properties. We are currently investigating this last possibility. Preliminary results on the nickel(II) complexes of these ligands indicate that the same type of electronic effect may also be operating.

Acknowledgment. We wish to thank S. R. Edmonson for first preparing Co(5-BrSALDAPS) and Co(5-BrSALDAPE); we also thank A. K. St. Clair for her preparation of Co(3-CH(CH$_3$)$_2$SALDAPS). This research is supported by the Research Corp.

Registry No. Co(3-CH$_3$OSALDAPE), 59831-25-3; Co(5-CH$_3$OSALDAPE), 59831-26-4; Co(5-ClSALDAPE), 59831-27-5; Co(5-BrSALDAPE), 59831-28-6; Co(3-NO$_2$SALDAPE), 59831-29-7; Co(3-CH(CH$_3$)$_2$SALDAPS), 59831-30-0; Co(5-ClSALDAPS), 59831-31-1; Co(5-BrSALDAPS), 59831-32-2; Co(3-CH$_3$OSALPhDPT), 59831-33-3; Co(5-CH$_3$OSALPhDPT), 59831-34-4; Co(5-ClSALPhDPT), 59831-35-5; Co(SAL-*p*-ClPhDPT), 59831-36-6; Co(SAL-*p*-CH$_3$OPhDPT), 59831-37-7; Co(SAL-*p*-CH$_3$PhDPT), 59831-38-8; Co(3-NO$_2$SAL-*p*-ClPhDPT), 59831-39-9.

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Conformational Dissymmetry. Conformational Isomers of Bis((*R*,*S*)-2,4-pentanediamine) Complexes

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Received March 22, 1976 AIC60206I

The five possible conformational isomers of the ion [Co(R,S-dmtn)$_2$X$_2$]$^+$ (R,S-dmtn = *meso*-2,4-pentanediamine), three cis and two trans isomers, have been prepared by a variety of kinetic and thermodynamic methods. All were isolated and characterized. It was found that unique and exclusive stereochemical relationships obtain in transferring from the cis to trans isomers, the isomerism of the trans complex being determined by that of the cis isomer from which it is derived. Under appropriately controlled conditions, the converse is true. The mechanistic implication of these observations is discussed. The equilibrium constant for the three *cis*-diaquo isomers has been determined.

Conformational calculations predict[1-3] and experimental studies confirm[4-9] that the isolated trimethylenediamine (tn) chelate ring prefers the chair conformation over any of the other possible conformations. This preference is further reinforced in the analogous dimethyl-substituted ligand, *meso*-2,4-pentanediamine (R,S-dmtn), where the chair chelate ring is stabilized by the requirement that the methyl groups are equatorially disposed. When two or more of either of these ligands is coordinated to a metal atom, the similarity between them diverges; the tn ligand is capable of inverting its chair rings and seeking the most stable relationship between adjacent rings, whereas the R,S-dmtn ligand locks a particular chair conformation so that, for a system containing two or more of these rings, particular isomers arise because of the fixed relationships between the rings.

This paper describes the isolation of all (five) possible conformational isomers of the [M(R,S-dmtn)$_2$X$_2$]$^{n+}$ system in pure crystalline forms. In order to achieve this, we have resorted to both thermodynamic and kinetic means. The kinetically based separations, we believe, are of considerable general importance for they imply a uniqueness about substitution and stereochemical rearrangement in octahedral systems.

I. Isomers

Figure 1 shows the five possible isomers of the octahedral [M(R,S-dmtn)$_2$X$_2$]$^{n+}$ system, two trans and three cis isomers. We refer to the two trans as *trans*-(C_{2v}) and *trans*-(C_{2h}) and the three cis isomers as *cis*-(C_2)-*anti*, *cis*-(C_2)-*syn*, and *cis*-(C_1). The syn and anti designations specify whether the two chelate rings both fold toward each other (syn) or both fold away from each other (anti); the *cis*-(C_1) has the rings folding in–out. We should point out that these isomers arise primarily because of the relative orientations of the (R or S) chiral centers of the ligands (Figure 1) and the fixed chair conformations are a secondary assumption although it is almost certainly correct. For example, *meso*-2,3-butanediamine would give the same number of isomers.

Of the two trans isomers the steplike *trans*-(C_{2h}) configuration is probably more stable. This is suggested by the determined crystal structures of *trans*-[M(tn)$_2$X$_2$]$^{n+}$ systems,[6,7,9] all of which have the *trans*-(C_{2h}) arrangement. The *cis*-(C_2)-*syn* isomer is undoubtedly less stable than the other two because of steric crowding,[10] but the other two may be of comparable energy. Thus the crystal structure of *cis*-[Co(tn)$_2$(NCS)$_2$][Sb((+)-tart)]·2H$_2$O[8] reveals the chair tn rings in a *cis*-(C_2)-*anti* configuration whereas the [Co(tn)$_2$CO$_3$]ClO$_4$ crystal structure has the tn rings in essentially chair conformations but in a *cis*-(C_1) configuration.[10]

II. Mechanism

The most intriguing aspect of this system is that it potentially provides a fine stereochemical probe into the mechanisms of stereochemical change in octahedral systems. In order to focus on this possibility, we assume that the elementary act by which one isomer interconverts to another is an edge displacement of one donor nitrogen atom to an adjacent cis position. In Figure 2 we show an interconversion scheme for the five isomers; in going from one isomer to another, only one edge displacement is invoked. Only a selected number of edge displacements are shown; these are sufficient to illustrate the basic features of the system.

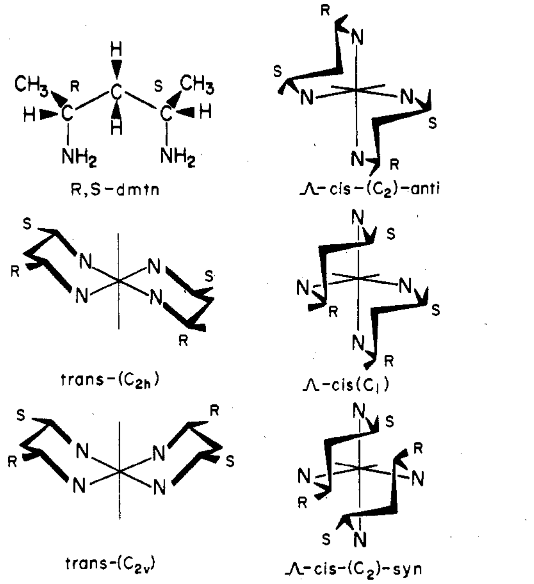

Figure 1. The structure of *meso*-2,4-pentanediamine and that of each of the five possible octahedral bis(bidentate) isomers.

