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Two Isomers of the *trans*-Dichlorobis((2*S*)-2-amino-4-azahexane)cobalt(III) Ion. Isolation, Structural Assignment, and Circular Dichroism

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Two geometric isomers of *trans*-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ (trans,trans (*RR*) and trans,trans (*SS*)) were prepared and isolated. The trans,trans configuration of the *RR* isomer is determined from the ^1H NMR spectrum of *trans,trans*(*RR*)-chloronitro complexes. The trans,trans configuration and the absolute configuration of asymmetric nitrogens are estimated from ^1H NMR and CD spectra. The CD spectra of these two isomers are reported. The calculated vicinal effects of *R* and *S* nitrogens are significantly different in sign from each other in the visible absorption regions. The CD spectrum of the *SS* isomer is mutarotated in methanol and finally coincided with that of the *RR* isomer. This result means that the *S* asymmetric nitrogen of the thermodynamically less stable *SS* isomer, which has two axial *N*-ethyl groups, is inverted. The precursor of the SS isomer, which is stereospecifically derived from the cis complex, is discussed.

In recent years, much attention has been devoted to the stereochemistry of transition metal complexes containing N-substituted 1,2-diamines, i.e., *N*-methylethylenediamine (=*N*-Meen),[1-6] (2*S*)-1-amino-2-methyl-3-azabutane (=N_1-Me-*S*-pn), (2*S*)-2-amino-4-azapentane (=N_2-Me-*S*-pn),[7,8] and *N,N'*-dimethylethylenediamine(=*N,N'*-Me_2en).[9,10] In these diamine complexes there are two stereochemically important interactions, which must be considered separately in examining individual complexes. One is interligand steric interactions which are evidently revealed in determining the geometry of dianionobis(diamine)cobalt(III) complexes. Only the trans,trans isomer could be obtained for the dichloro- and dinitrocobalt(III) complexes with *N*-Meen[2,3] and N_2-Me-*S*-pn.[7] The steric repulsions between the *N*-methyl groups and adjacent ligands (diamine or anionic ligands) would be the main reason for the trans,trans isomer's being the sole product.

The second interaction has intraligand features and occurs only for the diamines with C and N substituents such as N_2-Me-*S*-pn. It has been established that 1,2-diamines substituted at the C atom with methyl[11,12] or phenyl[13] groups take the restricted gauche conformation in which the substituent(s) adopts (adopt) an equatorial disposition. The N_2-Me-*S*-pn chelate rings were considered to be fixed in a similar manner to the δ conformation with an equatorial methyl group.[7] When this is the case, the orientation of *N*-methyl group will be such that the total steric repulsions are minimized. In the *trans,trans*-$[Co(N_2\text{-Me-}S\text{-pn})_2X_2]^+$ ($X^- = Cl^-, NO_2^-$) complexes, both *N*-methyl and *C*-methyl groups locate equatorially.[7]

A recent study indicates that for planar Pt(II) complexes two diastereomeric isomers which differ only in the orientation of the *N*-methyl groups coexist in equilibria.[8] For the Pt(IV) complexes containing one N_2-Me-*S*-pn chelate, the distribution of the isomer with an equatorial and that with an axial *N*-methyl group vary considerably with change of unidentate from NH_3 to Cl^-.[8] This suggests that certain small modifications in the N-substituted diamine will result in significant changes of the stereoisomerism of metal complexes.

Basolo tried to prepare the *trans*-dichloro complexes with some *N*-alkyl-substituted ethylenediamines by the air oxidation method and failed to obtain the complexes of *N*-isopropyl- and *N*-*n*-butylethylenediamine.[14] This suggests that changes in the chain length and/or bulkiness of the N-substituents result in significant influences on the stabilities of complexes. We consider that it is of interest to examine the intraligand steric effects of *N*-alkyl groups other than the methyl, along with the interligand effects. Hence, the stereoisomerism of cobalt(III) complexes with (2*S*)-2-amino-4-azahexane (abbreviated as N_2-Et-*S*-pn) was studied in some detail.

Experimental Section

(2*S*)-2-Amino-4-azahexane (N_2-Et-*S*-pn). L-Alanine ethylamide was obtained by the slightly modified method described for the L-alanine methylamide by Bergel and Peutherer.[15] N_2-Et-*S*-pn was obtained from L-alanine ethylamide by a similar manner to N_2-Me-*S*-pn in our previous work.[7]

***trans,trans*(*RR*)-$[Co(NO_2)_2(N_2\text{-Et-}S\text{-pn})_2]ClO_4$.** To an aqueous solution of $Na_3[Co(NO_2)_6]$ (2.02 g in 15 ml of H_2O) was added N_2-Et-*S*-pn (1.02 g). The solution stood at 60 °C for 1 h on a water bath, and then solid sodium perchlorate (5 g) was added and dissolved. Yellow crystals of *trans*-dinitro complexes appeared and were filtered off, washed with small volumes of water, alcohol, and ether, and air-dried; yield 1.36 g. Anal. Calcd: C, 31.75; H, 6.92; N, 18.51. Found: C, 31.35; H, 7.38; N, 18.64.

