needles; yield 0.10 g (27%),  $[\alpha]_D^{-181 \pm 5^\circ}$  ( $10^{-2} M$  in methanol- $\text{HCl}$ , 10:1).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)(\text{OH}_2)\text{Cl}]_2\cdot 2\text{H}_2\text{O}$ : C, 24.4; H, 7.2; N, 14.2. Found: C, 24.5; H, 7.3; N, 14.2.

*cis-ClH<sub>2</sub>O*  $\rightarrow \text{Cl}_2$ . Treatment of the active *cis*-chloroquo complex with  $\text{HCl-HClO}_4$  gave conversion to fully active *trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>ClO<sub>4</sub>]*.

4. (+)- $\Delta$ -*cis-β-R,R-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>ClO<sub>4</sub>]*. *trans-R,R-[Co(3,2,3-tet)Cl<sub>2</sub>Cl·H<sub>2</sub>O* (0.50 g,  $[\alpha]_D^{+30^\circ}$ ) and  $\text{Na}_2\text{C}_2\text{O}_4$  (0.30 g) in water (10 ml) were heated at  $60^\circ$  for 10 min. The pink-violet solution formed was filtered,  $\text{NaClO}_4$  (1.0 g) was added, and precipitation of the complex was induced by scratching the sides of the vessel. After being cooled 30 min at room temperature the fine pink needles deposited were collected, washed with ethanol-water (1:1), ethanol, and ether; yield 0.20 g (34%),  $[\alpha]_D^{+119 \pm 3^\circ}$  ( $10^{-2} M$  in water).

*Anal.* Calcd for  $[\text{Co}(\text{C}_8\text{H}_{22}\text{N}_4)\text{C}_2\text{O}_4]\text{ClO}_4$ : C, 28.5; H, 5.3; N, 13.3. Found: C, 28.1; H, 5.4; N, 13.1.

**Oxalato**  $\rightarrow$  **Cl<sub>2</sub>**. By heating the active complex in HCl-HClO<sub>4</sub> (each 5 M) on the steam bath for 2 hr it was quantitatively converted to fully active *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>.

**5. *trans-R,R*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>.** *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.06 g,  $[\alpha]_D +30^\circ$ ) was dissolved in aqueous NaOH (0.46 g in 5 ml, 0°) by stirring until a clear violet solution had formed. AgNO<sub>3</sub> (2.93 g) in water (3 ml, 0°) was added and the mixture stirred until the AgCl had coagulated. The AgCl was filtered off and washed with water (5 ml, 0°), and NaClO<sub>4</sub> (3.0 g) was added to the clear filtrate-wash. Maintaining the temperature of 0°, the solution was carefully neutralized with HClO<sub>4</sub> (12 M), fine, dark violet needles rapidly precipitating as this was done. The crystals were collected and washed with methanol and ether; yield 2.2 g (82%). They were recrystallized from HClO<sub>4</sub> (5 ml, 2 M, 0°) by addition of NaOH (5 M, 0°) to neutrality.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>: C, 20.6; H, 5.4; N, 12.0; Cl, 15.2. Found: C, 20.6; H, 5.5; N, 11.8; Cl, 15.0.

**(OH)(H<sub>2</sub>O)  $\rightarrow$  Cl<sub>2</sub>.** Racemization of the complex in neutral, room-temperature aqueous solution was so rapid as to preclude accurate measurement of its rotation. However, dissolution of the solid in warm HCl (5 M) resulted in precipitation of fully active *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>.

**6. (-)-*trans-R,R*-[Co(3,2,3-tet)Br<sub>2</sub>]Br·H<sub>2</sub>O.** *trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> (1.5 g,  $[\alpha]_D -19^\circ$  in water) dissolved in DMF (15 ml) was mixed with a solution of LiBr (0.60 g) in water (1 ml), giving an immediate precipitate of the dinitro bromide. This was recrystallized from water (5 ml, 80°) as long, yellow needles; yield 0.90 g,  $[\alpha]_D -20 \pm 1^\circ$  (10<sup>-2</sup> M in water).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)<sub>2</sub>]Br: C, 23.7; H, 5.5; N, 20.8. Found: C, 23.5; H, 5.2; N, 20.8.