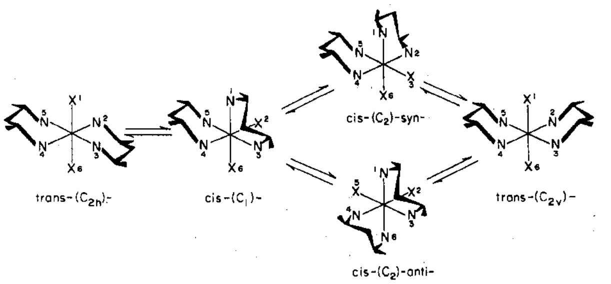

Figure 2. An interconversion scheme for the five [Co(R,S-dmtn)$_2$X$_2$]$^+$ isomers assuming a single act of edge displacement for each step.

A single act of edge displacement by the *trans*-(C_{2h}) isomer leads exclusively to the *cis*-(C_1) isomer. This result does not depend on which nitrogen atom of the trans complex is moved, nor to which apical position (of the trans isomer) it moves. There are two possible *single* acts of edge displacement which convert the *cis*-(C_1) isomer to a trans complex, namely, 1 to 2 and 4 to 6; both acts give the *trans*-(C_{2h}) isomer.

The *trans*-(C_{2v}) isomer has two avenues to the cis complexes arising from the inequivalence of the axial positions. Displacement of any one of the four nitrogen atoms to the crowded axial position, 1, gives only the *cis*-(C_2)-*syn* isomer, whereas displacement of any one of the four nitrogen atoms to the open axial position, 6, leads to the *cis*-(C_2)-*anti* isomer exclusively. However, the unit displacements, 1 to 3 or 5 to 6 in the *cis*-(C_2)-*syn* structure and 3 to 2 or 4 to 5 in the *cis*-(C_2)-*anti* isomer, all lead back to the *trans*-(C_{2v}) complex.

Thus on the assumption of unit edge displacement, there exist two independent sets of equilibria, namely, *trans*-(C_{2h})–*cis*-(C_1) and *trans*-(C_{2v})–*cis*-(C_2)-*syn*–*cis*-(C_2)-*anti*. In order to transfer from one equilibrium domain to the other requires a second displacement within the cis complexes. Figure 2 gives a representative set of displacements which interconvert cis complexes. It is notable that a particular single displacement of the *cis*-(C_1) structure gives either of the *cis*-(C_2) isomers, but to transfer from one *cis*-(C_2) structure to the other requires two unit displacements which include either the *cis*-(C_1) or the *trans*-(C_{2v}) as intermediates. The two trans complexes are interconverted by a minimum of three unit displacements involving cis isomers and by either of two possible paths (Figure 2).

We now show by experiment that the considerations above are apposite.

III. Chemistry

A methanol solution of cobaltous chloride, R,S-dmtn, and acetic acid is oxidized by air to give a variety of (R,S-dmtn)$_2$Co^{III} species which, when reacted with hydrochloric acid, are totally converted to the *trans*-[Co(R,S-dmtn)$_2$Cl$_2$]$^+$ ion. The resulting solution is a mixture of isomers containing mainly the *trans*-(C_{2h}) isomer and about 5% of the *trans*-(C_{2v}) species. These are difficult to separate cleanly either as their chloride or perchlorate salts, although the *trans*-(C_{2v}) isomer as either salt is more soluble in common solvents. In order to separate these isomers, the trans complexes were reacted with carbonate ions to give a small amount of the insoluble *cis*-(C_2)-*anti*-[Co(R,S-dmtn)$_2$CO$_3$]Cl salt and the very soluble *cis*-(C_1)-[Co(R,S-dmtn)$_2$CO$_3$]Cl compound. This soluble *cis*-(C_1)-carbonato species reacts with HCl to give the *trans*-(C_{2h})-[Co(R,S-dmtn)$_2$Cl$_2$]Cl isomer exclusively which can then be isolated pure.

The insolubility of the *cis*-(C_2)-*anti*-[Co(R,S-dmtn)$_2$CO$_3$]Cl salt provided a method for transferring from the *trans*-(C_{2h})–*cis*-(C_1) equilibrium domain to the other (Figure 2). Thus the reaction of the pure *trans*-(C_{2h})-[Co(R,S-dmtn)$_2$Cl$_2$]Cl complex with carbonate ions gives the *cis*-(C_1)-[Co(R,S-dmtn)$_2$CO$_3$]Cl complex initially, but, if this solution is heated, equilibration occurs, and the *cis*-(C_2)-*anti*-[Co(R,S-dmtn)$_2$CO$_3$]Cl salt begins to precipitate out of water solution. By collecting the crystals and repeating the equilibration a number of times, the system can be induced to convert nearly all the complex in solution into the *cis*-(C_2)-*anti* isomer. This "milking" of the less soluble complex almost certainly occurs because of Co(II)-induced catalytic equilibration; after each cycle, small amounts of cobalt oxide are deposited and equilibration does not occur without the appearance of this side product. Despite the catalytic equilibration, no evidence of the (crowded) *cis*-(C_2)-*syn* isomer could be found even after exhaustive fractional crystallization. It thus appears that, although the *cis*-(C_1) and *cis*-(C_2)-*anti* conformers have comparable stability, the *cis*-(C_2)-*syn* arrangement is much less stable.

When the *cis*-(C_2)-*anti*-[Co(R,S-dmtn)$_2$CO$_3$]$^+$ ion is treated with HCl, the only product is the second trans isomer, *trans*-(C_{2v})-[Co(R,S-dmtn)$_2$Cl$_2$]$^+$, which can be isolated pure as the perchlorate salt.

Since the remaining isomer, *cis*-(C_2)-*syn*, is not accessible thermodynamically, we have devised a kinetic method for obtaining it. The method is based on the following argument. It is now becoming clear that many, if not all, carbonate substitutions at a Co(III) center involve first the formation of a hydroxo complex which then adds to carbon dioxide forming, after deprotonation, a unidentate carbonato species which, if conditions allow, closes to form a bidentate chelate ring.[11,12] We note that the axial positions of the *trans*-(C_{2v})-[Co(R,S-dmtn)$_2$Cl$_2$]$^+$ ion are inequivalent, and hence two (*trans*-(C_{2v})-)hydroxochloro isomers are possible, the hydroxo ligand being either at the crowded side or at the exposed side (Figure 1). Addition of CO$_2$ to the crowded hydroxo ligand followed by chelation will produce the *cis*-(C_2)-*anti*-carbonato complex, whereas addition and chelation which involves the exposed hydroxo ligand produces the (crowded) *cis*-(C_2)-*syn*-carbonato complex (Figure 3).

