Chemistry, Stereochemistry, and Molecular Dissymmetry of Complexes Containing Quadridentate Ligands with Skew Six-Membered Chelate Rings

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Reaction between excess racemic 2,4-pentanediamine and ethylene dibromide leads to the formation of two quadridentate ligands, a racemic and a meso form. These two forms have been separated by means of their cobalt(III) complexes. The *trans*-dinitro complexes of both ligands have been resolved into their optically active forms from which an extensive series of optically active complexes have been prepared. The stereochemistries, conformations, and absolute configurations have been inferred from a variety of physical measurements and chemical interconversions and from the preparation of the active racemic ligand from the independently resolved 2,4-pentanediamine molecule. It was assumed that the methyl groups of the ligand, when complexed, would adopt equatorial dispositions, thus forcing the terminal six-membered chelate rings into skew conformations. As a consequence the racemic ligand was expected to be completely stereospecific. This is so. In general, both racemic and meso ligands were found to favor strongly planar arrangements of the four donor nitrogen atoms. The only cis compounds prepared were those having bidentate ligands in the remaining two octahedral positions.

In the preceding papers[1-4] we have described the preparations, the resolutions, and the optical activity of cobalt complexes derived from the 3,2,3-tet ligand and a (methyl) substituted analog which was assumed to prefer chair six-membered chelate rings. In order to compare the effects of changing the ring conformations, we now turn to a description of the preparations and resolutions of similar complexes in which the substituents are introduced in such a way as to engender a preference for skew six-membered rings. This has been achieved by the preparation of two quadridentate ligands from (*R,R:S,S* (or (*R,R*)))-2,4-pentanediamine (*R,R:S,S*-dmtn).

1. Conformations of *R,R*-dmtn

In Figure 1 we show some of the conformations that are possible when *R,R*-dmtn is coordinated to a metal. The chair conformation of the ring has one methyl group axial and the other equatorial; but in the λ-skew conformation both methyl groups are equatorially disposed. In addition to these, there are an infinite number of possible conformations which arise as the skew ring is twisted to a boat conformation. These other ring conformations, including the boat, are probably less stable than either the chair or skew conformers in isolated ring systems but may be important when the ring is linked to other saturated ring systems.[5] We show two intermediate forms between skew and boat which we call skew-boat conformations. It will be seen that for *R,R*-dmtn in the λ-skew-boat conformation, one methyl group occupies a position intermediate between the axial disposition of the boat and the equatorial position of the skew ring.

Theoretical calculations suggest[6,7] and experimental observations[8] confirm that an unsubstituted six-membered chelate ring is intrinsically more stable in the chair conformation than in the skew although distortions do occur when two or more rings are cis-disposed to each other[9,10] presumably because of neighboring interactions. The issue then arises, *ceteris paribus*, as to whether, in the *R,R*-dmtn system, the ring will prefer a chair conformation with one axial methyl group or a skew conformation with both methyl groups assuming equatorial dispositions. From a recent crystal structure[11] and circular dichroism data,[12,13] it appears that the skew conformation is more stable. We therefore assume that if other stereochemical effects do not predominate, the terminal six-membered ring systems of the complexed quadridentate ligands prepared from ethylene dibromide and racemic dmtn will prefer to adopt skew conformations. This is why we designate these quadridentate ligands as sk-3,2,3 which, although convenient, is not meant to imply that in all

isomers of the complexes perfect skew rings will be formed. In fact, as we shall see, rather distorted ring systems appear to form because of other effects which operate in some of the systems.

2. The Ligands and Their Mode of Chelation

As with the ch-3,2,3 ligand, two isomers are formed when ethylene dibromide is treated with racemic 2,4-diaminopentane, namely, *R,R,R,R:S,S,S,S*-sk-3,2,3 and *R,R,S,S*-sk-3,2,3 (Figure 2). The sequential order of the chiral centers corresponds to the normal numbering scheme for organic molecules. If optically active *R,R*-dmtn is used, then only the *R,R,R,R*-sk-3,2,3 ligand is formed (Figure 2). When complexed to an octahedral metal atom these ligands provide a large number of possible stereochemistries; but if we assume that the six-membered chelate rings will prefer to be in skew conformations with equatorial methyl groups, which implies stereospecificity, then the number of isomers is considerably restricted. In Figure 3 we show these possible isomers for the racemic and meso sk-3,2,3 ligands together with some which do not meet this criterion but which have actually been isolated.

In the trans isomer of the racemic ligand (I), the outer six-membered rings can adopt skew conformations having equatorial methyl groups and the inner five-membered ring can adopt a stable gauche conformation. The system appears to be without strain or serious nonbonding interactions. An edge displacement of one of the terminal chelate arms of I, without inverting the inner nitrogen atoms, leads to structure II in which the moved arm cannot adopt a skew conformation with equatorial methyl groups. At best a skew-boat conformation is possible with methyl groups in pseudoequatorial positions (Figure 3). An identical problem arises when both terminal arms in I are moved without inverting the nitrogen atoms to produce the cis-α geometry; neither ring can adopt a stable skew conformation in this Λ-cis-α-*S,S* geometry. By successively inverting the inner nitrogen atoms of I and successively displacing the terminal chelate arms, structures III and IV are formed where, in both cases, the terminal chelate arms can adopt slightly distorted skew conformations with equatorial methyl groups.

The meso ligand can assume two geometries where the six-membered rings are in stable skew conformations, namely, V and VI. In the meso-trans-*R,S* geometry (V), the central five-membered ring cannot assume a perfect gauche conformation and probably would experience strain. One of the rings in the trans-*S,S* complex (VII) can adopt a skew conformation but the other cannot adopt any stable conformation. Two conformations seem reasonable for this system: either
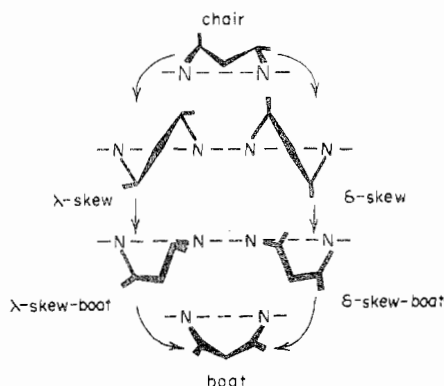
Figure 1. The conformations of the (R,R)-2,4-pentanediamine chelate ring and the orientations of substituents in the 2,4 positions as the chair ring is twisted in the two chiral senses to produce the boat conformation.
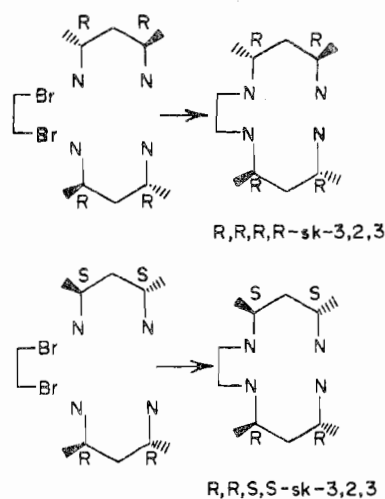

Figure 2.

Figure 3. The proposed conformations of octahedral metal complexes formed from the racemic ligand R,R,R,R-sk-3,2,3 (I–IV) and the meso ligand R,R,S,S-sk-3,2,3 (V–VII). The R and S labels after the specification of the geometry refer to the chirality of the coordinated inner nitrogen atoms.

a boat conformation where both methyl groups are roughly "equatorial" or a chair conformation with one axial and one equatorial methyl group (VII). We present evidence to support the latter.

Despite numerous attempts, we have only succeeded in isolating the isomers I, II, VI, and VII. This observation, when compared to the large number of isomers isolated for the ch-3,2,3 systems, indicates differences between these two systems which are suggested by molecular models. The first obvious difference is that in cis complexes with skew terminal arms there appears to be much more nonbonding interaction between neighboring rings than with chair terminal rings. In addition, the skew conformations appear to be somewhat strained in the cis complexes. Finally the two trans geometries of the meso ligand V and VII involve a decision between having an unfavorable five-membered ring and satisfactory six-membered rings (V) or unfavorable six-membered rings and a favorable five-membered ring (VII). We have only succeeded in isolating VII which suggests the greater importance of achieving a stable five-membered ring.