***trans,trans*-$[CoCl(NO_2)(N_2\text{-Et-}S\text{-pn})_2]ClO_4$.** *trans,trans*(*RR*)-$[Co(NO_2)_2(N_2\text{-Et-}S\text{-pn})_2]ClO_4$ (1.0 g) was dissolved in concentrated hydrochloric acid (20 ml) and warmed on a water bath at 40 °C for 3 h. The color of the solution turned from yellow to red, and red crystals began to precipitate. The crystals were filtered off, washed with small volumes of water, alcohol, and ether, and dried under reduced pressure; yield 0.35 g.

***trans,trans*(*RR*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]ClO_4$ (I).** *trans,trans*-$[CoCl(NO_2)(N_2\text{-Et-}S\text{-pn})_2]ClO_4$ (1.0 g) was dissolved in concentrated hydrochloric acid (30 ml) and heated on a boiling water bath at 95 °C. After the color of the solution turned from red to deep green, it was evaporated gradually until green crystals began to precipitate. The green crystals were filtered off, washed with small volumes of water, alcohol, and ether, and dried under reduced pressure. The crystals were recrystalized from a small volume of concentrated hydrochloric acid; yield 0.26 g. Anal. Calcd: C, 27.70; H, 6.51; N, 12.92. Found: C, 27.65; H, 6.83; N, 13.36.

A Mixture of *trans,trans*(*RR*)- and *trans,trans*(*SS*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]ClO_4$ (II). To an aqueous solution of $CoCl_2{\cdot}6H_2O$ (1.19 g in 25 ml of H_2O) was added 1.02 g of N_2-Et-*S*-pn and the solution was aerated for 6 h with carbon dioxide free air. After 20 ml of concentrated hydrochloric acid was added, the solution was concentrated to about 10 ml on a steam bath. Perchloric acid (60%, 3 ml) was added, and the green crystals formed were filtered off, washed with small volumes of cold water, ethanol, and ether, and dried under reduced pressure. The product was recrystallized from methanol; yield 0.89 g.

***trans,trans*(*RR*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]Cl$ (III).** A mixture of $CoCl_2{\cdot}6H_2O$ (2.38 g in 30 ml of H_2O) and N_2-Et-*S*-pn (2.04 g) was vigorously aerated for 6 h, with carbon dioxide free air. Concentrated hydrochloric acid (30 ml) was added to the red solution, and the mixture was warmed on a boiling water bath until the color of the solution changed from red to deep green. The solution was evaporated almost to dryness on a boiling water bath, occasionally triturating with a small volume of water. When green crystals began to precipitate, the heating was stopped and the solution was allowed to stand overnight at room temperature. The green crystals were filtered off and washed with small volumes of cold water, ethanol, and ether; yield 0.40 g. Anal. Calcd: C, 32.49; H, 8.08; N, 15.13. Found: C, 32.05; H, 7.64; N, 15.16.

The violet filtrate was reserved to obtain the following cis compounds.

***cis*-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]ClO_4$.** To the violet filtrate of *trans,*-*trans*-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]Cl$ (III), perchloric acid (60%, 1 ml) and sodium perchlorate (2 g) were added, successively, and the mixture

Table I. Absorption and CD Spectral Data

	Absorption		CD	
	$10^{-3}\,\tilde{\nu}$, cm^{-1}	ϵ_{max}	$10^{-3}\,\tilde{\nu}$, cm^{-1}	$\Delta\epsilon_{max}$
trans,trans(*RR*)-[Co$(NO_2)_2$-(N_2-Me-*S*-pn$)_2$]ClO_4[a]	22.5	199	21.65	+0.92
			24.39	−0.10
	28.8	3500	27.78	+2.02
trans,trans(*RR*)-[Co$(NO_2)_2$-(N_2-Et-*S*-pn$)_2$]ClO_4	22.5	220	19.7	−0.17
			21.8	+0.88
trans,trans(*RR*)-[$CoCl_2$-(N_2-Me-*S*-pn$)_2$]ClO_4[a]	15.9	37.5	14.93	+0.05
			16.95	−0.09
	21.1	29.6	21.1	−0.51
trans,trans(*RR*)-[$CoCl_2$-(N_2-Et-*S*-pn$)_2$]ClO_4	15.8	38.0	15.0	+0.17
	20.8	33.4	20.6	−0.77
	25.2	63.8	24.5	+0.23
trans,trans(*SS*)-[$CoCl_2$-(N_2-Et-*S*-pn$)_2$]$ClO_4\cdot$ CH_3OH	15.8	38.9	16.3	−1.08
	20.6	35.5	20.3	+0.52
	25.0	55.0	26.3	+0.34