The *trans*-(C_{2v})-[Co(R,S-dmtn)$_2$Cl$_2$]$^+$ ion was reacted with a cold solution of bicarbonate ions in the expectation that the mild pH conditions might prevent any unwanted hydroxide induced isomerization. The reaction is characterized by a rapid color change from green to ink-blue (the characteristic hydroxochloro color) and the copious evolution of CO$_2$. On warming, the solution develops the characteristic pink color

Table I. Methyl Proton Resonances of the $(R,S\text{-dmtn})_2\mathrm{Co^{III}}$ Isomers

Complex	Solvent (29 °C)	δ, ppm
trans-(C_{2h})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$[b]	Sulpholane-d_8[d]	1.32, 1.38
trans-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$[b]	Sulpholane-d_8[d]	1.31, 1.37
trans-(C_{2h})-$[\mathrm{Co}(R,S\text{-dmtn})_2(\mathrm{CH_3CO_2})_2]\mathrm{ClO_4}$[b]	$\mathrm{CD_3OD}$[d]	1.35, 1.41; 1.83[e]
trans-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2(\mathrm{CH_3CO_2})_2]\mathrm{ClO_4}$[b]	$\mathrm{CD_3OD}$[d]	1.36, 1.43; 1.86,[e] 1.88[e]
cis-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl}$[a]	$\mathrm{D_2O}$[c]	1.20, 1.23, 1.28, 1.33, 1.35, 1.39, 1.42
cis-(C_2)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl}$[a]	$\mathrm{D_2O}$[c]	1.17, 1.25, 1.27, 1.36
cis-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$[a]	$\mathrm{D_2O}$[c]	1.26, 1.32, 1.37, 1.42
cis-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{C_2O_4}]\mathrm{Cl}$[b]	$\mathrm{D_2O/DCl}$[c]	1.36, 1.37, 1.40, 1.42
cis-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{C_2O_4}]\mathrm{ClO_4}$[b]	$\mathrm{D_2O/DCl}$[c]	1.16, 1.17, 1.22, 1.23

[a] 60 MHz. [b] 100 MHz. [c] Internal NaDSS as reference. [d] Internal TMS as reference. [e] Methyl proton resonance of coordinated acetate (free acetic acid occurs at 1.99 ppm in the same solvent).

Table II. $^{13}\mathrm{C}$ NMR Data for *cis*-$(R,S\text{-dmtn})_2\mathrm{Co^{III}}$ Isomers (100 MHz)

	δ, ppm (290)[d]				
Complex	$\mathrm{CH_3}$	$\mathrm{CH_2}$	CH	$\mathrm{CO_3}$	$\mathrm{C_2O_4}$
cis-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl}$[a]	−43.74[c]	−25.24 −26.21	−18.94[c] −19.23 −19.67	+100.67	
cis-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$[b]	−43.85 −44.26	−25.90	−19.18 −20.14	+100.75	
cis-(C_2)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl}$[b]	−43.94[c]	−25.31	−19.26 −19.65	+100.54	
cis-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{C_2O_4}]\mathrm{Cl}$[a]	−44.25[c]	−25.56 −26.54	−19.22 −19.54 −19.89 −20.04		+101.90 +101.78
cis-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{C_2O_4}]\mathrm{ClO_4}$[a]	−43.94 −44.26	−25.97	−18.85 −19.87		+101.65

[a] $\mathrm{H_2O}$ as solvent; external reference $^{13}\mathrm{C}$ of dioxane in $\mathrm{D_2O}$; external lock, D of $\mathrm{D_2O}$. [b] $\mathrm{H_2O/D_2O}$ solvent (1:3); internal reference $^{13}\mathrm{C}$ of dioxane and internal lock, D of $\mathrm{D_2O}$. [c] Broad unresolved resonances. [d] "Noise" decoupled data.

of the chelated carbonato complexes and, mirable dictu, the product consists of 30% of *cis*-(C_2)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]^+$ and 70% of the desired, sterically congested *cis*-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]^+$ isomer. The two were isolated pure by crystallization. This same reaction with the *trans*-(C_{2h})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]^+$ ion produces exclusively the expected *cis*-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]^+$ ion.

Just as in the case of the *cis*-(C_2)-*anti* isomer, treatment of *cis*-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]^+$ with HCl leads to the exclusive production of the *trans*-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]^+$ ion.

All three carbonato isomers react with oxalic acid to give, with complete steric retention, the corresponding oxalato isomers. These were all isolated.

In order to assign the structures of the two trans complexes we have employed the following device. The three isomeric carbonato complexes were reacted in glacial acetic acid: the *cis*-(C_1)-carbonato complex gave exclusively a single *trans*-$[\mathrm{Co}(R,S\text{-dmtn})_2(\mathrm{CH_3CO_2})_2]^+$ isomer, whereas either the *cis*-(C_2)-*anti* or *cis*-(C_2)-*syn* gave a second *trans*-bisacetato complex exclusively. The first isomer, from *cis*-(C_1), showed a single sharp acetatomethyl proton resonance at 60 MHz whereas, the other *trans*-bisacetato species, obtained from either of the *cis*-(C_2) complexes, gave two equally intense acetatomethyl proton signals at 60 MHz. We thus conclude that the *cis*-(C_1)-derived complex is the *trans*-(C_{2h})-$[\mathrm{Co}(R,S\text{-dmtn})_2(\mathrm{CH_3CO_2})_2]^+$ isomer and that the *cis*-(C_2)-derived species is the *trans*-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2(\mathrm{CH_3CO_2})_2]^+$ conformer because of the magnetic inequivalence of the acetatomethyl groups. If the *trans*-(C_{2h})-bisacetato complex is treated with HCl it gives only the *trans*-(C_{2h})-dichloro isomer and the same reaction of the *trans*-(C_{2v})-bisacetato species gives exclusively the *trans*-(C_{2v})-dichloro complex. This together with other evidence provides almost conclusive proof of the isomerism of the *trans*-dichloro complexes. The structural assignments of these and the other complexes are provided by NMR and a crystal structure.

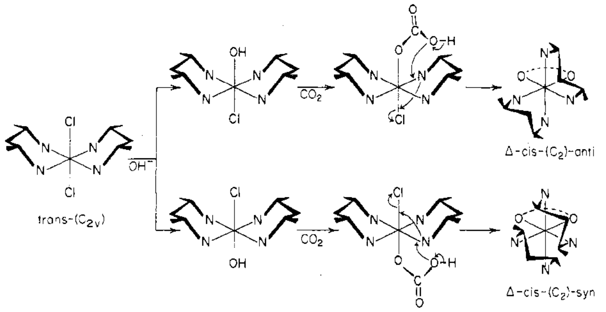

Figure 3. The proposed mechanism for the formation of the two carbonato isomers derived from the *trans*-(C_{2v}) complex when reacted with bicarbonate ions.

IV. Structural Assignments

The structures of these complexes were determined by their NMR spectra, their d–d electronic absorption spectra, and by a single-crystal x-ray structure of a key compound. Table I lists the methyl proton signals of the various isomers. By symmetry we expect each of the trans isomers should give only one methyl proton doublet because in either isomer the methyl groups are in identical magnetic environments; similarly the *cis*-(C_2) isomers should each give a pair of methyl doublets while the *cis*-(C_1) isomer, which is devoid of any symmetry, should show four sets of methyl doublets. The results collected in Table I bear out these expectations except that the *cis*-(C_1)-oxalato isomer is ambiguous because the signals are not resolved.