3. General Chemistry

The product of the reaction between ethylene dibromide and excess racemic dmtn is a high-boiling viscous oil which consists of the racemic and meso quadridentates (Figure 2). These could not be separated by fractional crystallization of their hydrochloride or hydrobromide salts but could be isolated as their cobalt complexes. When a methanol solution of cobalt chloride and the mixed ligands is oxidized by air, a brown (pero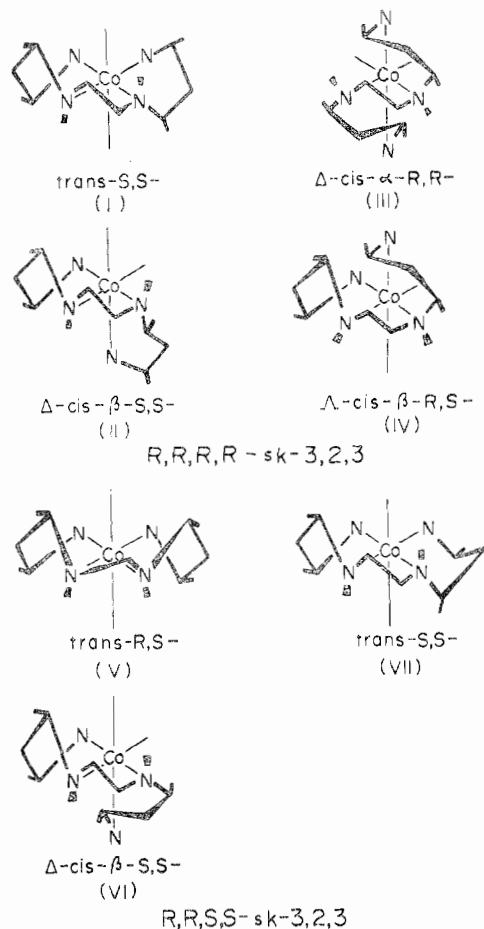xo) complex is formed with the racemic ligand. This complex is very soluble in both water and methanol and appears to be reasonably stable in neutral solutions. The meso ligand, in contrast, deposits a blue complex which is sparingly soluble in water, in which it gives a transient blue solution which turns pink. This blue complex is not a peroxo complex and is probably the *trans*-hydroxochloro complex of the meso ligand because an apparently identical material can be formed by addition of 1 mol of hydroxide ions to a water solution of the pure *trans*-R,R:S,S-$[Co(R,R,S,S$-sk-3,2,3)Cl_2]Cl salt. We have used this difference in behavior of the two ligands to separate the ligands, but the success of the procedure depends critically on the length of oxidation. Thus aeration of the solution for 30 min gives a poor yield of the blue complex and aeration for 12 hr gives no yield at all presumably because of the instability of the blue complex. The optimum time appears to be 2 hr whence the yield is poor but maximum. Thus after the oxidation in methanol, the deep brown solution was pumped to dryness at room temperature and the brown peroxo complex containing the racemic ligand was dissolved in cold water leaving the blue complex containing the meso ligand. Addition of HCl and HClO_4 to the brown solution and the blue solid gave the green *trans*-R,R:S,S-$[Co(R,R,R,R$:S,S,S,S-sk-3,-2,3)Cl_2]ClO_4 and *trans*-R,R:S,S-$[Co(R,R,S,S$-sk-3,2,3)-Cl_2]ClO_4 complexes, respectively. Both complexes are readily converted to the *trans*-dinitro derivatives and both of these can be resolved as their α-bromocamphor-π-sulfonate salts. Both resolved dinitro complexes can be converted to the fully active *trans*-dichloro species by reaction in HCl. The ligands may be taken off the two active complexes by reduction with SnCl_2

in HCl and it is found that the ligand from the active complex containing the racemic ligand is optically active while the ligand from the active complex containing the meso ligand is inactive. When the optically active ligand is put back on the metal, exactly the same rotation as for the starting complex is obtained. No other species are formed and we conclude that the ligand was cleanly separated from its meso analog and is completely stereospecific. Similarly, the meso ligand gave only one (inactive) complex. Furthermore, when ethylene dibromide is treated with (active) *R,R*-dmtn, only one ligand is formed (Figure 2) with a rotation identical with that of the racemic quadridentate ligand isolated from the resolved complex. And when the active quadridentate ligand prepared from active *R,R*-dmtn is complexed, the complex has a rotation identical with that of the analogous complex prepared and separated on the metal.

A. Complexes Containing the Racemic Ligand. Using methods similar to those described for the corresponding 3,2,3-tet and the racemic ch-3,2,3 complexes we have prepared a series of *trans-(R,R:S,S)*-di-X complexes where X = NO2⁻, N3⁻, NCS⁻, NO3⁻, and NH3. The *trans-(R,R:S,S)*-dicyano complex may be prepared from the reaction between AgCN and the *trans*-dichloro complex of the racemic ligand in boiling methanol, this being the only procedure we have found which does not lead to the formation of an uncharacterized tricyano complex as the almost exclusive product. *trans*-Nitro-X complexes, where X = Cl⁻, N3⁻, and NCS⁻, may be prepared by methods identical with those used for the racemic ch-3,2,3 complexes. Reaction of the *trans*-dichloro complex with oxalate and carbonate ions is rapid and produces the cis-β-*R,R:S,S* oxalato and carbonato complexes. Except for the oxalato complex which in the optically active form is exceedingly soluble in water and was found difficult to isolate in a pure state, all the above complexes have been obtained as their pure optical antipodes.

In general, the Co(III) complexes of the *R,R,R,R:S,S,-S,S*-sk-3,2,3 ligand show a considerably greater solubility in all solvents compared to their 3,2,3-tet and racemic ch-3,2,3 analogs and appear to be more labile. Thus, substitution of the dichloro complex by nitrite, azide, and thiocyanate ions is extremely rapid and complete within an approximately fivefold shorter time than the 3,2,3-tet reactions. The racemic sk-3,2,3 ligand enforces a marked preference for the trans geometry and appears to be even more stereochemically restrictive than the corresponding complexes of the 3,2,3-tet ligand or the racemic ch-3,2,3 ligand in that we have been able to detect only the trans-*R,R:S,S* and cis-β-*R,R:S,S* isomers, the latter only with bidentate ligands, even after exhaustive fractionation of charcoal-equilibrated carbonato and oxalato complexes and the *trans*-dichloro complexes generated from them.

B. Complexes Containing the Meso Ligand. The pale green *trans*-dichloro complex of the meso ligand is readily converted to the yellow dinitro complex which in turn can be resolved into its optical isomers. Upon reaction with HCl the resolved *trans*-dinitro complex gives the active *trans*-dichloro complex. These complexes racemize only in basic solutions where amino proton exchange can take place but not in acid solutions. This observation suggests that the optical stability of these trans complexes is associated with the asymmetric inner nitrogen atoms which therefore must be in the *R,R* or *S,S* configurations despite the fact that this geometry will not allow both terminal chelate rings to adopt conformationally stable skew conformations (Figure 3 (VII)). Several experiments aimed at converting the *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl2]⁺ ion to the *trans-R,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl2]⁺ ion, which can adopt skew-ring conformations (Figure 3 (V)), were unsuccessful. Thus, the *trans-R,R:S,S*-dichloro isomer was refluxed

in neutral methanol for several hours without detectable change, a procedure which was successful for the meso ch-3,2,3 complex. Reaction with azide ions gave deep blue solutions of the diazido complex but treatment with HCl only regenerated the starting complex, even though complete amino proton exchange had taken place both in neutral methanol and in the presence of azide ions. Similarly, reactions with carbonate and oxalate ions, with or without the presence of activated charcoal, gave products which, when treated with HCl, gave quantitative yields of the starting isomer.