[a] M. Saburi et al., *Inorg. Chem.*, 9, 1476 (1970).

was allowed to stand overnight. A mixture of green and violet salts was filtered off (3.70 g). Since the violet perchlorate salt was highly soluble in ethanol, the mixture was washed repeatedly with ethanol, until the color of the extract turned from violet to green. The ethanolic washings were combined and evaporated to dryness on a rotary evaporator at room temperature. The violet residue was again extracted with a small volume of ethanol and insoluble green perchlorates were removed. This procedure was repeated two or three times until the contamination of the green salts could not be acknowledged. From the final ethanolic extract of violet complexes (*cis*-dichloro isomers), we could obtain no crystalline compounds, but its absorption spectrum showed that the solution contained only *cis*-dichloro complexes.

A Mixture of *trans,trans*(*RR*)- and *trans,trans*(*SS*)-[$CoCl_2$(N_2-Et-*S*-pn$)_2$]ClO_4 (IV). Several fractions of green complexes obtained as residues of the extraction of *cis*-dichloro isomer were combined and recrystallized from a small volume of methanol; yield 0.77 g.

***trans,trans*(*SS*)-[$CoCl_2$(N_2-Et-*S*-pn$)_2$]$ClO_4\cdot CH_3OH$ (V).** The ethanolic extract described above was evaporated to dryness at room temperature on a rotary evaporator, the residue was dissolved in methanol (10 ml), and then a drop of methanol saturated by dry hydrogen chloride gas was added. The solution was refluxed until the color of the solution turned from violet to green. Green needlelike crystals were obtained as the perchlorate after the solution stood overnight at room temperature; yield 0.13 g. Anal. Calcd: C, 28.37; H, 6.92; N, 12.03. Found: C, 28.41; H, 7.09; N, 12.08.

A Mixture of *trans,trans*(*RR*)- and *trans,trans*(*SS*)-[$CoCl_2$(N_2-Et-*S*-pn$)_2$]ClO_4 (Preparation from $Na_3[Co(CO_3)_3]$). To a cold suspension of $Na_3[Co(CO_3)_3]\cdot 3H_2O$[16] (1.54 g in 30 ml of H_2O) was added N_2-Et-*S*-pn (1.02 g) and the mixture was mechanically stirred for 10 min in an ice-cold bath. Then the temperature was raised gradually to 70 °C. After the color of the solution turned violet, the solution was concentrated on a rotary evaporator to about 10 ml. After the addition of concentrated hydrochloric acid (30 ml), the solution was concentrated to about 10 ml on a water bath at 70 °C and 60% perchloric acid (10 ml) was added. Green crystals were obtained after the solution stood in a refrigerator overnight; yield 0.65 g (30%). These compounds were not purified further and their absorption and CD spectra were measured.

The syntheses of the complexes in this work are illustrated in Scheme I.

Spectral Measurements. Electronic absorption spectra were recorded on a Shimazu MPS-50L spectrophotometer for methanol solutions at room temperature.

Circular dichroism (CD) spectra were recorded on a Jasco J-20 spectropolarimeter for methanol solution at room temperature. Proton magnetic resonance spectra (^1H NMR) were recorded on a JEOL PS-100 (100 MHz) spectrometer for CD_3OD solutions using TMS or DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as the internal standard.

Results and Discussion

***trans,trans*(*RR*)-[$CoCl_2$(N_2-Et-*S*-pn$)_2$$]^+$ and -[Co$(NO_2)_2$(N_2-Et-*S*-pn$)_2$$]^+$ Ions.** The dinitrocobalt(III) complex of N_2-Et-*S*-pn, [Co$(NO_2)_2$(N_2-Et-*S*-pn$)_2$$]^+$, was prepared from $Na_3[Co(NO_2)_6]$ and N_2-Et-*S*-pn and isolated as the perchlorate. The dinitro complex showed absorption maxima at 444 and 352 nm, which indicates that the complex has the trans configuration with regard to the nitro groups (Table I). It has been recognized that $[Co(N)_4(NO_2)_2]^+$ type complexes exhibit λ_{max} at about 330 nm for the cis isomers and at about 350 nm for the trans isomers.[3,7]