(-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Br was added in small portions over 15 min to hot HBr (9 M, 30 ml, 80°) and the resultant deep green solution was kept at 80° a further 20 min. Addition of ethanol (100 ml) and storage at 0° for 24 hr precipitated fine, yellow-green needles, which were washed with ethanol and ether; yield 0.90 g. The product appeared to be a hemihydrobromide.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Br<sub>2</sub>]Br·1/2(H<sub>2</sub>O): C, 18.1; H, 4.5; N, 10.5; Br, 52.7. Found: C, 17.9; H, 4.5; N, 10.6; Br, 52.3.

However on recrystallization from methanol the simple hydrate was obtained;  $[\alpha]_D -52 \pm 3^\circ$  (10<sup>-2</sup> M in methanol).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Br<sub>2</sub>]Br·H<sub>2</sub>O: C, 19.6; H, 4.9; N, 11.4. Found: C, 20.0; H, 4.7; N, 11.4.

The perchlorate salt may be obtained by addition of HClO<sub>4</sub> to a cold aqueous solution of the bromide or may be formed directly as very large, deep yellow needles by treatment of the dinitro perchlorate with hot HBr;  $[\alpha]_D -19 \pm 1^\circ$  (2 × 10<sup>-2</sup> M in DMF).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Br<sub>2</sub>]ClO<sub>4</sub>: C, 19.5; H, 4.5; N, 11.4. Found: C, 19.4; H, 4.6; N, 11.6.

**Br<sub>2</sub>  $\rightarrow$  (NO<sub>2</sub>)<sub>2</sub>.** Reaction of both the bromide and perchlorate salts of (-)-*trans-R,R*-[Co(3,2,3-tet)Br<sub>2</sub>]<sup>+</sup> with a tenfold molar ratio of NaNO<sub>2</sub> in water for 5 hr at room temperature gave a yellow solution identical in spectrum and rotation with an equimolar solution of pure *trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> ( $[\alpha]_D -19^\circ$  in water).

**7. (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>.** (-)-*trans-R,R*-[Co(3,2,3-tet)Br<sub>2</sub>]Br·H<sub>2</sub>O (0.40 g) was added in small portions to a boiling solution of AgNO<sub>3</sub> (0.43 g) in methanol (40 ml). The mixture was stirred vigorously while heating for a further 10 min; then the AgBr was filtered off and washed with methanol (20 ml). Dilution of the filtrate-wash with ether (20 ml) and storage at 0° for 12 hr led to deposition of fine, dull green, efflorescent needles, which were washed with methanol-ether (1:5) and ether; yield 0.25 g (75%),  $[\alpha]_D -780^\circ$  (2 × 10<sup>-3</sup> M in methanol). The complex was recrystallized from methanol as lustrous, gray-green flakes by the rapid addition of ether.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>: C, 22.9; H, 5.3; N, 23.4. Found: C, 23.0; H, 5.4; N, 23.1.

**(NO<sub>3</sub>)<sub>2</sub>  $\rightarrow$  Cl<sub>2</sub>.** Addition of HCl and HClO<sub>4</sub> to an aqueous solution of the complex and allowing the mixture to stand for 12 hr gave a quantitative precipitate of fully active *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>.

**8. (+)-*trans-R,R*-[Co(3,2,3-tet)(NCS)<sub>2</sub>]ClO<sub>4</sub>.** A solution of (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> ( $[\alpha]_D -780^\circ$  in methanol; 0.60 g) and NaNCS (0.60 g) in methanol (100 ml) was allowed to stand at room temperature for 15 hr. The methanol was removed under vacuum, the residue was taken up in water (45 ml, 40°), and small red crystals were precipitated by the addition of NaClO<sub>4</sub> (5.0

g); yield 0.43 g. This material was taken up in hot water (15 ml, 80°) and the mixture was allowed to stand for 12 hr at 0° to precipitate small crystals (0.12 g) with a CD spectrum approximately half as intense as that of the initial 0.43 g of solid. HClO<sub>4</sub> (12 M, 2 ml) was added to the filtrate and, after again cooling the mixture for 12 hr at 0°, magnificent, long, red needles (0.20 g, 31%) were precipitated. These showed much stronger CD which was not improved by further recrystallization.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NCS)<sub>2</sub>]ClO<sub>4</sub>: C, 26.7; H, 4.9; N, 18.7. Found: C, 26.4; H, 5.1; N, 18.7.