4. Stereochemistry and Diastereoisomerism

A. The Racemic Ligand. The stereochemistry of the *trans*-dichloro, *trans*-diazido, and *trans*-dinitrato complexes of the racemic ligand is established from the absorption spectra which are characteristic of these *trans*-di-X-(N4) chromophores. The presence of racemic inner nitrogen atoms in the dichloro and diazido complexes is confirmed by their nmr spectra (in (CD3)2SO) which show well-separated amino proton resonances integrating as even ratios. In addition, the methyl proton resonances are reasonably well resolved and show a quartet of (overlapping) lines due to the two pairs of environmentally distinct methyl group proton resonances which are split by coupling to the adjoining methine protons. The dinitrato species was too insoluble in solvents which did not dissociate the nitrato groups to measure its nmr spectrum, but this complex, as well as the diazido, is converted in HCl to the *trans*-dichloro species without proton exchange. The presence of a twofold axis in the *trans*-diisothiocyanato, -dinitro, -dicyano, and -diammine complexes is also suggested by the nmr spectra of their amino and methyl protons. Thus the complexes can only be either cis-α or trans with racemic inner nitrogen atoms (Figure 3 (I and III)). The absorption spectra, however, are virtually superimposable on those of other complexes with the same donor atom chromophores of known topology,[1] and, as we shall see subsequently, the component splittings of the ¹T1g manifold as observed by their circular dichroism spectra are consistent with the trans assignment. Of these four complexes (NCS⁻, NO2⁻, CN⁻, and NH3), the structure of the diammine remains uncertain and our assignment is an assumption based on the strong preference for the trans configuration that this ligand shows for a variety of unidentate ligands. The assignment of the trans configuration to the nitrochloro, nitroisothiocyanato, and nitroazido complexes is based on the similarity of their absorption spectra to those of the other quadridentate ligand complexes described previously[1,3] and by the splittings of the ¹T1g manifold shown by their circular dichroism spectra. These assignments are circumstantially supported by their conversion to the *trans*-dichloro complex without proton exchange.

The carbonato complex, prepared from the *trans*-dichloro complex, shows an nmr spectrum with a well-isolated amino proton resonance (at τ 3.8 in (CD3)2SO) of area representing one proton which indicates an unsymmetrical cis-β geometry. Addition of HCl to this complex rapidly produces the *trans*-dichloro complex with racemic inner nitrogen atoms; the process involves no proton exchange, and even under carefully controlled low-temperature conditions, there is no detectable amount of the cis-dichloro species. This establishes the cis-β-*R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)CO3]⁺ geometry of this ion, despite the fact that molecular models indicate that the cis-β-*R,S* system (Figure 3 (IV)) might be more stable. The instability of this system without an enforcing bidentate ligand is, therefore, perhaps not surprising.

B. The Meso Ligand. The green dichloro complex of the meso ligand has a characteristic *trans*-Cl2(N4) absorption spectrum and the stability of its optical isomers establishes the racemic configuration of its inner nitrogen atoms. The racemic configuration of the inner nitrogen atoms of the dinitro complex
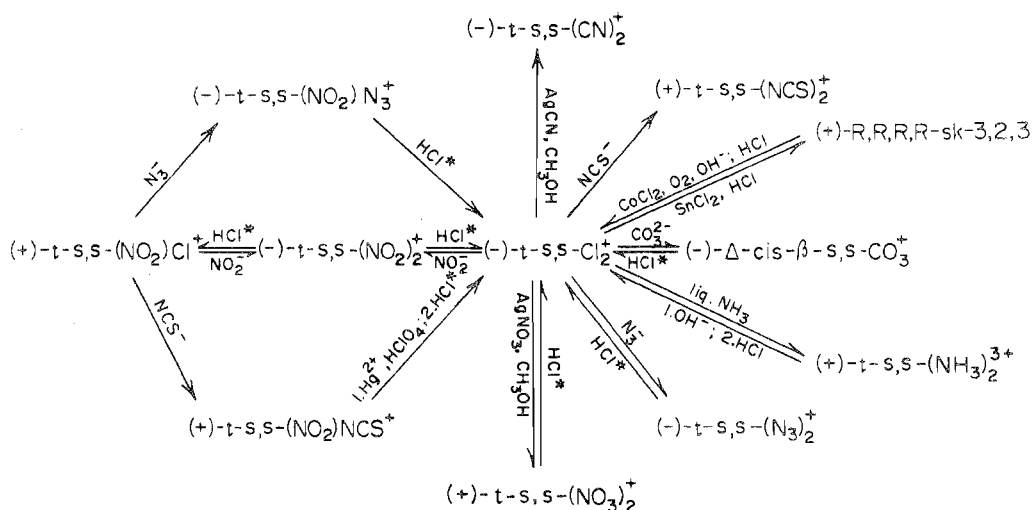
$(-)$-t-s,s-(CN)$_2^+$

$(-)$-t-s,s-(NO$_2$) N$_3^+$ AgCN, CH$_3$OH $(+)$-t-s,s -(NCS)$_2^+$

$(+)$-R,R,R,R-sk-3,2,3

N$_3^-$ HCl* NCS$^-$ CoCl$_2$, O$_2$, OH$^-$; HCl HCl

SnCl$_2$, HCl

$(+)$-t-s,s -(NO$_2$)Cl $\xrightleftharpoons[NO_2^-]{HCl^*}$ $(-)$-t-s,s-(NO$_2$)$_2^+$ $\xrightleftharpoons[NO_2^-]{HCl^*}$ $(-)$-t-s,s -Cl$_2^+$ $\xrightleftharpoons[HCl^*]{CO_3^{2-}}$ $(-)$-Δ-cis-β-s,s -CO$_3^+$

NCS$^-$ Hg^{2+}, HClO$_4$, 2·HCl* lig. NH$_3$ OH$^-$; 2·HCl N$_3^-$ HCl*

AgNO$_3$, CH$_3$OH HCl* $(+)$-t-s,s-(NH$_3$)$_2^{3+}$

$(+)$-t-s,s-(NO$_2$)NCS$^+$ $(-)$-t-s,s -(N$_3$)$_2^+$

$(+)$- t-s,s-(NO$_3$)$_2^+$

Figure 4. Chemical interconversions involving complexes of the $(+)$-R,R,R,R-sk-3,2,3 ligand. The S,S nomenclature refers to the absolute configuration of the inner (complexed) nitrogen atoms and t = *trans*. Transformations marked with an asterisk involve processes where no proton exchange occurs.

is established by its resolution and its conversion to the active *trans*-dichloro complex without proton exchange; its trans configuration is postulated on the basis of its absorption and circular dichroism spectra. The oxalato complex prepared from the *trans*-dichloro complex can be converted back to its starting *trans*-dichloro complex without proton exchange and hence the oxalato complex has the same racemic inner nitrogen configuration. We assume this oxalato complex has the cis-β topology because there is a general tendency of the 3,2,3-tet ligand and its substituted derivatives to form cis-β rather than cis-α complexes with oxalate and because the cis-β geometry seems to be conformationally more stable than the cis-α geometry. Other than this we have no firm evidence for the topological assignment.

Because of the unsymmetrical nature of the meso ligand the nmr spectra of its complexes are not useful in deciding the stereochemistries. In general the nmr signals of the methyl protons appear as a broad manifold of peaks at about τ 8.8 in (CD₃)₂SO except for the *trans*-dinitro complex which, in addition to a manifold of resonances at τ 8.7, shows an isolated well-resolved methyl doublet at τ 9.1 (6.5 Hz) which integrates for three protons. This leads us to suggest that one of the outer six-membered rings is skew with methyl groups equatorial and the other is in a chair conformation with one axial and one equatorial methyl group, *i.e.*, Figure 3 (VII). We suppose that the axial methyl group is the one that occurs at τ 9.1. A similar pattern does not obtain for the *trans*-dichloro complex where all the methyl resonances occur at τ 8.8. This observation, however, does not exclude the possibility that the *trans*-dichloro complexes have the same conformations; we have observed that, of all the complexes we have studied, the nitro complexes generally show large shifts in the ligand resonances compared to the others which show only small variations from compound to compound. This may be due to the shielding ability of the nitro group which, in the dinitro complex of the meso ligand, lies close by and parallel to the axial methyl group if we assume the conformation shown in Figure 3 (VII).