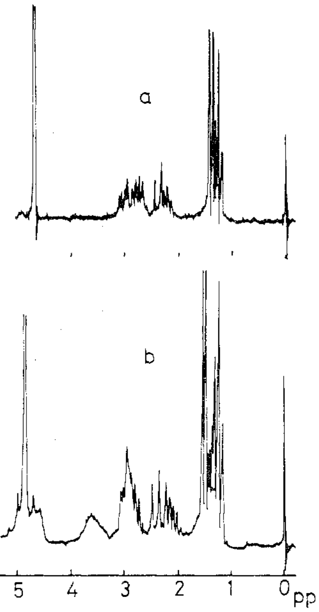


Figure 1. The 100-MHz ^1H NMR spectra of trans,trans (*RR*) complexes: (a) [Co$(NO_2)_2$(N_2-Et-*S*-pn$)_2$$]^+$ in D_2O; (b) [CoCl-(NO_2)(N_2-Et-*S*-pn$)_2$$]^+$ in 0.1 N DCl.

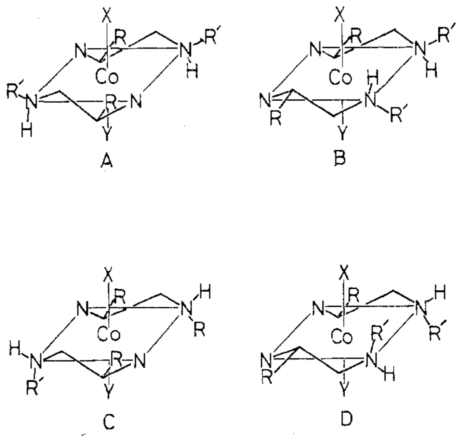
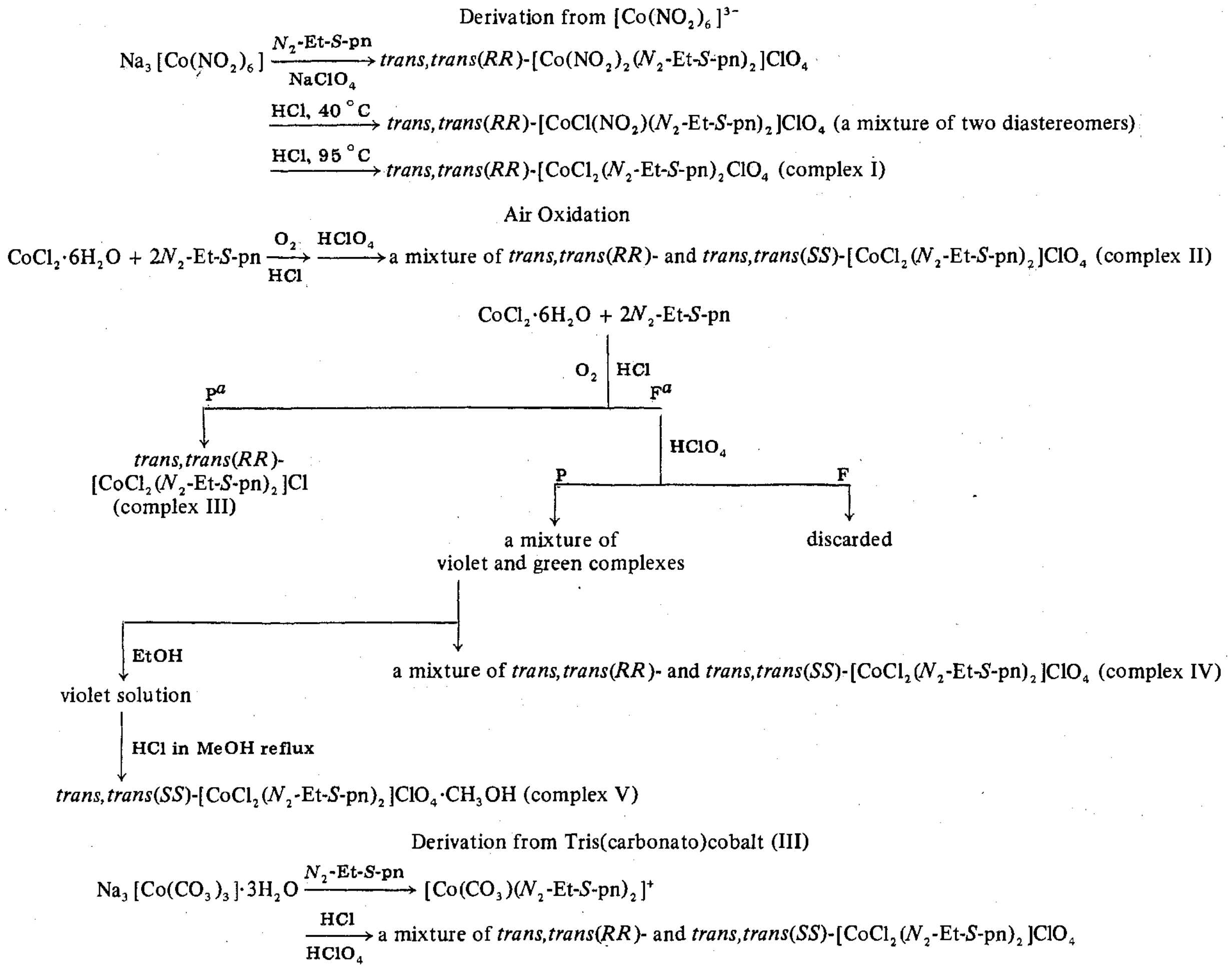