Because of its intense absorption at the sodium D line only a very approximate value of its rotation,  $[\alpha]_D +30 \pm 10^\circ$  (2 × 10<sup>-4</sup> M in methanol), could be obtained.

**9. (-)-*trans-R,R*-[Co(3,2,3-tet)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O.** Over a period of 5 min, a solution of NaN<sub>3</sub> (1.0 g) in water (5 ml) was added to a magnetically stirred solution of *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (1.0 g,  $[\alpha]_D +30^\circ$ ) in water (40 ml). (Rapid admixture precipitates the dichloro azide salt.) Stirring was continued for 55 min, when NaClO<sub>4</sub> (4.0 g) was added and the deep blue solution was allowed to stand at 0° for 1 hr. The green-blue precipitate was collected and washed with cold water, ethanol-ether (1:5), and ether. It was recrystallized from water (30 ml, 80°) to give very large, broad, black needles;  $[\alpha]_D -110 \pm 30^\circ$  (2 × 10<sup>-4</sup> M in methanol—as with the isothiocyanato complex, intense absorption limited the accuracy of rotation measurements).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O: C, 22.1; H, 5.5; N, 32.2. Found: C, 22.7; H, 5.4; N, 32.2.

**(N<sub>3</sub>)<sub>2</sub>  $\rightarrow$  Cl<sub>2</sub>.** Dissolution in HCl-HClO<sub>4</sub> (each 5 M), addition of a twofold molar amount of NaNO<sub>2</sub>, and standing for 12 hr quantitatively converted the azido complex to fully active *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>.

**10. (-)-*trans-R,R*-[Co(3,2,3-tet)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>·H<sub>2</sub>O.** *trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (0.30 g,  $[\alpha]_D +30^\circ$ ) was dissolved in anhydrous liquid ammonia (30 ml); a pale orange solid precipitated immediately. The NH<sub>3</sub> was allowed to evaporate off and the residue crystallized as fine, orange needles by the addition of ethanol (50 ml) to its solution in HCl (0.1 M, 10 ml); yield 0.23 g. This solid was fractionally crystallized from HCl (0.1 M, 3 ml) by the consecutive addition of two aliquots (each 9 ml) of ethanol. The more soluble fraction (0.10 g,  $[\alpha]_D -40^\circ$ , 2 × 10<sup>-3</sup> M in 0.1 M HCl) showed the higher activity and this was not improved by further fractionation.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>·H<sub>2</sub>O: C, 24.5; H, 7.7; N, 21.5. Found: C, 24.5; H, 7.8; N, 21.2.

**11-14. Active *trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)X]ClO<sub>4</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>).** These complexes were all prepared from (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> ( $[\alpha]_D -19^\circ$  in water) by exactly the methods given for their racemates.

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)Cl]ClO<sub>4</sub>: C, 23.2; H, 5.4; N, 16.9. Found: C, 23.3; H, 5.4; N, 16.8.  $[\alpha]_D -70 \pm 2^\circ$  (10<sup>-2</sup> M in DMF).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)Br]ClO<sub>4</sub>: C, 20.9; H, 4.8; N, 15.3. Found: C, 21.2; H, 4.7; N, 15.3.  $[\alpha]_D -25 \pm 1^\circ$  (10<sup>-2</sup> M in DMF).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)NCS]ClO<sub>4</sub>: C, 24.7; H, 5.1; N, 19.2. Found: C, 24.9; H, 5.3; N, 19.1.  $[\alpha]_D -24 \pm 1^\circ$  (10<sup>-2</sup> M in DMF).