This matter, however, is settled by the $^{13}\mathrm{C}$ NMR data listed in Table II. Symmetry predicts that all the carbon atoms of the *cis*-(C_1) isomer are magnetically inequivalent whereas the *cis*-(C_2) isomers should show two methyl carbon signals, two methylene carbon signals, and one methine carbon atom signal. Although not all the resonances are fully resolved, there is for each complex at least two kinds of carbon atoms which show

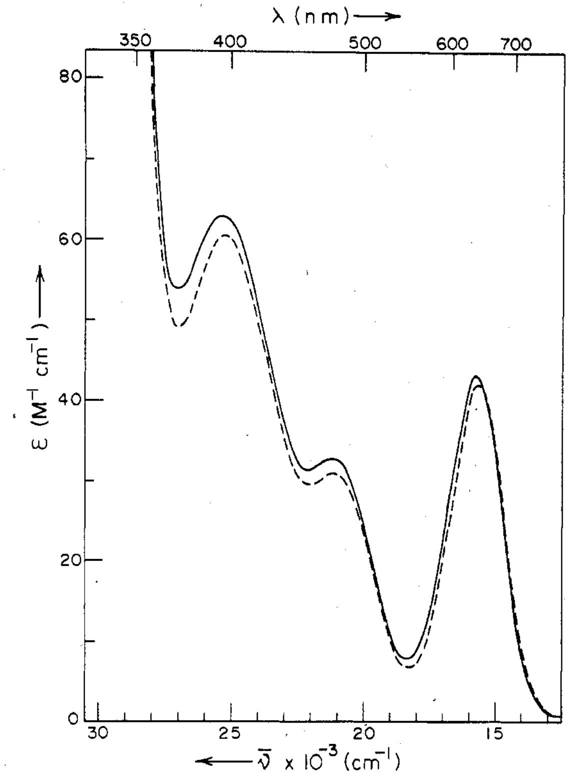

Figure 4. The visible absorption spectra of the *trans*-(C_{2h})-[Co(*R*, *S*-dmtn)$_2$Cl$_2$]ClO$_4$ (–) and *trans*-(C_{2v})-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]ClO$_4$ (- - -) complexes in methanol solutions.

the expected multiplicity (Table II). The *cis*-(C_1)-oxalato complex, which gave an ambiguous proton NMR, is seen to show the expected inequivalence of its oxalato carbon atoms. The assignments of the resonances is readily established by the multiplicity of the (proton) coupled spectra, as each type of carbon atom has a different number of attached hydrogen atoms.

Neither Table I nor II gives any data for the *cis*-(C_2)-*anti*-oxalato isomer because both the chloride and perchlorate salts are not sufficiently soluble to obtain acceptable NMR spectra. However, a single-crystal x-ray structure[13] of *cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$C$_2$O$_4$]ClO$_4$ shows it to be the correct isomer. At the same time this structure allows the assignment of the *cis*-(C_2) isomers which cannot be assigned by NMR on the basis of symmetry.

Thus most of the structural assignments are independent of any mechanistic assumptions; the two that rely on mechanism are the assignments of the *trans*-dichloro structures and of the *cis*-(C_2)-carbonato isomers, but the interconnected consistency of the chemical results is such as to leave little doubt that these assignments are correct.

Figures 4 and 5 show the visible absorption spectra of the *trans*-dichloro and *trans*-bisacetato isomers. It will be seen that, as expected, the pairs of isomers show very similar absorption. Of particular interest is the fact that the position of the $^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ transition derived from $^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h is at the same (19 250 cm^{-1}) energy position for the two sets of isomers. This is precisely what theory predicts should be the diagnostic feature of the *trans*-[Co(N)$_4$X$_2$]$^{n+}$ chromophore.[14,15]

The exact extinction coefficients and energy positions of the d–d bands of the other isomers are given in the Experimental Section.

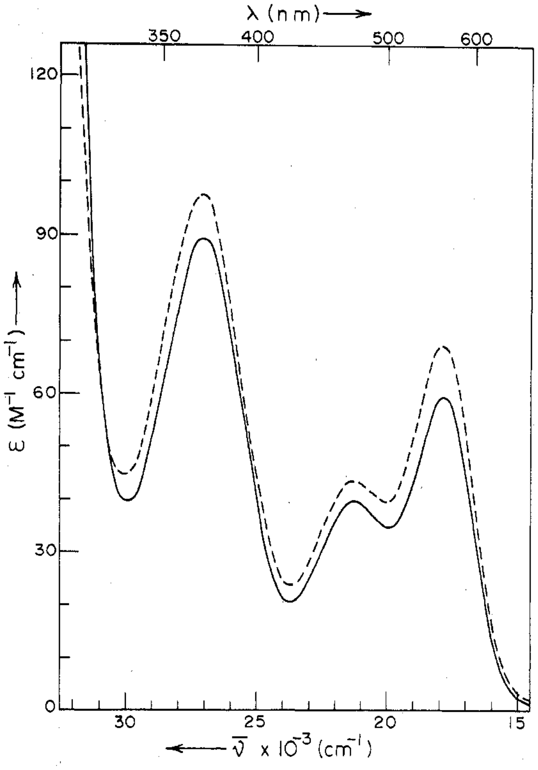

Figure 5. The visible absorption spectra of the *trans*-(C_{2h})-[Co(*R*, *S*-dmtn)$_2$(CH$_3$CO$_2$)$_2$]ClO$_4$·H$_2$O (–) and *trans*-(C_{2v})-[Co(*R*,*S*-dmtn)$_2$(CH$_3$CO$_2$)$_2$]ClO$_4$·CH$_3$CO$_2$H (- - -) complexes in methanol solutions.

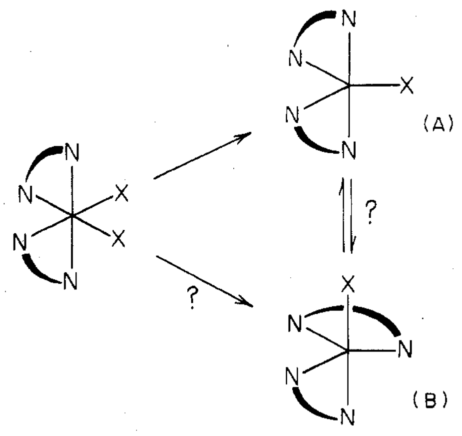

Figure 6. Two possible quasi-trigonal-bipyramidal intermediates which may be formed after dissociation of an X group from the octahedral complex.

V. Equilibration and Mechanism

The most remarkable result of the present study in relation to stereochemical change is that the carbonato isomers react with acids to give uniquely and exclusively one trans isomer. This observation strongly suggests that the cis to trans interconversions do not involve any intervening cis to cis edge displacements, for, were these to occur, the strict stereochemical connection between factor and product would not obtain (Figure 2). The fact that the three cis isomers, with their varying degrees of nonbonded interactions, all display this unique feature suggests that the relief of nonbonded interaction is not the primary factor in the steric course but, rather, that a similar (five coordinate) intermediate which retains the original chelate ring relationship and which has a preferred position of attack is formed in each of the three cases.