5. Stereochemical Equilibria and Optical Stability

A. The Racemic Ligand. Unlike the complexes of the methyl-substituted ligand described in the previous papers,[3,4] the complexes of the R,R,R,R:S,S,S,S-sk-3,2,3 ligand appear to be highly restrictive in the isomers than can be formed at equilibrium. Thus, for all the [Co(R,R,R,R:S,S,S,S-sk-3,-2,3)X₂]$^{n+}$ complexes where X is a unidentate ligand, the only species we were able to detect was the *trans-R,R:S,S*-di-X isomer despite considerable effort. Similarly, for complexes

with acetylacetonate, oxalate, or carbonate as ligands only the cis-β-R,R:S,S isomer was detected after methods which had been successful in equilibrating the complexes of the other ligands were attempted. Stereospecific coordination of the ligand is indicated by these observations. We have observed no mutarotation or racemization of any of these complexes.

B. The Meso Ligand. Molecular models suggest that perhaps the trans-R,S isomer would be the more stable of the two trans isomers (Figure 3 (V, VII)). In fact, the only trans isomer we have been able to detect has been the one with racemic inner nitrogen atoms (Figure 3 (VII)). We have observed that the *trans*-dichloro, -dinitro, and -diazido complexes racemize in neutral water and methanol and more quickly in the presence of such basic anions as OH⁻, N₃⁻, and NO₂⁻; but the complexes are quite optically stable in acid media. Presumably a trans-R,S complex is formed during the racemization process but its standing concentration and stability must be very small as we have not been able to detect it although we have not used any elaborate kinetic methods in our search for this species. Reactions of the *trans*-R,R:S,S-dichloro species with carbonate and oxalate ions, processes accompanied by complete amino proton exchange, give only the cis-β-R,R:S,S isomers even if the reaction mixture is refluxed for 3 hr in the presence of activated charcoal.

6. Optical Purity and Absolute Configurations

A. The Racemic Ligand. (The R,R,R,R-sk-3,2,3 ligand is sterically compatible with the trans-S,S inner nitrogen configuration and demands a λ, δ, λ sequence of chelate rings (Figure 3 (I))). The optical purity of these racemic ligand complexes is strongly suggested by three kinds of circumstantial evidence. First, each optical isomer of the *trans*-dinitro complex was fractionally crystallized to maximum, equal, and opposite rotation. Second, an elaborate series of chemical interconversions was carried out (Figure 4) where each new complex was isolated by crystallization. In all cases the same rotation was observed for the starting *trans*-dichloro species after each cycle of the interconversions. Third, the optically active quadridentate ligand prepared from the independently resolved (−)-dmtn ligand gave a *trans*-dichloro complex with a rotation identical with that obtained from the resolved *trans*-dinitro complex.

The absolute configuration of the Δ-[Co((−)-dmtn)₃]$^{3+}$ ion has been determined. This structure establishes that (−)-dmtn is R,R-dmtn.[14] Assuming this assignment and that the quadridentate ligand coordinates stereospecifically, as it does, then the (−)-*trans*-dichloro species prepared originally from
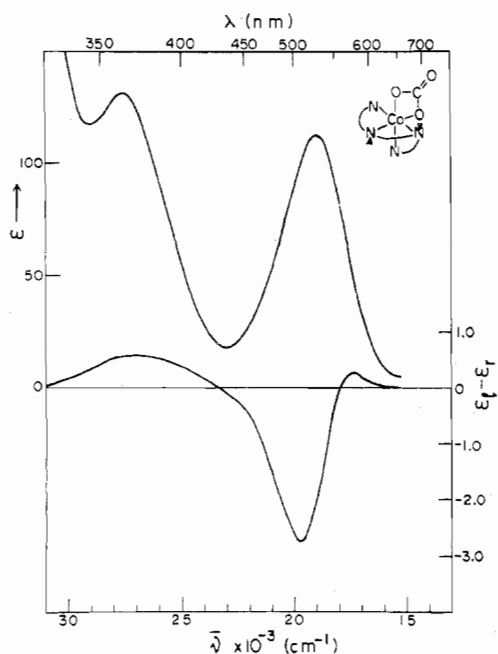
Figure 5. The absorption and circular dichroism spectra of Δ-*cis*-β-*S,S*-[Co(*R,R,R,R*-sk-3,2,3)CO₃]Cl in water solution.
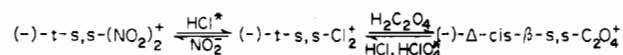
$$(-)\text{-}t\text{-}s,s\text{-}(NO_2)_2^+ \underset{\overline{NO_2^-}}{\overset{HCl^*}{\rightleftharpoons}} (-)\text{-}t\text{-}s,s\text{-}Cl_2^+ \xrightarrow[HCl,\, HClO_4^-]{H_2C_2O_4} (-)\text{-}\Delta\text{-}cis\text{-}\beta\text{-}s,s\text{-}C_2O_4^+$$

Figure 6. Chemical interconversions involving the *R,R,S,S*-sk-3,2,3 ligand complexes. The *S,S* nomenclautre refers to the absolute configurations of the inner (complexed) nitrogen atoms and t = *trans*. Transformations marked with an asterisk involve no proton exchange. The reaction involving NO_2^- ions proceeds with greater than 95% retention.

(−)-*R,R*-dmtn has the absolute configuration *trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]⁺. This assignment is the same as that inferred from the circular dichroism spectrum of the (−)-cis-β carbonato complex, which is converted without proton exchange to the (−)-*trans*-dichloro complex, namely, the conversion II → I in Figure 3. The circular dichroism spectrum (Figure 5) of the (−)-cis-β carbonato complex is very similar to that of Δ-*cis*-β-*R,R*-[Co(3,2,3-tet)CO₃]⁺ of known absolute configuration,[1] and hence we assign the same Δ-cis-β topology to the present (−) carbonato complex. The absolute configurations of the other complexes, therefore, unambiguously follow from these assignments; the chemical interconnections are shown in Figure 4.

B. The Meso Ligand. The only evidence of optical purity of these complexes is the maximized equal and opposite rotations of the directly resolved antipodes of the dinitro complex and the retention of constant maximum activity through a series of chemical interconversions of isolated complexes (Figure 6).

The absolute configurations of these complexes have been deduced from the circular dichroism spectrum of the oxalato complex (Figure 7). The circular dichroism spectrum of the (+)-cis-β-[Co(*R,R,S,S*-sk-3,2,3)C₂O₄]⁺ ion is very similar to that of the Λ-*cis*-β-*S,S*-[Co(3,2,3-tet)C₂O₄]⁺ ion of known configuration[1] and is assigned the same absolute configuration (Λ). Thus, the (+)-*trans*-dichloro complex generated without proton exchange from this oxalato complex must be *trans*-*R,R*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]⁺ in order that the two complexes have compatible configurations, Figure 3 (VI → VII). The absolute configuration of the *trans*-dinitro species then follows from the chemical interconversions (Figure 6). Apart from the empirical nature of the initial assignment, the conclusions hinge on the topological assignment of the oxalato complex which is probably correct but is not certain.
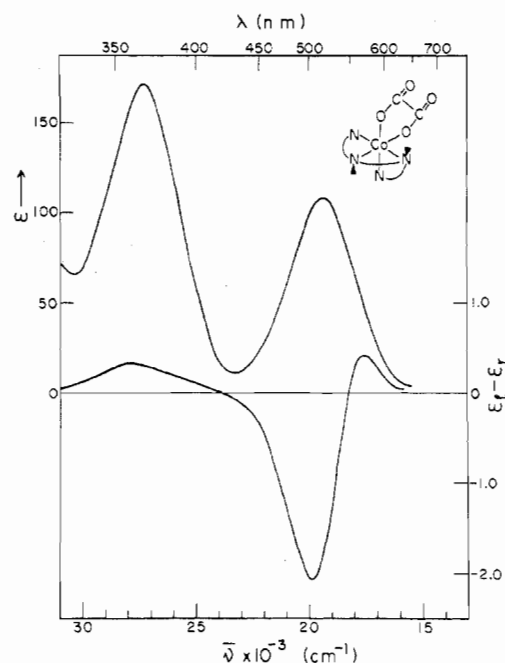

Figure 7. The absorption and circular dichroism spectra of Δ-*cis*-β-*S,S*-[Co(*R,R,S,S*-sk-3,2,3)C₂O₄]ClO₄ in water solution.