*Anal.* Calcd for [Co(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)(NO<sub>2</sub>)N<sub>3</sub>]ClO<sub>4</sub>: C, 22.8; H, 5.3; N, 26.6. Found: C, 22.8; H, 5.2; N, 26.4.  $[\alpha]_D +10^\circ \pm 1^\circ$  (10<sup>-2</sup> M in DMF).

That no racemization occurred in the formation of these complexes was shown by their conversions back to fully active (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> by the following methods.

**NO<sub>2</sub>Cl or Br  $\rightarrow$  (NO<sub>2</sub>)<sub>2</sub>.** The complexes and a tenfold molar amount of NaNO<sub>2</sub> were allowed to react in water at room temperature for 5 hr.

**NO<sub>2</sub>NCS  $\rightarrow$  (NO<sub>2</sub>)<sub>2</sub>.** The complex was heated on the steam bath with an equimolar amount of 0.1 M Hg(ClO<sub>4</sub>)<sub>2</sub> solution (1 M in HClO<sub>4</sub>) for 30 min. Sufficient NaNO<sub>2</sub> to render the solution neutral was added, and it was then allowed to stand 12 hr at room temperature.

**NO<sub>2</sub>N<sub>3</sub>  $\rightarrow$  (NO<sub>2</sub>)<sub>2</sub>.** The complex in a solution of 0.1 M HCl was allowed to react with a two molar amount of NaNO<sub>2</sub> for 10 min; it was then mixed with sufficient NaNO<sub>2</sub> to give a neutral solution which was allowed to stand for 12 hr.



All four solutions showed a visible absorption spectrum and rotation identical with those of the optically pure (-)-*trans-R,R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ion.

**Preparation and Resolution of *trans-R,R,R,S*-[Cr(3,2,3-tet)Cl<sub>2</sub>]-Cl·H<sub>2</sub>O.** Preparation. A solution of anhydrous CrCl<sub>3</sub> (2.3 g) in DMF (50 ml) was prepared by bringing the mixture of the solid and solvent to the boil in the presence of Zn powder (0.05 g). 3,2,3-tet (2.5 g) was added to the violet solution and the boiling was continued for 5 min; a copious precipitate of the green product formed in this time. On cooling, the solid was collected and washed with DMF, acetone, and ether; yield 3.3 g (65%). The complex was recrystallized from the minimum volume of HCl (2 M, 80°) by the addition of four volumes of acetone, followed by one of ether, forming as fine, pale green needles;  $\Delta\epsilon = 82 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Cr(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]Cl·H<sub>2</sub>O: Cr, 14.8; C, 27.4; H, 6.9; N, 16.0. Found: Cr, 14.5; C, 27.5; H, 6.9; N, 15.9.

**Resolution.** Hot solutions of *trans-R,R,R,S*-[Cr(3,2,3-tet)Cl<sub>2</sub>]-Cl·H<sub>2</sub>O (4.00 g) in methanol (100 ml) and Ag(+)BCS (4.76 g) in methanol (100 ml) were quickly mixed and then boiled on the steam bath for 5 min. The coagulated AgCl was filtered off and washed well with methanol; the filtrate-wash was taken to dryness under vacuum. The pale green residue was dissolved in methanol (70 ml, 66°), filtered, and allowed to stand at 0° for 12 hr. The very fine, pale green needles thus precipitated were washed with ethanol and ether; yield 2.5 g (66% optical yield),  $[\alpha]_D +6 \pm 2^\circ$  ( $2 \times 10^{-3} \text{ M}$  in CH<sub>3</sub>OH). Recrystallization of this material from methanol caused no change in its activity.

*Anal.* Calcd for [Cr(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>](C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>S Br)·3H<sub>2</sub>O: C, 32.6; H, 6.4; N, 8.5. Found: C, 32.7; H, 6.4; N, 8.4.