The intermediate A (Figure 6) represents a five-coordinate species where the original ring relationships have been retained and for convenience it is drawn as a trigonal bipyramid although such a classification is illusionary to the extent that any intermediate is likely to be distorted from any idealized geometry. Addition of a sixth ligand X, cis to the X group in A, to occupy the "equatorial" plane leads to the original (cis) isomer. However, addition in the "equatorial" plane trans to X, followed by displacement of the "equatorially" disposed nitrogen atoms, leads to a trans product which, as it were, remembers from which isomer it came. The present results preclude any intermediate which, after attack, allows either of the trans disposed nitrogen atoms (of the starting octahedral species) to be displaced, for were this to occur a new relationship between the rings would obtain (Figure 2) and the trans product eventually obtained would not have the observed direct relationship with the original cis isomer. Under somewhat forcing conditions, however, scrambling of the ring relationships can be induced.

When any of the three carbonato perchlorate isomers is reacted in 3 M perchloric acid at 30 °C, *cis*-diaquo complexes are rapidly formed which have the same configuration as each of the starting complexes. That this is so is readily established by their methyl proton (NMR) signals which show distinct and characteristic cis patterns (Experimental Section). These *cis*-diaquo complexes are isomerically stable at 30 °C for at least 2 h in the perchloric acid solutions for their NMR spectra remain constant. When each is reacted with hydrochloric acid the pink solutions rapidly turn violet-red (*cis*-chloroaquo) and shortly thereafter the appropriate green trans isomer is produced exclusively. In view of the fact that the anation is very rapid at 30 °C (~1 min), it is probable that many acts of water exchange occur[16] within 2 h at 30 °C; yet the cis complexes retain their isomerisms.

If, however, any of these *cis*-diaquo isomers dissolved in 3 M $HClO_4$ is held at 90 °C for about 1 h, equilibration between the *cis*-diaquo species does occur. The same mixture is observed when derived from any of the three isomers. A precise NMR analysis of the methyl proton signals is made difficult by the overlap but we find that the equilibrium mixture consists of 75 ± 10% of the *cis*-(C_1) isomer and 25 ± 10% of the *cis*-(C_2)-*anti* species. There is no evidence for the *cis*-(C_2)-*syn* isomer at equilibrium. These ratios are perhaps surprising in that it might have been expected that the more open structured *cis*-(C_2)-*anti* isomer would have been the more stable. It is probable that the ratio does depend on the nature of the other two ligands but, even so, it is clear that the *cis*-(C_2)-*anti* and *cis*-(C_1) isomers of *R*,*S*-dmtn are of comparable energy.

The mechanism of the cis–cis equilibrations could involve either the formation of a new intermediate, in which, either directly or indirectly (Figure 6), one of the trans disposed nitrogen atoms has been displaced such as to give a new ring relationship (intermediate B), or attack by the incoming ligand on intermediate A to cause displacement of one of the trans disposed nitrogen atoms. The present experiments do not distinguish these possibilities although electronic reasons have been advanced to exclude axial attack in an idealized trigonal-bipyramidal intermediate.[16]

VI. Experimental Section

The instrumentation and the method of obtaining the ^{13}C NMR spectra were the same as those described in a previous paper.[17]

***trans*-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]Cl·0.5H$_2$O.** A methanolic solution (200 ml) containing cobalt chloride hexahydrate (18.1 g), glacial acetic acid (1 ml), and freshly distilled *R*,*S*-dmtn·H_2O[18] (18.5 g) was aerated for 6 h, then hydrochloric acid (25 ml; 12 M) was added to yield a clear green solution. This was reduced to dryness under vacuum. The residue was treated with 20% excess lithium carbonate in hot water (450 ml) for 20 min and the insoluble solids were removed by filtration. The solids were washed with water (50 ml at 90 °C) and the combined filtrates were reduced in vacuo to about 100 ml. The pink solid (the insoluble *cis*-(C_2)-*anti*-carbonato species (6 g)) which separated from the cooled solution was filtered and set aside. Treatment of the deep purple filtrate with hydrochloric acid (60 ml; 6 M) caused precipitation of small green crystals, which were collected after cooling the mixture at 5 °C for 2 h and washed with water (40 ml), then with ethanol (50 ml), and finally with ether (10 g). Workup of the filtrate yielded a further 4 g.

This material consists mainly (>95%) of the *trans*-(C_{2h}) isomer and is a convenient starting material for obtaining the pure isomers. $\Lambda_M = 85.0\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in methanol at 25 °C). Anal. Calcd for $[Co(C_5H_{14}N_2)_2Cl_2]Cl{\cdot}0.5H_2O$: C, 31.7; H, 7.7; N, 14.8; Cl, 28.2. Found: C, 31.6; H, 7.7; N, 15.1; Cl, 28.2.

***cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$.** Finely ground *trans*-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]Cl·0.5H$_2$O (18.5 g), obtained from the above preparation, dissolved in water (50 ml) at 60 °C containing sodium carbonate (5.5 g) was heated at 80 °C for 15 min. The resulting deep purple solution was cooled in ice to 5 °C and then filtered. Sodium perchlorate (10 g) was added to precipitate deep purple crystals which were collected after the mixture was held at 0 °C for 1 h. The solid was washed with cold water (20 ml) and then with anhydrous ether. The product (18.2 g) was taken up in water (180 ml) at 80 °C and then sodium perchlorate (8.5 g) in water (20 ml) was added to the hot solution. On cooling, large dark purple needles of the pure *cis*-(C_1) isomer formed (16 g). This material slowly effloresces in air; it was kept at 100 °C for 12 h and then analyzed.

$\Lambda_M = 89.8\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in water at 26°); ϵ_{max} = 112.5 at 520 mμ and ϵ_{max} = 129 at 360 mμ. Anal. Calcd for $[Co(C_5H_{14}N_2)_2CO_3]ClO_4$: C, 31.2; H, 6.6; N, 13.3; Cl, 8.4. Found: C, 31.4; H, 6.9; N, 13.4; Cl, 8.4.

***cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]Cl·0.5H$_2$O.** A suspension of *trans*-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]Cl·0.5H$_2$O (37 g) in water (50 ml) containing sodium carbonate (11 g) was heated with stirring at 60 °C until dissolution was complete. The temperature was then raised to 80 °C and the solution was stirred until small pink needles began to separate, ~10 min. The solution was then allowed to cool slowly to room temperature whereafter the product was collected, washed with water (15 ml), and then with ethanol and finally with ether. The filtrate and aqueous wash was then reequilibrated at 80 °C. Six fractions, representing a combined total of 18.5 g of product, were thus collected. The final filtrate was retained for isolation of the more soluble *cis*-(C_1)-carbonato chloride isomer. The product was quickly taken up in water (750 ml) at 85 °C, the solution was filtered, and sodium chloride (30 g) was added. On cooling in ice, small pink red needles of the pure *cis*-(C_1) isomer deposited. These were collected and washed with ice water, then with ethanol, and finally with ether (14.7 g). $\Lambda_M = 83.0\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in water at 25 °C); ϵ_{max} = 110 at 518 mμ and ϵ_{max} = 109 at 360 mμ. Anal. Calcd for $[Co(C_5H_{14}N_2)_2CO_3]Cl{\cdot}0.5H_2O$: C, 35.9; H, 7.9; N, 15.2; Cl, 9.7. Found: C, 35.6; H, 7.9; N, 15.3; Cl, 10.0.

***cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$CO$_3$]Cl.** The reaction filtrate remaining after the isolation of the crude *cis*-(C_2)-*anti* isomer was reduced in volume in vacuo, with periodic removal of solids (NaCl and the *cis*-(C_2)-*anti* isomer) to a thick syrup. This was diluted with acetone (50 ml) and cooled for 12 h at 5 °C. The precipitated solids were collected and discarded. The filtrate was evaporated to dryness. Dissolution of the residue in water (28 ml) at 60 °C and cooling for 1 week at 4 °C afforded dark purple needles. These were collected and washed with methanol–acetone (30:1, 40 ml) and then with ether (11.1 g). The product was taken up in water (10 ml) at 65 °C and on cooling, dark purple needles of the pure *cis*-(C_1) isomer deposited (10 g). The compound rapidly effloresces in air. $\Lambda_M = 83.3\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in water at 25 °C). Anal. Calcd for $[Co(C_5H_{14}N_2)_2CO_3]Cl$: C, 36.8; H, 7.8; N, 15.6; Cl, 9.9. Found: C, 36.6; H, 7.8; N, 15.5; Cl, 10.0.

***cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$.** Addition of sodium perchlorate (10 g) to *cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]Cl·0.5H$_2$O (2.0 g) in water (90 ml) at 70 °C caused the precipitation of small deep red blocks of the perchlorate salt. It was cooled at 0 °C for 2 h and then was collected and washed with water (15 ml), followed by methanol, and finally with ether (1.9 g). $\Lambda_M = 89.9\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in water at 26 °C). Anal. Calcd for $[Co(C_5H_{14}N_2)_2CO_3]ClO_4$: C, 31.2; H, 6.6; N, 13.3; Cl, 8.4. Found: C, 31.1; H, 6.7; N, 13.3; Cl, 8.7.

***trans*-(C_{2h})-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]ClO$_4$.** Finely ground *cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$ (2.0 g) was allowed to react with perchloric acid (5 ml; 5 M) for 5 min at 25 °C, then hydrochloric acid (3 ml; 12 M) was added, whereupon dark green crystals began to deposit. After cooling, the product was collected and washed with absolute ethanol–ether (1:3, 20 ml) and with ether. Yield 2.05 g (100%).

This (pure) material may be recrystallized from methanol (150 ml) at 60 °C by the addition of $\mathrm{LiClO_4{\cdot}3H_2O}$ (1 g) in methanol (5 ml) to give dark green plates (0.93 g). Depending on the crystallization history, irregular, dull, light-green crystals may also form, which show identical solution properties to the regular plates. $\Lambda_M = 85.8\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in methanol at 25 °C); $\epsilon_{max} = 43.1$ at 636 mμ, $\epsilon_{max} = 32.9$ at 472 mμ, $\epsilon_{max} = 63.0$ at 395 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2Cl_2]ClO_4}$: C, 27.7; H, 6.5; N, 12.9; Cl, 24.6. Found: C, 27.8; H, 6.5; N, 13.0; Cl, 24.7.

trans-(C_{2v})-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$.** Either *cis*-($C_2$)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$ or *cis*-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$ (0.88 g) was dissolved in perchloric acid (2 ml; 5 M) at 25 °C. After 5 min, hydrochloric acid (0.5 ml; 12 M) was added and the solution was allowed to stand at 25 °C until a deep green solution resulted above the deposited green crystals. After cooling at 5 °C for 5 h, the product was collected and washed with ethanol–ether (1:20) and then with ether. Yield 0.90 g (100%). This material is pure but may be recrystallized from methanol (25 ml) at 70 °C by the addition of $\mathrm{LiClO_4{\cdot}3H_2O}$ (1 g) in methanol (2 ml). On cooling, this solution deposited long green needles (0.74 g). $\Lambda_M = 86.1\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in methanol at 25 °C); $\epsilon_{max} = 42.0$ at 640 mμ, $\epsilon_{max} = 31.0$ at 473 mμ, $\epsilon_{max} = 60.5$ at 396 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2Cl_2]ClO_4}$: C, 27.7; H, 6.5; N, 24.6; Cl, 13.6. Found: C, 27.7; H, 6.5; N, 24.6; Cl, 13.6.

cis-(C_2)-*syn*-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4{\cdot}H_2O}$.** Finely ground *trans*-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$ (1.9 g) was suspended in a chilled solution of sodium bicarbonate (1.9 g) in water (30 ml) and the mixture was vigorously shaken in a stoppered flask for 15 min. The mixture rapidly turned an intense ink-blue color and the solution began to froth; a small amount of blue solid may also deposit during this time. After the shaking was finished, the mixture was warmed on a steam bath for about 5 min, during which time a clear red solution developed. Sodium perchlorate (4.0 g) was added and the solution was cooled in an ice bath and held at 0 °C for 5 min and then, without delay, the crystals of the *cis*-(C_2)-*anti* isomer (0.35 g) were filtered. (The desired isomer may also crystallize at this stage if cooling is prolonged.) The violet filtrate was reduced in volume under vacuum to about 8 ml and, after the solution was cooled in ice, the violet-purple powder was collected and washed with absolute ethanol and ether (1.4 g).

The product was dissolved in water (15 ml) at 65 °C and sodium perchlorate (1.5 g) was added and after 1 min at 65 °C the solution was filtered rapidly to remove the residual *cis*-(C_2)-*anti* isomer. More sodium perchlorate (0.75 g) in water (3 ml) was added to the filtrate. Cooling afforded pink-violet needles of the pure *cis*-(C_2)-*syn* isomer (0.45 g). $\Lambda_M = 95.0\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in water at 25 °C); $\epsilon_{max} = 114.0$ at 527 mμ, $\epsilon_{max} = 153.5$ at 362 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2CO_3]ClO_4{\cdot}H_2O}$: C, 30.0; H, 6.8; N, 12.7; Cl, 8.1. Found: C, 30.1; H, 6.9; N, 12.9; Cl, 8.3.

cis-(C_1)-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2\mathrm{Ox}]\mathrm{Cl{\cdot}H_2O{\cdot}0.5(CH_3)_2CO}$.** A solution of *cis*-(C_1)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl{\cdot}0.5H_2O}$ (0.64 g) in water (5 ml) containing oxalic acid (0.7 g) was allowed to react at 30 °C for 15 min. It was then heated at 80 °C for a further 15 min. Addition of absolute ethanol (2 ml) and acetone (50 ml) induced the precipitation of a pink powder which was collected and washed with acetone and ether. Recrystallization from water (6 ml) by the successive addition of ethanol (2 ml) and acetone (100 ml) gave red-pink needles. Yield 0.69 g (100%); $\Lambda_M = 87.1\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in water at 26 °C); $\epsilon_{max} = 86.0$ at 510 mμ, $\epsilon_{max} = 160.2$ at 360 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(C_2O_4)]Cl{\cdot}H_2O{\cdot}0.5(CH_3)_2CO}$: C, 37.4; H, 7.6; N, 12.9; Cl, 8.2. Found: C, 37.3; H, 7.7; N, 12.8; Cl, 8.1.