Figure 2. Possible structures of *trans*-[CoXY(N_2-Et-*S*-pn$)_2$$]^+$ (R = CH_3, R′ = C_2H_5): A, trans,trans (*RR*); B, trans,cis (*RR*); C, trans,trans (*SS*); D, trans,cis (*SS*).

The 100-MHz ^1H NMR spectrum of the dinitro complex (Figure 1a) shows only one triplet and doublet assignable to the methyl protons of the *N*-methyl and *C*-methyl groups, respectively. Therefore, both N_2-Et-*S*-pn chelates should be in the same chemical environment and have the same configuration for the asymmetric N centers and the chelate ring conformations. There are four possible structures which satisfy the ^1H NMR spectral features, as illustrated in Figure 2. In the trans,trans (*RR*)[17] and trans,cis (*RR*)[17] isomers the *N*-ethyl groups adopt the equatorial orientation, whereas in the trans,trans (*SS*) and trans,cis (*SS*) forms they are disposed in the axial orientation. The difference in the secondary N configuration should reflect on the CD pattern of the complexes.

The CD curve of the *trans*-[Co$(NO_2)_2$(N_2-Et-*S*-*pn*$)_2$$]^+$ is very similar to that of *trans,trans*(*RR*)-[Co$(NO_2)_2$(N_2-Me-

Scheme I. Synthesis of *trans*-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ Complexes



[a] P = precipitate; F = filtrate.

S-pn)$_2]^+$.[7] Since the contribution of the asymmetric secondary N centers to the CD was considered not to vary significantly due to the change of the N substituents (vide infra), the similarity in CD suggests that the absolute configuration of the two N centers is the same, i.e., *RR*.

The dinitro complex of N_2-Et-S-pn was transformed into the chloronitro form under acidic conditions necessary to retain the secondary N configuration. When two anionic ligands are different as in the chloronitro complex, the trans,trans (*RR*) form should yield two diastereomeric isomers ($X^- = Cl^-$, $Y^- = NO_2^-$ and $X^- = NO_2^-$, $Y^- = Cl^-$ in Figure 2A). The yield of these isomers should be generally different. In each isomer, the two diamine chelates are magnetically equivalent. Therefore, the ^{1}H NMR spectrum of the *trans,trans*(*RR*)-chloronitro complex is expected to show two kinds of triplets (N-ethyl) and doublets (C-methyl) with different intensities.

On the other hand, the trans,cis (*RR*) form should result in the single isomeric form ($X^- = Cl^-$, $Y^- = NO_2^-$ and $X^- = NO_2^-$, $Y^- = Cl^-$ are identical in Figure 2B), but the two chelates are not magnetically equivalent. Hence, the ^{1}H NMR spectrum for this isomer would give rise to two N-ethyl and C-methyl resonances with equal intensity.

The ^{1}H NMR spectrum of the chloronitro complex (Figure 1b) shows a pair of triplets and doublets with unequal intensities, indicating the trans,trans (*RR*) configuration. It is obvious that the parent dinitro complex also has the trans,trans (*RR*) configuration (Figure 2A, $X^- = Y^- = NO_2^-$). The dichlorocobalt(III) complex obtained by a reaction of the chloronitro complex with concentrated hydrochloric acid and designated as complex I should have the same configuration, since no structural change was expected for the above reaction.[3,7] The CD and ^{1}H NMR spectra of complex I are shown