(-)-*trans-R,R,R*-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>. Dissolution of the diastereoisomer (2.5 g) in HCl (2 M, 75 ml, 80°) and addition of HClO<sub>4</sub> (12 M, 5 ml) led to precipitation of long, green-red needles of *trans-R,R,R*-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> which, after cooling (2 hr), were collected and washed with water, ethanol, and ether; yield 1.3 g (87%),  $[\alpha]_D -58 \pm 2^\circ$  ( $2 \times 10^{-3} \text{ M}$  in DMF). Recrystallization from HCl (2 M, 100°) did not change the rotation.

*Anal.* Calcd for [Cr(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 24.3; H, 5.6; N, 14.1. Found: C, 24.4; H, 5.5; N, 14.2.

(+)-*trans-S,S*-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>. Only by very tedious fractionation of the material in the filtrate obtained from the initial diastereoisomer precipitate could optically pure materials be obtained, and, as these repeated crystallizations led to considerable decomposition, it was more convenient simply to mix the methanolic filtrate with aqueous HCl-HClO<sub>4</sub> (1:1, both 2 M, 100 ml) and precipitate optically impure (+)-*trans*-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> (2.2 g,  $[\alpha]_D +30^\circ$ ,  $2 \times 10^{-3} \text{ M}$  in DMF). Four recrystallizations from HCl (2 M, 100°, c 50 ml/g) gave material of constant rotation: *trans-S,S*-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>; 0.2 g,  $[\alpha]_D +58 \pm 2^\circ$ .

*Anal.* Calcd for [Cr(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 24.3; H, 5.6; N, 14.1. Found: C, 24.5; H, 5.3; N, 14.3.

**Preparation and Resolution of *trans-R,R,R,S*-[Rh(3,2,3-tet)Cl<sub>2</sub>]-Cl·H<sub>2</sub>O.** Preparation. 3,2,3-tet (0.85 g) was added to a solution of *trans*-[Rh(py)<sub>4</sub>]Cl<sub>2</sub>·5H<sub>2</sub>O (3.0 g) in water (100 ml) and the mixture was refluxed for 2 hr. The clear yellow solution was acidified with HCl (2 M, 10 ml) and evaporated to dryness. The residue was taken up in water (25 ml), filtered, and diluted with acetone (125 ml), and small yellow needles were then precipitated by the slow addition of ether (50 ml). These were collected and washed with acetone and ether; yield 1.4 g. On taking the filtrate to dryness and fractionally crystallizing the residue from methanol by the addition of acetone and ether, another 0.4 g of complex was obtained (total yield 94%). The combined fractions were recrystallized from water by the addition of acetone and ether;  $\Delta\epsilon = 74 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$  (in water).

*Anal.* Calcd for [Rh(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]Cl·H<sub>2</sub>O: C, 24.0; H, 6.0; N, 13.9; Cl, 26.6. Found: C, 24.1; H, 5.9; N, 14.1; Cl, 26.3.

**Resolution.** Resolution of the complex with  $\alpha$ -bromocamphor- $\pi$ -sulfonate (BCS<sup>-</sup>) is complicated by the formation, above about 5°, of large block-like crystals which are racemic with respect to the complex cation. The optically active material deposits as needles below about 5°. Hence, without rigid adherence to the conditions of resolution described below, an adequate resolution is not achieved.

To a solution of *trans-R,R,R,S*-[Rh(3,2,3-tet)Cl<sub>2</sub>]Cl·H<sub>2</sub>O (4.01 g) in water (45 ml, 80°) contained in a 150-ml conical flask was added a solution of NH<sub>4</sub>(+)BCS (1.64 g) in water (40 ml, 80°). The flask was stoppered and the clear solution rapidly cooled by vigorous swirling in an acetone-ice slush bath until the solution became solid. The flask