7. Experimental Section

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

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

A. Preparation of *R,R,R,R:S,S,S,S*-sk-3,2,3 and *R,R,S,S*-sk-3,2,3. (*R,R:S,S*)-2,4-Diaminopentane (94 g) was heated on the steam bath as 1,2-dibromoethane (10 ml) was added drop by drop over 45 min. The mixture was heated another 30 min to complete reaction; then the bulk of the excess diamine was removed by distillation under water pump vacuum (the distillation temperature should not be allowed to rise above 65° at this stage). KOH (14 g) in methanol (100 ml) was cautiously mixed with the viscous, pale yellow residue, and, after cooling, ether (200 ml) was added to complete precipitation of KBr. The solution was filtered, the ether and methanol removed on the rotary evaporator, and the residual liquid was fractionally distilled from glass wool under vacuum. The mixed quadridentates were collected as a well-isolated fraction between 170 and 200° (*ca.* 5–10 mm); yield 15.5 g (63%).

B. Preparation of *R,R,R,R*-2,11-Diamino-4,9-dimethyl-5,8-diazadodecane (*R,R,R,R*-sk-3,2,3). Using (−)-*R,R*-2,4-diaminopentane (12.8 g) and 1,2-dibromoethane (1.5 ml) this active ligand was prepared by the same method as described for the mixed inactive ligands except that, on this small scale, it was more convenient to add the methanolic KOH to the reaction mixture before removal of the excess diamine, which was then recovered as its hydrochloride from a methanolic distillate; yield 2.3 g.

HCl (12 M, 1.0 ml) was added to a solution of *R,R,R,R*-sk-3,2,3 (0.5 g) in ethanol (20 ml). Slow addition of acetone (50 ml) gave an oil which, on stirring, solidified to a white powder. This was recrystallized from boiling methanol (50 ml) by the gradual addition of ether (40 ml) to the cooled solution, giving clusters of fine, white needles. These were weakly deliquescent except under conditions of very low humidity and appeared to contain methanol of crystallization which was readily lost on oven-drying; [α]D +17.6 ± 0.5° (dried solid, 10^{-2} M in 0.1 M HCl).

Anal. Calcd for C₁₂H₃₀N₄·4HCl: C, 38.3; H, 9.1; N, 14.9. Found (dried solid): C, 38.2; H, 9.1; N, 14.8.

C. Separation of *R,R,R,R:S,S,S,S*- and *R,R,S,S*-sk-3,2,3. A

solution of mixed quadridentates (11.0 g) and CoCl₂·6H₂O (11.0 g) in methanol (200 ml) was oxidized by a rapid passage of air for 2 hr. The methanol was removed under vacuum and the brown residue triturated with ice-cold water (50 ml). The insoluble blue-violet crystals were filtered off and washed with water (10 ml, 0°), methanol–ether (1:10), and finally ether. They were then dissolved in HCl (5 M, 20 ml, 80°), and upon the addition of HClO₄ (12 M, 5 ml), pale green needles of *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,-3)Cl₂]ClO₄ precipitated. These were collected and washed with water, ethanol–ether (1:10), and finally ether; yield 4.0 g (18%). The complex was recrystallized from boiling HCl (1 M, 200 ml) by the addition of HClO₄ (12 M, 4 ml); Λ_M = 76 cm² ohm⁻¹ mol⁻¹ (in methanol).

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]ClO₄: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.5; H, 6.7; N, 12.2; Cl, 23.4.

The aqueous extract of the oxidation residue was mixed with HCl (12 M, 10 ml) and HClO₄ (12 M, 5 ml) and heated on the steam bath for 10 min to precipitate lustrous, bright green flakes of *trans-R,R:S,S*-[Co(*R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]ClO₄; yield 10.0 g (42%). The complex was recrystallized as for the meso-ligand complex; Λ_M = 76 cm² ohm⁻¹ mol⁻¹ (in methanol).

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]ClO₄: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.5; H, 6.6; N, 12.2; Cl, 23.2.

D.   [Co(*R,R,R:S,S,S,S*-sk-3,2,3)X₂]ⁿ⁺ Complexes.   (i) *trans-R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]Cl. *trans-R,R:-S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]ClO₄ was converted to its chloride salt by twice shaking its methanolic solution with a tenfold excess of Dowex 2-X8 Cl⁻ form anion-exchange resin. The dilute methanolic solution of the chloride thus produced was evaporated to dryness under vacuum and the residue was recrystallized from methanol (100 ml) by the addition of ether (200 ml), forming long, dark green needles which effloresced to a yellow green powder on drying; yield 8.0 g (94%).

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]Cl: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.6; H, 7.4; N, 14.1; Cl, 26.9.

(ii)   *trans-R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)(NO₂)₂]I. NaNO₂ (5.0 g) was added to a solution of *trans-R,R:S,S*-[Co(*R,-R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]Cl (7.4 g) in water (80 ml, 80°) and the mixture was heated on the steam bath for 15 min. Excess NaI was added to the then clear yellow-orange solution and, after cooling for 1 hr at 0°, the precipitated glistening golden needles were collected and washed with water (20 ml), ethanol, and finally ether; yield 7.6 g (80%). The complex was recrystallized from boiling methanol; Λ_M = 82 cm² ohm⁻¹ mol⁻¹ (in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]I: C, 28.4; H, 5.9; N, 16.5; I, 25.0. Found: C, 28.5; H, 5.9; N, 16.6; I, 25.2.

Resolution of *trans-R,R:S,S*-[Co(*R,R,R:S,S,S,S*-sk-3,2,3)-(NO₂)₂]I. Resolution of this complex with α-bromocamphor-π-sulfonate was quite straightforward, its efficiency being limited only by a decomposition process which occurred after repeated fractional crystallization of the diastereoisomers. Because the D line rotations of the pure diastereoisomers were, within experimental error, equal, the resolution was more conveniently followed by circular dichroism than by rotation measurements.

trans-R,R:S,S-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)(NO₂)]I (12.36 g) was added rapidly to a hot solution of Ag(+)BCS (10.17 g) in methanol (200 ml). The mixture was kept hot while being shaken vigorously for 10 min. The AgI was filtered off and washed well with boiling methanol (ten 20-ml portions). The filtrate–wash was taken to dryness under vacuum and the yellow residue was redissolved in the minimum volume of absolute ethanol (125 ml, 78°). The solution was filtered and allowed to stand at 0° for 12 hr to deposit a mass of fine golden needles; these were collected and washed with ethanol–ether (3:1) and finally ether [9.0 g; $(\epsilon_l - \epsilon_r)_{458nm}$ = +0.52, in water]. Recrystallization of this material from ethanol (150 ml, 78°) gave a precipitate of greater activity [5.3 g; $(\epsilon_l - \epsilon_r)_{458nm}$ = +1.12], but repeated recrystallization caused no further increase.

The filtrate from the first precipitate was taken to dryness under vacuum and the residue was recrystallized from methanol (50 ml, 66°) by the addition of ether (25 ml). This provided fine yellow needles [4.2 g, $(\epsilon_l - \epsilon_r)_{458nm}$ = −1.12], the activity of which was not increased by recrystallization. This filtrate was combined with that from the recrystallization of the initial precipitate and evaporated to dryness, and the residue was recrystallized from ethanol (35 ml, 78°). This gave material [2.7 g; $(\epsilon_l - \epsilon_r)_{458nm}$ = +0.30] contaminated with a sparingly soluble, yellow decomposition product and two recrystallizations were required to obtain pure (+) CD diastereoisomer

(0.8 g). The filtrate residue from the contaminated precipitate was recrystallized from methanol–ether (25 ml + 25 ml) to give pure diastereoisomer [1.7 g; $(\epsilon_l - \epsilon_r)_{458nm}$ ≈ −1.12]. Further crystallizations by the above methods gave another 0.8 g of each diastereoisomer before the decomposition product became so abundant as to render further fractionation unrewarding.