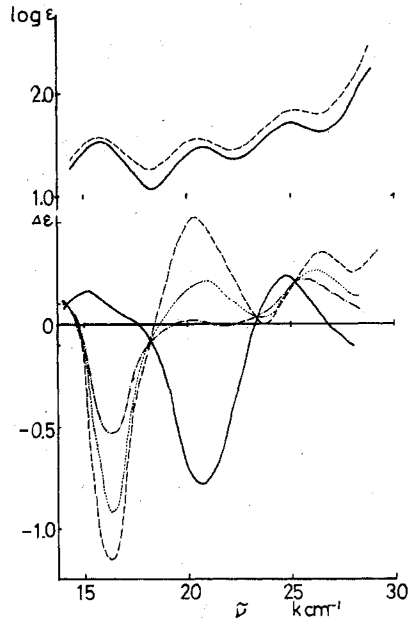


Figure 3. Visible absorption and CD spectra of *trans,trans*-(*RR*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ (I = III) (—) and of *trans,trans*-(*SS*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ (V) (- - -) and CD spectra of complex II (– · –) and complex IV (· · · ·).

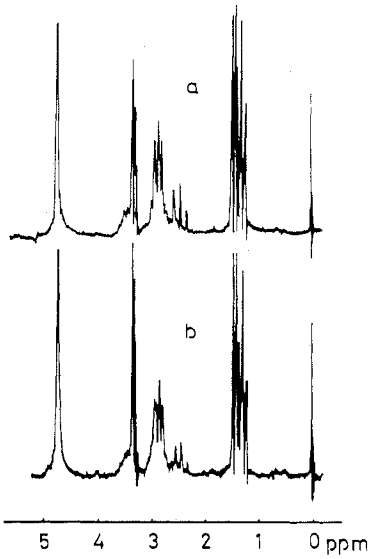


Figure 4. The 100-MHz ^{1}H NMR spectra of *trans*-dichloro isomers: (a) *trans,trans*(*RR*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ in CD_3OD; (b) *trans,trans*(*SS*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ in CD_3OD.

in Figures 3 and 4, respectively.

***trans,trans*(*SS*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ Ion.** It was found unexpectedly that the *trans*-dichloro complex of N_2-Et-*S*-pn obtained by a typical air oxidation procedure and designated as complex II gave a CD curve remarkably different from that of the trans,trans (*RR*) isomer, but the visible absorption spectra of these complexes are very similar. The 100-MHz ^{1}H NMR spectrum of complex II was more complicated than that of the trans,trans (*RR*) complex, with two kinds of triplets and doublets for the methyl resonances. One set of triplet and doublet signals was identical with that of the trans,trans (*RR*) isomer. This suggests, therefore, that at least one diastereomeric isomer other than the trans,trans (*RR*) form should exist for the *trans*-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$ ion.

When a solution of air oxidation products mixed with concentrated hydrochloric acid was carefully evaporated, green crystals were separated out in the chloride form (designated as complex III). This complex gave ^{1}H NMR, visible absorption, and CD spectra strictly identical with those of the *trans,trans*(*RR*)-dichloro perchlorate (complex I). It is clear that complex III can be assigned as *trans,trans*(*RR*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]Cl$.

From the filtrate of complex III was recovered a mixture of green and violet perchlorate crystals. These complexes were separated by utilizing these different solubilities in ethanol. The violet crystals could be extracted with ethanol because of their higher solubility. The ethanol extracts were concentrated to give a glassy violet residue, which was hard to crystallize from ethanol or methanol solution. Several fractions of green complex recovered during the separation and purification of violet complex were combined and recrystallized from methanol (designated as complex IV).

The violet residue from the ethanol extracts was considered to be composed of *cis*-dichloro complexes based on its absorption maxima at 540 and 390 nm. The color of a methanol solution of this residue, acidified with hydrogen chloride gas, turned green under reflux and green needlelike crystals (designated as complex V) were obtained. The ^{1}H NMR spectrum of complex V exhibited one triplet and doublet for the methyl resonances as shown in Figure 4b. This means that the complex V consisted of a single species, in which the two chelate rings take identical configurations. The CD curve of complex V (Figure 3) is markedly different from that of the trans,trans (*RR*) isomer, indicating that these *trans*-dichloro complexes are diastereomeric to each other. Furthermore, it is noteworthy that the CD curves of complexes II and IV pass through the isodichroic points (684, 546, 427, and 398 nm) of complexes I and V. This means that both II and IV are isomeric mixtures of I (trans,trans (*RR*)) and V (trans, trans (*SS*)), although the relative ratios of I and V are not equal.

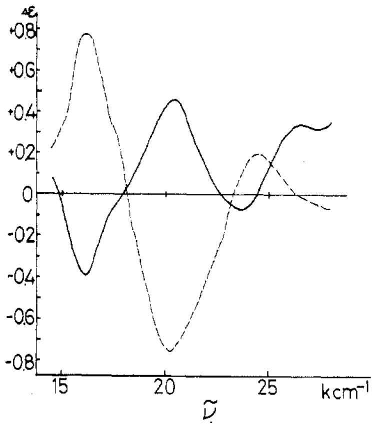


Figure 5. Calculated vicinal effects of *R* and *S* nitrogens in *trans,trans*(*RR*)- and *trans,trans*(*SS*)-$[CoCl_2(N_2\text{-Et-}S\text{-pn})_2]^+$: *R*, - - -; *S*, —.