was taken out of the bath and shaken until the ice melted, whereupon very fine, pale yellow needles suddenly began to precipitate. After 5 min at 0° a flocculent yellow mass resulted. This precipitate was quickly filtered off and washed with acetone-ether (1:1) and ether; yield 1.5 g. Reduction of the filtrate volume to 45 ml and similar rapid cooling gave another fraction of 0.8 g. A third fraction of 0.5 g was obtained on subsequent reduction of the volume to 30 ml. Though not of identical optical purity, these three diastereoisomer precipitates were combined and recrystallized from water (25 ml, 100°) after standing at 0° for 12 hr; yield 2.4 g,  $[\alpha]_D +30 \pm 1^\circ$  ( $5 \times 10^{-3} \text{ M}$  in water). Recrystallization of this material from water (60 ml, 80°), after standing at 0° for 24 hr, gave pure *trans-R,R*-[Rh(3,2,3-tet)Cl<sub>2</sub>]BCS as clusters of fine, yellow needles; 1.2 g,  $[\alpha]_D +19 \pm 1^\circ$  ( $5 \times 10^{-3} \text{ M}$  in water). This material showed no change in rotation with further recrystallization.

*Anal.* Calcd for [Rh(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>](C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>SBr)·3H<sub>2</sub>O: C, 30.4; H, 5.7; N, 7.9. Found: C, 30.7; H, 5.9; N, 8.1.

(-)-*trans-R,R,R*-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>. Dissolution of the pure diastereoisomer (1.0 g) in water (50 ml, 80°) and the addition of HNO<sub>3</sub> (14 M, 2 ml) caused deposition of long, yellow needles of *trans-R,R,R*-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>, which, after standing to cool, were collected and washed with acetone and ether; yield 0.4 g (71%),  $[\alpha]_D -35 \pm 1^\circ$  ( $10^{-2} \text{ M}$  in water).

*Anal.* Calcd for [Rh(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]NO<sub>3</sub>: C, 23.5; H, 5.4; N, 17.1; Cl, 17.3. Found: C, 23.7; H, 5.4; N, 16.9; Cl, 17.3.

(+)-*trans-S,S*-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>. Addition of NH<sub>4</sub>NO<sub>3</sub> (2.0 g) to the filtrate from the third diastereoisomer fraction precipitated optically impure (+)-*trans*-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>; 1.8 g,  $[\alpha]_D +20^\circ$  ( $10^{-2} \text{ M}$  in water). Recrystallization from water (25 ml, 80°), after standing at 0° for 12 hr, gave large needles of pure *trans-S,S*-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>; 0.8 g,  $[\alpha]_D +35^\circ$  ( $10^{-2} \text{ M}$  in water).

*Anal.* Calcd for [Rh(C<sub>8</sub>H<sub>22</sub>N<sub>4</sub>)Cl<sub>2</sub>]NO<sub>3</sub>: C, 23.5; H, 5.4; N, 17.1; Cl, 17.3. Found: C, 23.7; H, 5.5; N, 17.0; Cl, 17.2.