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]C₁₀H₁₄O₄SBr: C, 38.2; H, 6.4; N, 12.2. Found (for Δε₄₅₈nm > 0 isomer): C, 38.7; H, 6.7; N, 12.2. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]C₁₀H₁₄O₄SBr·CH₃OH: C, 38.2; H, 6.7; N, 11.6. Found (for Δε₄₅₈nm < 0 isomer): C, 37.9; H, 6.6; N, 11.6.

Both diastereoisomers gave [α]D +38 ± 1° (3 × 10⁻³ M in water).

Addition of NaClO₄ to concentrated aqueous solutions of the diastereoisomers rapidly precipitated glistening, golden flakes of (−)₅₄₆nm-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)₂]ClO₄ [[α]₅₄₆nm −42°, 2 × 10⁻³ M in water; $(\epsilon_l - \epsilon_r)_{458nm}$ = −1.12] and (+)₅₄₆nm-*trans-R,R*-[Co(*S,S,S,S*-sk-3,2,3)(NO₂)₂]ClO₄ [[α]₅₄₆nm +42°; $(\epsilon_l - \epsilon_r)_{458nm}$ = +1.12]. These complexes were recrystallized from boiling water (ca. 50 ml g⁻¹) without detectable change in activity.

(i)   (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄. (−)₅₄₆nm-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)₂]ClO₄ (1.3 g) in HCl (12 M, 20 ml) was heated on the steam bath for 30 min, giving a clear green solution. HClO₄ (5 M, 5 ml) was added and the solution was allowed to stand at 0° for 12 hr to precipitate long, thin, green plates of (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄, which were collected and washed with water, ethanol–ether (1:1), and finally ether; yield 1.1 g (88%); [α]D −310° (2 × 10⁻³ M in methanol). The complex was recrystallized from HCl (2 M, 100 ml, 80°) by the addition of HClO₄ (12 M, 5 ml), without any change in optical activity.

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]ClO₄: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.1; H, 6.8; N, 12.4; Cl, 23.0.

Reaction with NaNO₂ in aqueous solution gave the dinitro complex of activity identical with that of the starting material.

(ii) *R,R,R,R*-sk-3,2,3 (1.8 g) and CoCl₂·6H₂O (1.8 g) in methanol (50 ml) were oxidized by rapid passage of air for 2 hr. The methanol was removed under vacuum and the brown residue was dissolved in HCl (2 M, 50 ml) and heated to give a green solution. Addition of HClO₄ (12 M, 5 ml) precipitated green crystals (2.9 g, 81%) with physical, spectral, and optical properties identical with those of the product of (i).

Anal. Found: C, 31.1; H, 6.6; N, 12.1; Cl, 23.1.

For the completion of the cycle of reactions and as another proof of the nature of the ligand bound in the directly resolved complex, the free ligand was isolated from the product of (i).

***R,R,R,R*-sk-3,2,3.** (−)-*trans*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.9 g) and SnCl₂·2H₂O (0.25 g) in methanol (25 ml) containing HCl (12 M, 5 ml) were heated on the steam bath for 30 min, giving a solution with the characteristic blue color of CoCl₄²⁻. The solution was evaporated to dryness under vacuum and the bright blue residue redissolved in methanolic HCl (1 M). This solution was passed through a column of Dowex 2-X8 Cl⁻ form anion-exchange resin to remove CoCl₄²⁻ (and SnCl₆²⁻), and the effluent was again taken to dryness. The white residue was recrystallized from methanol (15 ml, 66°) by the addition of ether (10 ml), giving clusters of long, white needles (0.75 g, 90%). These were analyzed without oven-drying to remove solvent of crystallization; [α]D +15.8° (10⁻² M in 0.1 M HCl).

Anal. Calcd for C₁₂H₃₀N₄·4HCl·H₂O·CH₃OH: C, 36.6; H, 9.4; N, 13.1; Cl, 33.5. Found: C, 36.1; H, 9.2; N, 12.9; Cl, 33.1.

Reconversion to the *trans*-dichlorocobalt(III) complex gave a solid identical with the starting material.

(−)₅₄₆nm-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(N₃)₂]ClO₄·H₂O. (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.42 g) and NaN₃ (0.30 g) in water (20 ml) were heated on the steam bath for 30 min. Excess NaClO₄ was dissolved in the deep blue solution, which was then allowed to stand at 0° for 3 hr to deposit black-violet blocks (0.40 g, 90%), which were collected and washed with water, ethanol–ether (1:1), and ether. The complex was recrystallized from water (20 ml, 100°) as long, broad needles which appeared violet-black but which crushed to a blue-green powder; Λ_M = 69 cm² ohm⁻¹ mol⁻¹ (in water); [α]₅₄₆nm −610° (10⁻⁴ M in methanol).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(N₃)₂]ClO₄·H₂O: C, 29.4; H, 6.6; N, 28.5. Found: C, 29.2; H, 6.5; N, 28.7.

Dissolution of the complex and NaNO₂ in methanolic HCl results in quantitative conversion to (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,-3)Cl₂]⁺ ion having properties identical with those of the starting *trans*-dichloro complex.

(+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NCS)₂]ClO₄·H₂O. (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.40 g) and NaNCS (0.30 g) in water (15 ml) were heated on the steam bath for 15 min, giving a rose red solution from which considerable precipitation of red crystals had occurred. Precipitation was completed by the addition of excess NaClO₄ and cooling the solution for 2 hr at 0°. The resulting solid (0.38 g, 86%) was collected and washed with water, ethanol–ether (1:1), and ether. Recrystallization from water (60 ml, 100°) provided long, deep red rods; $\Lambda_M = 79$ cm² ohm⁻¹ mol⁻¹ (in methanol); $[\alpha]_D$ +220° (10⁻³ *M* in methanol); $[\alpha]_{436nm}$ +560° (10⁻³ *M* in CH₃OH).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NCS)₂]ClO₄·H₂O: C, 32.2; H, 6.2; N, 16.1; S, 12.2. Found: C, 32.4; H, 6.3; N, 16.1; S, 11.9.

(+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₃)₂]NO₃. (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.348 g) was converted to the chloride salt by anion exchange in methanol. A solution of AgNO₃ (0.390 g) in methanol (30 ml) was added to the solid and the mixture was heated on the steam bath until the AgCl had coagulated and a brown-violet solution formed (5 min). The AgCl was filtered off and the filtrate was diluted with ether (50 ml) to precipitate rapidly a dull brown-violet powder (0.280 g, 78%) which was collected and washed with ether. The complex was recrystallized from boiling methanol (15 ml) as clusters of fine, fawn needles; $\Lambda_M = 80$ cm² ohm⁻¹ mol⁻¹ (in methanol); $[\alpha]_D$ +1305° (10⁻³ *M* in CH₃OH).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₃)₂]NO₃: C, 30.3; H, 6.4; N, 20.6. Found: C, 30.2; H, 6.6; N, 20.5.

Addition of HCl to a solution of the complex in methanol generated the optically pure (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]⁺ ion.

(−)₅₄₆nm-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(CN)₂]ClO₄. The preparation of this complex was rendered difficult by the necessity of its separation from a tricyano species formed as the predominant product in all reactions investigated for the substitution of CN⁻ on the dichloro complex.

AgCN (0.268 g) was added to a solution of (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.460 g) in methanol (50 ml). The mixture was refluxed for 1 hr, in which time the solution slowly became clear yellow and a well-coagulated precipitate of AgCl formed. The AgCl was filtered off and the filtrate evaporated to dryness under vacuum. The gummy residue was redissolved in methanol, filtered to remove a trace of AgCl, and again taken to dryness. Trituration with acetone (three 10-ml portions) was then used to remove the very soluble tricyano species and the insoluble residual powder (*ca.* 0.1 g) was taken up in water (3 ml, 80°). NaClO₄ (0.5 g) was added and the solution was allowed to stand at 0° for 72 hr to precipitate clusters of golden needles (0.02 g). Reduction of the filtrate volume to near dryness gave more complex as a powder (0.05 g) and the combined fractions were recrystallized from methanol (5 ml) by the addition of ether (10 ml); $\Lambda_M = 100$ cm² ohm⁻¹ mol⁻¹; $[\alpha]_{546nm}$ −90° (in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(CN)₂]ClO₄: C, 38.2; H, 6.9; N, 19.1. Found: C, 38.2; H, 7.0; N, 18.6.