The (half) acetone of crystallization could not be removed under the usual conditions but its presence and proportion was confirmed by NMR.

cis-(C_2)-*anti*-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2\mathrm{Ox}]\mathrm{Cl{\cdot}1.5H_2O}$.** A suspension of *cis*-(C_2)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{Cl{\cdot}0.5H_2O}$ (2.0 g) in water (100 ml) containing oxalic acid (2.0 g) was allowed to react at 25 °C for 1 h. It was then refluxed for 5 min. The solution was reduced to dryness under vacuum, and the residue was slurried with acetone, collected, and washed well with acetone and ether. The solid was dissolved in water (180 ml) at 90 °C and then sodium chloride (5.0 g) in water (25 ml) was added. On slow cooling the solution deposited small shiny pink flakes, which were collected and washed successively with cold water (10 ml), absolute ethanol, and ether (1.1 g). $\Lambda_M = 83.8\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in water at 25 °C); $\epsilon_{max} = 95.7$ at 510 mμ, $\epsilon_{max} = 156.7$ at 363 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(C_2O_4)]Cl{\cdot}1.5H_2O}$: C, 34.8; H, 7.5; N, 13.5; Cl, 8.6. Found: C, 34.9; H, 7.5; N, 13.5; Cl, 8.6.

The perchlorate salt is prepared by adding sodium perchlorate (2.0 g) in water (3 ml) to a hot solution of the chloride salt (0.4 g) in water (70 ml) at 80 °C. On cooling, deep red blocks form. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(C_2O_4)]ClO_4}$: C, 32.0; H, 6.2; N, 12.4; Cl, 7.9. Found: C, 32.2; H, 6.0; N, 12.3; Cl, 7.9.

cis-(C_2)-*syn*-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2\mathrm{Ox}]\mathrm{ClO_4{\cdot}H_2O}$.** Finely ground *trans*-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$ (2.0 g) was shaken for 15 min in cold aqueous sodium bicarbonate solution (2 g in 40 ml) and then the solution was heated at 80 °C for 10 min. Sodium perchlorate (4 g) was added to the hot solution and, on cooling at 10 °C for 10 min, the *cis*-(C_2)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$ isomer deposited. It was collected and oxalic acid (1.5 g) was added to the filtrate which was then heated for 5 min at 80 °C to give a clear red solution. This was pumped to dryness under vacuum. The residue was dissolved in water (4 ml) and then methanol (25 ml) followed by acetone (200 ml) were added to precipitate both the sodium salts and the remaining *cis*-(C_2)-*anti* isomer. These were collected and the filtrate was pumped to dryness under vacuum. The residue was suspended in warm water (10 ml) and after cooling at 5 °C for $^1/_2$ h the crude product was filtered (1.1 g). It was taken up in water (25 ml) at 80 °C and sodium perchlorate (2.0 g) in water (3 ml) was added. On cooling, the pure *cis*-(C_2)-*syn* isomer formed as deep red needles (0.72 g). $\Lambda_M = 84.4\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in water at 26 °C); $\epsilon_{max} = 91.6$ at 512 mμ, $\epsilon_{max} = 193.4$ at 360 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(C_2O_4)]ClO_4{\cdot}H_2O}$: C, 30.7; H, 6.4; N, 12.0; Cl, 7.6. Found: C, 30.4; H, 6.3; N, 12.0; Cl, 7.6.

trans-(C_{2h})-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2(\mathrm{CH_3CO_2})_2]\mathrm{ClO_4{\cdot}H_2O}$.** *cis*-($C_1$)-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$ (1.5 g) was suspended in glacial acetic acid (15 ml) and heated at 80 °C for 5 min. Ether (70 ml) was added to the clear red violet solution and, on cooling for $^1/_2$ h at 5 °C, the purple powder was collected and washed well with ether (1.3 g). The solid was taken up in hot methanol (15 ml) and then sodium perchlorate (3 g) in methanol (10 ml) was added to yield, upon cooling, very large dark red blocks of pure *trans*-(C_{2h}) isomer (0.70 g). These were collected and washed with methanol–ether (1:20, 20 ml) and with ether. The crystals effloresce on drying in air. The vacuum dried product was analyzed. $\Lambda_M = 81.3\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in methanol at 24 °C); $\epsilon_{max} = 59.7$ at 560 mμ, $\epsilon_{max} = 39.9$ at 470 mμ, $\epsilon_{max} = 89.7$ at 370 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(CH_3CO_2)_2]ClO_4{\cdot}H_2O}$: C, 33.7; H, 7.2; N, 11.2; Cl, 7.2. Found: C, 33.7; H, 7.2; N, 11.2; Cl, 7.7. The compound dissolves in 12 M HCl and the pure *trans*-(C_{2h})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$ is precipitated quantitatively.

trans-(C_{2v})-**$[\mathrm{Co}(R,S\text{-}\mathbf{dmtn})_2(\mathrm{CH_3CO_2})_2]\mathrm{ClO_4{\cdot}CH_3COOH}$.** *cis*-($C_2$)-*anti*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4}$ or *cis*-(C_2)-*syn*-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{CO_3}]\mathrm{ClO_4{\cdot}H_2O}$ (1.5 g) was heated in glacial acetic acid (30 ml) for $^1/_2$ h at 60 °C. Then methanol (4 ml) was added and the product was precipitated by the slow careful addition of ether (150 ml). The resulting deep purple needles (1.45 g) were collected and recrystallized from glacial acetic acid (27 ml) by the slow addition of ether; 0.92 g of the pure *trans*-(C_{2v}) isomer was collected as deep purple needles. The product effloresces on drying but a tightly held acetic acid of crystallization could not be removed even upon prolonged vacuum drying; its presence was quantitatively confirmed by NMR. $\Lambda_M = 77.2\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ (1×10^{-3} M in methanol at 24 °C); $\epsilon_{max} = 69.3$ at 560 mμ, $\epsilon_{max} = 43.5$ at 470 mμ, $\epsilon_{max} = 97.8$ at 370 mμ. Anal. Calcd for $[\mathrm{Co(C_5H_{14}N_2)_2(CH_3CO_2)_2]ClO_4{\cdot}CH_3COOH}$: C, 35.5; H, 6.9; N, 10.4; Cl, 6.6. Found: C, 35.5; H, 6.9; N, 10.3; Cl, 6.6.

When dissolved in 12 M HCl, the compound reacts to form *trans*-(C_{2v})-$[\mathrm{Co}(R,S\text{-dmtn})_2\mathrm{Cl_2}]\mathrm{ClO_4}$ quantitatively.