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**Registry No.** *trans-R,R,R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl, 53625-30-2; *trans-R,R,R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 53625-32-4; *cis-R,R,R,S*-[Co(3,2,3-tet)CO<sub>3</sub>]Cl, 53625-37-9; *cis-β-R,R,R,S*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>, 53625-36-8; *cis-β-R,R,R,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)Cl]Cl<sub>2</sub>, 53625-38-0; *cis-β-R,R,R,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 53567-15-0; *trans-R,R,R,S*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>, 53625-40-4; *cis-β-R,R,R,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>, 53567-17-2; *cis-β-R,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>, 53648-33-2; [Co<sup>III</sup>(3,2,3-tet)(OH)<sub>2</sub>Co<sup>II</sup>](ClO<sub>4</sub>)<sub>5</sub>, 53716-41-9; *trans-R,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 53625-34-6; *cis-β-R,S*-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>]ClO<sub>4</sub>, 53648-35-4; *cis-β-R,R,R,S*-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>]Cl, 53625-41-5; *cis-β-R,R,S*-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>]Br, 53625-42-6; *trans-R,R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>, 53701-30-7; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]I, 53701-31-8; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Cl, 53701-32-9; *trans-R,R,S*-[Co(3,2,3-tet)Br<sub>2</sub>]ClO<sub>4</sub>, 53625-44-8; *trans-R,R,S*-[Co(3,2,3-tet)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 53625-46-0; *trans-R,R,R,S*-[Co(3,2,3-tet)(NCS)<sub>2</sub>]ClO<sub>4</sub>, 53567-19-4; *trans-R,R,S*-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>, 53567-21-8; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>, 53567-23-0; *trans-R,R,S*-[Co(3,2,3-tet)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 53567-24-1; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)Cl]ClO<sub>4</sub>, 53567-26-3; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)Br]ClO<sub>4</sub>, 53567-28-5; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)NCS]ClO<sub>4</sub>, 53567-30-9; *trans-R,R,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)N<sub>3</sub>]ClO<sub>4</sub>, 53567-32-1; (+)-*trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]BCS, 53625-47-1; (+)-*trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]Cl, 53567-33-2; (+)-*trans-R,R*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 25878-84-6; (-)-*trans-S,S*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 53567-34-3; *trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]BCS, 53625-48-2; (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>, 53567-36-5; (+)-*trans-S,S*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>, 53701-34-1; *trans-R,R*-[Co(3,2,3-tet)(CN)<sub>2</sub>]BCS, 53625-50-6; (-)-*trans-R,R*-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>, 53625-51-7; (+)-*trans-S,S*-[Co(3,2,3-tet)(CN)<sub>2</sub>]ClO<sub>4</sub>, 53625-53-9;  $\Delta$ -*cis-β-S*-[Co(3,2,3-tet)acac](AsOC<sub>4</sub>H<sub>6</sub>O<sub>6</sub>)<sub>2</sub>, 53625-55-1; (-)- $\Delta$ -*cis-β-S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>, 53625-56-2; (+)- $\Delta$ -*cis-β-R,R*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>, 53625-58-4; (+)- $\Delta$ -*cis-β-R,S*-[Co(3,2,3-tet)acac](ClO<sub>4</sub>)<sub>2</sub>, 53625-60-8; (+)- $\Delta$ -*cis-β-R,R*-[Co(3,2,3-tet)CO<sub>3</sub>]ClO<sub>4</sub>, 53648-37-6; (+)- $\Delta$ -*cis-β-R,R*-[Co(3,2,3-tet)C<sub>2</sub>O<sub>4</sub>]ClO<sub>4</sub>, 53648-39-8; *trans-R,R*-[Co(3,2,3-tet)(OH<sub>2</sub>)OH](ClO<sub>4</sub>)<sub>2</sub>, 53625-62-0; (-)-*trans-R,R*-[Co(3,2,3-tet)(NO<sub>2</sub>)<sub>2</sub>]Br, 36802-21-8; (-)-*trans-R,R*-[Co(3,2,3-tet)Br<sub>2</sub>]Br<sup>1/2</sup>(H<sub>5</sub>O<sub>2</sub>Br), 53567-39-8; (-)-*trans-R,R*-



[Co(3,2,3-tet)Br<sub>2</sub>]Br, 53567-37-6; (-)-*trans*-R,R-[Co(3,2,3-tet)-(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>, 53625-64-2; (+)-*trans*-R,R-[Co(3,2,3-tet)(NCS)<sub>2</sub>]ClO<sub>4</sub>, 53625-66-4; (-)-*trans*-R,R-[Co(3,2,3-tet)(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 36490-58-1; (-)-*trans*-R,R-[Co(3,2,3-tet)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 53625-67-5; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)Cl]ClO<sub>4</sub>, 53625-69-7; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)Br]ClO<sub>4</sub>, 53625-71-1; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)NCS]ClO<sub>4</sub>, 53625-73-3; (+)-*trans*-R,R-[Co(3,2,3-tet)(NO<sub>2</sub>)N<sub>3</sub>]ClO<sub>4</sub>, 53625-75-5; *trans*-R,R,S,S-[Cr(3,2,3-tet)Cl<sub>2</sub>]Cl, 53567-41-2; *trans*-R,R-[Cr(3,2,3-tet)Cl<sub>2</sub>]BCS, 53625-77-7; (-)-*trans*-R,R-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 53625-78-8; (+)-*trans*-S,S-[Cr(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>, 53625-80-2; *trans*-R,R,S,S-[Rh(3,2,3-tet)Cl<sub>2</sub>]Cl, 53567-42-3; *trans*-R,R-[Rh(3,2,3-tet)Cl<sub>2</sub>]BCS, 53625-82-4; (-)-*trans*-R,R-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>, 53625-83-5; (+)-*trans*-S,S-[Rh(3,2,3-tet)Cl<sub>2</sub>]NO<sub>3</sub>, 53625-85-7; (3,2,3-tet), 10563-26-5; 1,2-dibromoethane, 106-93-4; 1,3-diaminopropane, 109-76-2; *trans*-[Rh(py)<sub>4</sub>Cl<sub>2</sub>]Cl, 14077-30-6.