There are three structures possible for complex V, which meet the requirements from the ^{1}H NMR data, i.e., trans,trans (*SS*), trans,cis (*RR*), and trans,cis (*SS*) (Figure 2B–D, $X^- = Y^- = Cl^-$). It was observed that the CD curve of complex V in basic methanol changed to the same with the trans,trans (*RR*) isomer. The stereochemical conversion from trans,cis to trans,trans geometry would be improbable even in basic methanol. Hence, the most probable structure for complex V is the trans,trans (*SS*) configuration. The changes from trans,trans (*SS*) to trans,trans (*RR*) and vice versa in methanol are acceptable; the thermodynamically less stable isomer, trans,trans (*SS*), with axial *N*-ethyl groups, turns into the more stable isomer, trans,trans (*RR*). A tendency to prefer the isomers having the equatorial N substituent to those having the axial N substituent was noticed for octahedral Pt(IV) complexes of N_2-Me-*S*-pn.[8]

Circular Dichroism. The CD spectra in d–d transition regions of the transition metal complexes are considered to be constituted from three effects,[18] namely, the configurational, the conformational, and the vicinal effects. For the *trans*-dianiono complexes, only the latter two effects contribute to the optical activity. Further, it has been acknowledged that these effects are additive qualitatively in CD spectra.[19] When the conformations of the chelate rings are presumable as in the N-substituted pn complexes, the absolute configuration of asymmetric nitrogens can be estimated from the vicinal contributions evaluated from the difference in CD curves between the complex with N-substituted ligand and the corresponding complex with nonsubstituted ligand.

The difference in the CD curves between *trans,trans*-$[CoCl_2(N_2\text{-Me-}S\text{-pn})_2]^+$ and *trans*-$[CoCl_2(S\text{-pn})_2]^+$, in both of which the conformations of the chelate rings are considered to be fixed to δ, has been caused by the contribution of the asymmetric *R* nitrogen with the *N*-methyl group in an equatorial position.[18]

The first absorption band of the cobalt(III) complex in an octahedral ligand field is $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h), which splits into two components in a tetragonal field, $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ (D_{4h}). In the case of *trans*-$[CoCl_2N_4]^+$, these two bands are observed about 16 000 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$) and 21 000 cm^{-1} ($^1A_{1g} \rightarrow {}^1A_{2g}$). The calculated vicinal effects of asymmetric *R* nitrogens were shown to have a positive and a negative maximum for the above transition, respectively.

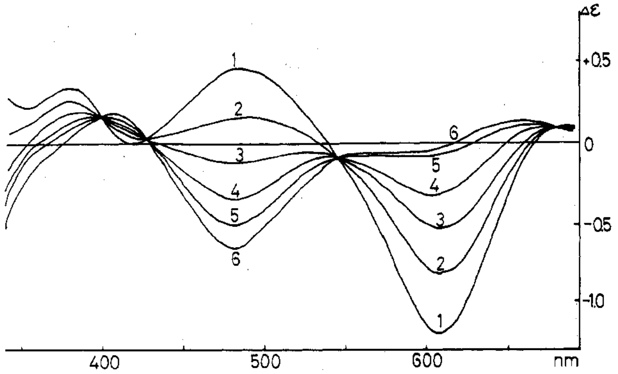


Figure 6. Mutarotation of CD spectra of *trans,trans(SS)*-[$CoCl_2$(N_2-Et-*S*-pn)$_2$]ClO_4 in CH_3OH after (1) 0, (2) 3 h, (3) 9 h, (4) 24 h, (5) 2 days, and (6) 10 days (at 40 °C).

The calculated vicinal effects of *R* and *S* nitrogens of *trans,trans(RR)*- and *trans,trans(SS)*-[$CoCl_2$(N_2-Et-*S*-pn)$_2$]$^+$, shown in Figure 5, apparently have similar patterns and are opposite in sign to each other in the first absorption regions. The contribution of the *R* nitrogen shows a positive and a negative maximum for ^1E_g and $^1A_{2g}$ transitions, respectively, as in the case of the N_2-Me-*S*-pn complexes. On the other hand, the *S* nitrogen shows a negative and a positive maximum.