Equilibrations. The three carbonato isomers were dissolved in deuterated 3 M $\mathrm{HClO_4}$ at 30 °C, 0.1 g of complex in 0.6 ml of $\mathrm{DClO_4}$. After the effervescence had subsided, the NMR spectra were measured. Heating of each of the solutions at 90 °C for 1 h caused equilibration and the isomer ratios were analyzed by NMR at 30 °C. The following 60 MHz methyl proton resonances were observed: *cis*-(C_2)-*anti*-diaquo, δ 1.21, 1.31, 1.43, 1.54; *cis*-(C_1)-diaquo, δ 1.27, 1.38, 1.45, 1.49, 1.56, 1.60; *cis*-(C_2)-*syn*-diaquo, δ 1.30, 1.40, 1.50, 1.60.

Acknowledgment. This work was partly supported by the National Research Council of Canada.

Registry No. *trans*-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]Cl, 60045-92-3; *cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$, 59982-68-2; *cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]Cl, 60018-58-8; *cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$CO$_3$]Cl, 59982-69-3; *cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$, 60018-60-2; *trans*-(C_{2h})-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]ClO$_4$, 60045-94-5; *trans*-(C_{2v})-[Co(*R*,*S*-dmtn)$_2$Cl$_2$]ClO$_4$, 59982-71-7; *cis*-(C_2)-*syn*-[Co(*R*,*S*-dmtn)$_2$CO$_3$]ClO$_4$, 60018-62-4; *cis*-(C_1)-[Co(*R*,*S*-dmtn)$_2$Ox]Cl, 59982-72-8; *cis*-(C_2)-*anti*-[Co(*R*,*S*-dmtn)$_2$Ox]Cl, 60239-27-2; *cis*-(C_2)-*syn*-[Co(*R*,*S*-dmtn)$_2$Ox]ClO$_4$, 60045-96-7; *trans*-(C_{2h})-[Co(*R*,*S*-dmtn)$_2$(CH$_3$CO$_2$)$_2$]ClO$_4$, 59982-74-0; *trans*-(C_{2v})-[Co(*R*,*S*-dmtn)$_2$(CH$_3$CO$_2$)$_2$]ClO$_4$, 60018-64-6; ^{13}C, 14762-74-4.

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Competition between Ammonia and the Nitrite Ion as Leaving Groups in Cobalt(III) Complexes. 3. Hydrolysis of Nitroamminecobalt(III) Complexes

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Received April 6, 1976 AIC602590

A kinetic study is reported on the spontaneous aquation of nitroamminecobalt(III) complexes in weakly alkaline ammoniacal solutions using a spectrophotometric technique. The results could be interpreted by the assumption of a duality of mechanism for the aquation: loss of NH$_3$ or NO$_2^-$. Independent measurements of liberated NH$_3$ and NO$_2^-$ by way of gas-detecting electrodes have confirmed the photometric results. The determining factor for the mechanism in this class of complexes is suggested to be a trans-labilizing effect of the NO$_2^-$ group.

Introduction

In the preceding parts[1,2] of the present series on the competition between ammonia and the nitrite ion as leaving groups in cobalt(III) complexes a dual mechanism has been proposed for the spontaneous aquation of the nitroamminecobalt(III) complexes. It has been shown[1] that the spontaneous aquation of the nitropentaamminecobalt(III) ion involves as the first step the loss of the ammine group trans to the nitro group to form the *trans*-aquo(hydroxo)nitrotetraamminecobalt(III) ion. Further we have found indications[2] that the same mechanism is operative for some of the remaining nitroamminecobalt(III) complexes.

To test the proposed mechanism experiments are reported on the *cis*- and *trans*-dinitrotetraamminecobalt(III), the *mer*-trinitrotriamminecobalt(III), and the *trans*-tetranitrodiamminecobalt(III) complexes in the ammonia/ammonium perchlorate buffer system. The reason for choosing this medium is that it can stop further degradation of the complexes in alkaline solution after the first hydrolysis step. In this way the route via loss of an ammine group can be separated from other reaction paths.[3,4] Apart from the mechanistic criterion the aquation rate obtained by extrapolation from weakly alkaline conditions is more reliable than the one obtained from the extrapolation of acid-catalyzed rate values. In this series we have discussed this problem in relation to the fact that the values for the aquation of nitropentaamminecobalt(III)[5] and *trans*-tetranitrodiamminecobalt(III)[6] obtained as the acid-independent part of the rate in strongly acidic solutions are not in agreement with the values in slightly acidic to alkaline media.[1,2,7,8] As a probable cause for this discrepancy we have suggested the presence of a saturation effect with regard to the hydrogen ion concentration for the acid-catalyzed hydrolysis. The conclusion reached by a kinetic analysis of the hydrolysis rates in the ammonia buffers has been tested independently in a more direct way by monitoring the loss of ammonia and nitrite during the reaction with the help of gas-detecting electrodes.

Experimental Part

Chemicals. The preparation, recrystallization, and analysis of the compounds used has been described.[1,2]

In this paper previously introduced[2] abbreviations will be used: [Co(NH$_3$)$_5$(NO$_2$)][ClO$_4$]$_2$, A5N; *cis*-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$, *cis*-A4N2; *trans*-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$, *trans*-A4N2; *mer*-[Co(NH$_3$)$_3$(NO$_2$)$_3$], *mer*-A3N3; *trans*-K[Co(NH$_3$)$_2$(NO$_2$)$_4$], *trans*-A2N4.

The other chemicals used were of reagent grade.

Spectrophotometric Measurements of the Reaction Rate. The solutions were made up at room temperature from ammonia/ammonium perchlorate buffers at a constant ionic strength (1.00 M) obtained by adding sodium perchlorate. Concentrations will refer to the temperature at which the reaction was followed. The reacting solutions were monitored spectrophotometrically, using the procedure described in our study of the nitropentaamminecobalt(III) ion.[1] The reactions are not photosensitive as far as the amount of irradiation inherent in the photometric measurements is concerned.

Product Analysis with Gas-Detecting Electrodes. A direct determination of the concentrations of the leaving groups was performed with a nitrogen oxide electrode (Model 95-46, Orion) and an ammonia probe (Model 8002-2, E.I.L.) connected to an Electrofact 36200 pH meter. The pH was measured with Electrofact 7G111 or 7G112 glass electrodes and a Hg/HgSO$_4$/Na$_2$SO$_4$ reference electrode (E.I.L. 33-1352-330).

Solutions were prepared by dissolving the required amount of the complex (concentration 0.01 M) in a sodium perchlorate solution at a fixed ionic strength (0.10 M). The use of this value for the ionic strength is imperative from the composition of the internal solutions of the electrodes which is about 0.10 M. The neutral (unbuffered) perchlorate solutions were brought into a darkened thermostated bath and allowed to equilibrate to the bath temperature before addition of the complex. At appropriate time intervals aliquot portions of the reacting solution were withdrawn and cooled in ice to quench the