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## Conformational Dissymmetry. Circular Dichroism Spectra of a Series of Complexes Containing a Quadridentate Amine Ligand

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The circular dichroism spectra associated with the d-d transitions of an extensive series of conformationally dissymmetric metal complexes are recorded. All of the complexes are of the general type *trans*-R,R-[M(3,2,3-tet)XY]<sup>n+</sup>, where 3,2,3-tet is a linear quadridentate amine, where M = Co(III), Cr(III), and Rh(III), and where, for the Co(III) complexes, the X and Y axial ligands represent a wide variety of types. It was found that the general form of the circular dichroism patterns exhibited by the d-d bands was extremely sensitive to the environment of the complex and to the nature of X and Y. The type of spectrum observed was dependent on the way the axial groups split the upper state d-electron manifolds, but for any given complex, large variations in the circular dichroism were observed from one solvent to another and in the solid state. These environmental variations are ascribed to varying amounts of donor atom distortions and possibly also to changes in the twist sense of the donor atom displacements. Dissymmetric solvation and, in appropriate cases, dissymmetric rotamer orientations of the axial groups are also considered as contributing factors. In view of these variations, the problems associated with deriving regional rules for conformational isomers are discussed.

Of all the stereochemical properties of molecules the assignment of absolute configuration remains the single most intractable feature which is not subject to routine physical methods for its elucidation. While it is true that, for certain restricted and closely specified systems, correlations between chirality and circular dichroism show a consistency necessary for the advancement of predictive regional rules, it is also true that these quasiempirical rules encompass only a limited number of chromophores and structural types.<sup>1</sup> Even the purely theoretical methods,<sup>2-5</sup> which are unambiguous in principle, require a very detailed knowledge of both the electronic and nonchiral structure of the molecule.

Unlike the studies of organic chromophores where detailed and extensive studies have been made, no comparable systematic effort has been reported for the correlations between absolute configuration and the circular dichroism of the d-d transitions of transition metal complexes. Despite this, regional rules, purporting to correlate structure with absolute configuration, have been put forward for these systems with disconcerting profusion. Not surprisingly, few of these have proved to be general or revealing.

The problems associated with deriving regional rules for the d-d bands of transition metal chromophores are generally more

complicated than those encountered for many of the organic chromophores. The most obvious complication is the fact that d-d transitions show a high orbital multiplicity in their upper states and these components almost invariably show a variety of sign patterns within the closely spaced upper state manifolds. The circular dichroism, thus observed, is a result of overlapped bands of varying signs and intensities, a proper interpretation of which would require a knowledge of the separations between assigned levels, the individual band shapes, the individual signs, and the individual intensities. Partly because of this problem, a prevalent device has been simply to use the sign of the "major band" associated with a particular manifold of transitions as the correlative index for assigning configurations. It is not difficult to see, however, that the sign of the major band would reverse simply because of variations in the circular dichroism intensities of overlapped transitions even if, for a series of complexes of the same absolute configuration, the spacings between levels and the signs of the components were the same. It is not surprising, therefore, that the major band hypothesis has proved to be of little value for configurationally dissymmetric complexes and we show here that the same applies for conformationally dissymmetric compounds.

The present series of papers is an attempt at providing