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

(+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NH₃)₂]Cl₃. (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ (0.20 g) was added to anhydrous liquid ammonia (*ca.* 15 ml), giving an immediate orange precipitate. The excess NH₃ was removed by vacuum evaporation (it is essential that the presence of water be avoided in this preparation as the complex reacts rapidly with OH⁻ to lose its ammine groups) and the orange residue was taken up in HCl (1 *M*, 5 ml). After filtration and the addition of acetone (30 ml), the solution was stored at 0° for 12 hr, whereafter small orange crystals (0.15 g, 80%) were deposited. These were collected and washed with acetone and ether; $\Lambda_M = 296$ cm² ohm⁻¹ mol⁻¹ (in water); $[\alpha]_D$ +116° (2 × 10⁻³ *M* in 0.1 *M* HCl).

On warming the complex with dilute NaOH for a few minutes and then adding HCl and HClO₄, (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ of full activity was recovered.

(+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)Cl]ClO₄. HCl (12 *M*, 0.5 ml) was added to a solution of (−)₅₄₆nm-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)₂]ClO₄ (0.69 g) and urea (0.10 g) in water (75 ml, 80°). The mixture effervesced and rapidly turned red as heating on the steam bath was continued for 10 min. Excess NaClO₄ was added and the solution was allowed to stand to cool for 1 hr at 0° as red-brown crystals (0.50 g, 74%) rapidly precipitated. These were collected, washed with water (5 ml), ethanol–ether (1:1), and ether, and recrystallized from methanol (30 ml, 66°) to give large brown-red

rods; $\Lambda_M = 80$ cm² ohm⁻¹ mol⁻¹ (in methanol); $[\alpha]_D$ +73° (3 × 10⁻³ *M* in methanol).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)Cl]ClO₄: C, 30.6; H, 6.4; N, 14.9; Cl, 15.1. Found: C, 30.6; H, 6.8; N, 15.1; Cl, 15.9.

On heating a known mass of the complex in HCl (12 *M*) for 10 min and then making the solution up to a known volume with methanol, the CD spectrum was identical with that of (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ in the same solvent.

(−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)N₃]ClO₄. (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)Cl]ClO₄ (0.422 g) was dissolved in a boiling mixture of water (10 ml) and methanol (5 ml) to give an orange-brown solution. NaN₃ (0.059 g) was added, causing a very rapid color change to deep burgundy. After heating for 1 min on the steam bath, excess NaClO₄ was added and the solution was allowed to stand to cool at 0° for 2 hr. The thin burgundy-colored plates (0.35 g, 82%) were collected and washed with water (5 ml), ethanol–ether (1:1), and ether. The complex was recrystallized from methanol (20 ml) by the addition of ether (20 ml); $\Lambda_M = 75$ cm² ohm⁻¹ mol⁻¹ (in methanol); $[\alpha]_D$ −120° (3 × 10⁻³ *M* in methanol).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)N₃]ClO₄: C, 30.2; H, 6.3; N, 23.5. Found: C, 30.1; H, 6.3; N, 23.3.

The complex was quantitatively converted to (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄ under the same conditions as described for the conversion of the nitrochloro species and gave the optically pure *trans*-dichloro complex.

(+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)NCS]ClO₄. (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)Cl]ClO₄ (0.492 g) was dissolved in a boiling mixture of water (10 ml) and methanol (5 ml). NaNCS (0.100 g) was added and heating was continued for 5 min as the solution rapidly turned orange-red. Addition of excess NaClO₄ caused immediate precipitation of fine pink needles of the diisothiocyanato complex (0.12 g; the result of disproportionation) which, after cooling at 0° for 2 hr, were filtered off. Addition of water (20 ml) to the filtrate and storage at 0° for another 1 hr led to deposition of large orange needles (0.25 g, 49%), which were collected and washed with water, ethanol–ether (1:3), and ether. The complex was recrystallized from water (15 ml, 80°) by the addition of NaClO₄ (1.0 g); $\Lambda_M = 82$ cm² ohm⁻¹ mol⁻¹ (in water); $[\alpha]_D$ +26° (3 × 10⁻³ *M* in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)NCS]ClO₄: C, 31.7; H, 6.1; N, 17.1; S, 6.5. Found: C, 31.4; H, 6.3; N, 17.3; S, 6.0.

A known mass of complex was heated on the steam bath with a 2 molar excess of Hg(ClO₄)₂ solution (0.1 *M* in 1 *M* HClO₄) for 5 min. A large excess of HCl (12 *M*) was then added; the mixture was made up to an exact volume with CH₃OH and allowed to stand 24 hr. The CD spectrum was then identical with that of the (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]⁺ ion.

(−)-Δ-*cis*-β-*S,S*-[Co(*R,R,R,R*-sk-3,2,3)CO₃]Cl·2H₂O. (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]Cl (0.20 g) and Li₂CO₃ (0.10 g) in water (2 ml) were heated on the steam bath for 15 min to give a pink-violet solution. This was filtered and diluted with ethanol (20 ml) and ether (200 ml) to precipitate a pink-violet powder, which was collected and redissolved in methanol (10 ml) containing water (1 ml) and mixed with acetone (20 ml). Storage at 0° for 48 hr led to very slow deposition of small pink-violet blocks (0.12 g, 56%) which were filtered off and washed with ethanol and ether; $\Lambda_M = 80$ cm² ohm⁻¹ mol⁻¹ (in water); $[\alpha]_D$ −300° (2 × 10⁻³ *M* in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)CO₃]Cl·2H₂O: C, 37.1; H, 8.1; N, 13.3; Cl, 8.4. Found: C, 36.5; H, 8.0; N, 13.5; Cl, 8.5.

On dissolution in warm methanolic HCl the complex gave a CD spectrum identical with that of pure (−)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄.

E. [Co(*R,R,S,S*-sk-3,2,3)X₂]ⁿ⁺ Complexes. (i) *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]Cl. The perchlorate salt was converted to the chloride by the method described for the *R,R,R,R:S,S,S,S* ligand complex. The chloride was recrystallized from methanol by the addition of 5 vol. of ether. The lustrous, yellow-green flakes were collected and washed with ether.

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]Cl: C, 36.4; H, 7.6; N, 14.2; Cl, 26.9. Found: C, 36.4; H, 7.7; N, 14.1; Cl, 27.1.

(ii) *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]I. *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]Cl (2.3 g) and NaNO₂ (1.6 g) in water (20 ml) were heated on the steam bath for 15 min. The dinitro complex was formed very rapidly and reaction appeared to be complete within a few minutes. Excess NaI was added to the clear yellow-orange solution, causing immediate precipitation of small golden

crystals, which, after cooling for 1 hr at 0°, were collected and washed with water, ethanol, and ether; yield 2.7 g (91%). The complex was recrystallized from water–methanol (1:4) as fine golden needles; Λ_M = 79 cm² ohm⁻¹ mol⁻¹ (in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]I: C, 28.4; H, 5.9; N, 16.5; I, 25.0. Found: C, 28.5; H, 5.9; N, 16.6; I, 25.3.