In the methanol solutions, the CD of the trans,trans (*SS*) isomer changed slowly (at 40 °C, $\tau_{1/2}$ = 7.5 h) with four isodichroic points at 684, 546, 427, and 398 nm and finally coincided with the CD of trans,trans (*RR*) isomer (Figure 6). The observation of these isodichroic points means that only two isomers, trans,trans (*SS*) and trans,trans (*RR*), exist during the inversion of two asymmetric nitrogens; the formation of the intermediate trans,trans (*RS*) form, in which one of the two *S* nitrogens has inverted, is practically negligible. In other words, two asymmetric *S* nitrogens of the trans,trans (*SS*) isomer inverted simultaneously.

Precursors of *trans,trans(SS)*-[$CoCl_2$(N_2-Et-*S*-pn)$_2$]$^+$. As the *trans*-dichloro complex with axial *N*-ethyl groups was stereospecifically derived from the purple dichloro complex, probably a *cis*-dichloro isomer, through cis → trans isomerization, it is postulated that the cis forms are the precursors of this complex. In the trans forms, the axial ethyl groups appear thermodynamically less stable than equatorial ones due to steric repulsions between the apical ligands and the ethyl groups; this is supported by the complete inversion of *S* (axial) nitrogens in methanol solutions. It is reasonable to suppose that in *trans*-dichloro complexes derived from [$Co(NO_2)_6$]$^{3-}$ in moderately basic conditions, the *N*-ethyl groups orient to the most preferred configuration, i.e., *R*. If the cis forms are the precursors for the *trans*-dichloro complex, the absolute configuration of the asymmetric nitrogens could be *R* and/or *S*, though it is difficult to estimate the differences of the steric repulsions between *N*-ethyl groups and others in a cis geometry. In any case it is probable that the equatorial *N*-ethyl groups are not always the more stable. It has been shown by Yano, et al., that Λ-[$Co(C_2O_4)(Me_2en)_2$]ClO_4 has two axial *N*-methyl groups.[20] It is assumed that the axial *N*-ethyl groups of complex V were formed in the cis precursor and were maintained during the cis → trans isomerization. Hence, we prepared *trans*-dichloro complexes from carbonato complexes to illustrate this assumption.

Tris(carbonato)cobalt(III), $Na_3[Co(CO_3)_3]$ (1 mol), was converted to carbonatobis(N_2-Et-*S*-pn) complexes in aqueous solution by the addition of N_2-Et-*S*-pn (2 mol), and the carbonato ion was replaced by Cl^- by adding hydrochloric acid with the evolution of gaseous carbon dioxide. The color of the solution was immediately turned from red to violet and we obtained green precipitates from this violet solution by adding ClO_4^- ion. It is presumed that *cis*-dichloro complexes (violet) were produced, followed by cis → trans isomerization and precipitation of the trans (green) complexes.

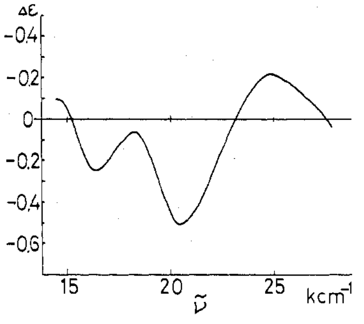


Figure 7. CD spectrum of *trans,trans*-[$CoCl_2$(N_2-Et-*S*-pn)$_2$]$^+$ derived from the tris(carbonato)cobalt(III) complex. The compound is a mixture of trans,trans (*RR*) and trans,trans (*SS*).

The CD and the absorption spectra of the *trans*-dichloro complexes are shown in Figure 7. Since the CD spectrum has the isodichroic points as well as the spectra of II and IV, we considered that these were also the mixture of I (*RR*) and V (*SS*). These results supported strongly that cis forms were the precursors of the *trans*-dichloro complex with the axial *N*-ethyl groups (complex V).

Registry No. I, 61483-15-6; II, 61521-18-4; III, 61505-84-8; *trans,trans(RR)*-[$Co(NO_2)_2$(N_2-Et-*S*-pn)$_2$]ClO_4, 61483-17-8; *trans,trans*-[$CoCl(NO_2)$(N_2-Et-*S*-pn)$_2$]ClO_4, 61483-19-0; *trans,trans(SS)*-[$CoCl_2$(N_2-Et-*S*-pn)$_2$]ClO_4, 61521-20-8; $Na_3[Co(NO_2)_6]$, 13600-98-1; $Na_3[Co(CO_3)_3]$, 23311-39-9.

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(17) trans,trans (trans,cis) means that the complex has the trans configuration with regard to the monodentate ligands and has the trans (cis) configuration with regard to the secondary nitrogen. *RR* (*SS*) means that the absolute configuration of secondary nitrogen is *R* (*S*).
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