Resolution of *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]I. This resolution was complicated by slow formation of a decomposition product during repeated crystallizations. In addition, a partial asymmetric transformation (of the second kind) was obtained, it being possible to cause enantiomeric displacement in either direction if water or methanol was used as the only crystallizing solvent.

trans-R,R:S,S-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]I (2.57 g) was rapidly added to a boiling solution of Ag(+)BCS (2.12 g) in methanol (150 ml) and the mixture was vigorously shaken for 5 min. The AgI was filtered off and washed with boiling methanol (five 20-ml portions), and the filtrate–wash was taken to dryness under vacuum. The yellow residue was dissolved in boiling methanol (50 ml) and filtered; the solution was allowed to stand at 0° for 2 hr to precipitate rapidly clusters of fine yellow needles, which were collected and washed with acetone (25 ml) and ether [1.3 g (37%); [α]D –12° (3 × 10⁻³ M in water); (ε₁ – εᵣ)₄₆₂ₙₘ = –1.22]. Recrystallization did not alter the activity of this material. The filtrate–wash was taken to dryness under vacuum and the residue was dissolved in water (75 ml, 100°). Storage at 0° for 12 hr provided shiny, yellow needles [0.7 g (20%); [α]D +81°; (ε₁ – εᵣ)₄₆₂ₙₘ = +1.17], the activity of which was slightly improved by recrystallization ([α]D +84°) but unchanged by further fractionation. The residue from the filtrate of the [α]D +81° material was recrystallized from methanol (30 ml) to give the impure (–) isomer [0.5 g (23%)] contaminated with decomposition product. Two recrystallizations from methanol gave pure (–) diastereoisomer (0.3 g). Two further fractionations of the bulk residue material from water and methanol gave 0.25 g of (+) and 0.35 g of (–) isomer, respectively.

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]C₁₀H₁₄O₄SBr: C, 38.2; H, 6.4; N, 12.2. Found for (–) diastereoisomer: C, 38.4; H, 6.6; N, 12.3. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]C₁₀H₁₄O₄SBr·1.5H₂O: C, 36.7; H, 6.6; N, 11.7. Found for (+) diastereoisomer: C, 36.7; H, 6.5; N, 11.3.

Excess LiNO₃ was added to aqueous solutions of the (+) and (–) diastereoisomers to precipitate fine yellow needles of (+)-*trans-R,R*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]NO₃ and (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]NO₃, respectively. These complexes were recrystallized from water (80°) made slightly acidic by the addition of CH₃COOH; [α]D ±78° (5 × 10⁻³ M in water). The perchlorate salts may also be readily precipitated but are of such low solubility as to make their crystallization difficult.

Anal. Calcd for [Co(C₁₂H₃₀N₄)(NO₂)₂]NO₃: C, 32.5; H, 6.8; N, 22.1. Found for (+) isomer: C, 32.7; H, 6.8; N, 22.2. Found for (–) isomer: C, 32.6; H, 6.8; N, 22.1.

(–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄. Excess NaClO₄ was added to a solution of (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)-(NO₂)₂]BCS (1.0 g) in water (50 ml), and the glistening golden flakes of the dinitro perchlorate were collected in quantitative yield. This material was dissolved in HCl (12 M, 50 ml) and heated on the steam bath for 20 min, giving a clear green solution. Addition of HClO₄ (6 M, 10 ml) and cooling for 1 hr at 0° caused precipitation of fine, pale green needles of (–)-*trans*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄ [0.55 g (83%)], which were collected and washed with water, ethanol–ether (1:1), and ether. The complex was recrystallized as for its racemate; [α]D –242° (2 × 10⁻³ M in CH₃OH).

Anal. Calcd for [Co(C₁₂H₃₀N₄)Cl₂]ClO₄: C, 31.3; H, 6.6; N, 12.2; Cl, 23.2. Found: C, 31.3; H, 6.7; N, 12.3; Cl, 23.2.

Reaction of this complex with NaNO₂ in aqueous solution regenerated the dinitro complex which was only partly active [(ε₁ – εᵣ)₄₆₂ₙₘ = –0.78] as a result of racemization occurring at a rate similar to that of substitution.

***R,R,S,S*-sk-3,2,3·4HCl.** As direct proof of the optically unresolvable nature of the free ligand present in the above complexes, the ligand was removed from the active *trans*-dichloro complex.

(–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄ (0.40 g) and SnCl₂·2H₂O (0.15 g) were dissolved in ethanol (50 ml) containing HCl (12 M, 5 ml) and heated on the steam bath for 30 min. Shiny white crystals began to precipitate after a few minutes of heating and their deposition was completed by the addition of ether (25 ml) and standing at 0° for 1 hr. The white solid [0.30 g (92%)] was washed with ethanol and ether and recrystallized from HCl (1 M, 5 ml) by

the addition of methanol (5 ml) and acetone (25 ml) to give white plates. In HCl solution these showed no D-line rotation and on conversion back to the Co(III) complex no activity was detectable in the CD 400–600-nm region.

Anal. Calcd for C₁₂H₃₀N₄·4HCl: C, 38.3; H, 9.1; N, 14.9; Cl, 37.7. Found: C, 38.4; H, 9.1; N, 14.8; Cl, 37.5.

(–)-Δ-*cis-β-S,S*-[Co(*R,R,S,S*-sk-3,2,3)C₂O₄]ClO₄·1.5H₂O. (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄ (0.30 g) and H₂C₂O₄·H₂O (0.30 g) in water (5 ml) were heated on the steam bath for 30 min, giving a clear, pink-violet solution. This was diluted with methanol (25 ml) and ether (200 ml) and allowed to stand at 0° for 12 hr to give a flocculent pink precipitate, which was taken up in methanol (25 ml) containing HClO₄ (12 M, 0.5 ml), filtered, and diluted with ether (10 ml). Storage at 0° for 12 hr gave chunky, pink-violet crystals [0.15 g (46%)], which were collected and washed with ethanol and ether; Λ_M = 85 cm² ohm⁻¹ mol⁻¹ (in water); [α]D –105° (10⁻³ M in water).

Anal. Calcd for [Co(C₁₂H₃₀N₄)C₂O₄]ClO₄·1.5H₂O: C, 33.3; H, 6.6; N, 11.1. Found: C, 33.2; H, 6.6; N, 11.3.

By heating the complex in HCl (12 M) for 30 min, the optically pure (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]⁺ ion was regenerated quantitatively.

Registry No. *R,R,S,S*-sk-3,2,3, 53783-18-9; (*R,R:S,S*)-2,4-diaminopentane, 29745-97-9; 1,2-dibromoethane, 106-93-4; *R,R,R,-R*-sk-3,2,3, 53833-93-5; (–)-*R,R*-2,4-diaminopentane, 34998-98-6; *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄, 53783-23-6; *trans-R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]ClO₄, 53860-81-4; *trans-R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)Cl₂]Cl, 53833-94-6; *trans-R,R:S,S*-[Co(*R,R,R,R:S,S,S,S*-sk-3,2,3)(NO₂)₂]I, 53783-24-7; (+)-*trans-R,R*-[Co(*S,S,S,S*-sk-3,2,3)(NO₂)₂](+)BCS, 53860-94-9; (–)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)₂](+)BCS, 53861-01-1; (–)₅₄₆ₙₘ-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)₂]ClO₄, 53833-98-0; (+)₅₄₆ₙₘ-*trans-R,R*-[Co(*S,S,S,S*-sk-3,2,3)(NO₂)₂]ClO₄, 53834-00-7; (–)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)Cl₂]ClO₄, 53833-96-8; (–)-₅₄₆ₙₘ-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(N₃)₂]ClO₄, 36535-50-9; (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NCS)₂]ClO₄, 53783-26-9; (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₃)₂]NO₃, 53860-99-4; (–)₅₄₆ₙₘ-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(CN)₂]ClO₄, 53783-28-1; (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NH₃)₂]Cl₃, 53783-29-2; (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)Cl]ClO₄, 53783-31-6; (–)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)N₃]ClO₄, 53783-33-8; (+)-*trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO₂)NCS]ClO₄, 53783-35-0; (–)-Δ-*cis-β-S,S*-[Co(*R,R,R,R*-sk-3,2,3)CO₃]Cl, 53783-36-1; *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]Cl, 53834-01-8; *trans-R,R:S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]I, 53834-02-9; (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂](+)BCS, 53860-97-2; (+)-*trans-R,R*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂](+)BCS, 53861-00-0; (+)-*trans-R,R*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]NO₃, 53834-04-1; (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO₂)₂]NO₃, 53860-82-5; (–)-*trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)Cl₂]ClO₄, 53834-06-3; (–)-Δ-*cis-β-S,S*-[Co(*R,R,S,S*-sk-3,2,3)C₂O₄]ClO₄, 53783-38-3.

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