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THE STEREOCHEMISTRY OF THE DICHLOROCOBALT(III) COMPLEXES WITH (2*S*,5*S*,9*S*)- AND (2*S*,5*R*,9*S*)-TRIMETHYLTRIETHYLENETETRAAMINES

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Abstract—Dichlorocobalt(III) complexes of (2*S*,5*S*,9*S*)-trimethyltriethylenetetraamine (L_1) and (2*S*,5*R*,9*S*)-trimethyltriethylenetetraamine (L_2) have been prepared. Both L_1 and L_2 coordinate to the cobalt(III) ion to give three isomers: Λ-*cis*-α, Δ-*cis*-β, *trans* isomers for L_1 and Δ-*cis*-α, Δ-*cis*-β, *trans* isomers for L_2. Each of the *trans*-dichloro complexes of the two ligands have been isomerized stereospecifically to the *cis*-α-dichloro complex in methanol, and each of the *cis*-α-dichloro complexes stereospecifically to the *trans*-diaqua complex in water. Both the geometrical and optical inversions took place at the same time in the observed stereospecific isomerizations.

Stereochemical studies of the cobalt(III) complexes of the optically active flexible tetraamines have shown the importance of the asymmetric carbon in the stereospecific coordination of the ligands.[1-3] The remarkable effect of the asymmetric substituent on the stereochemistry of the cobalt(III) complexes of those tetraamines is more pronounced in the dichloro complexes than in other forms, such as the dinitro complexes.[4-6]

This paper describes the preparation and stereochemistry of dichloro cobalt(III) complexes containing (2*S*,5*S*,9*S*)-trimethyltriethylenetetraamine (L_1) and (2*S*,5*R*,9*S*)-trimethyltriethylenetetraamine (L_2). Yoshikawa *et al.*[6] have reported the preparation of dinitro cobalt(III) complexes of L_1 and L_2 in which only the Δ-*cis*-β isomer was obtained for L_1, while both Λ-*cis*-α and Δ-*cis*-β isomers were obtained for L_2. It is interesting to see which geometrical and optical isomers will be formed in the dichloro cobalt(III) complexes of L_1 and L_2. It will be shown here that, quite different from the dinitro complexes,[6] the optically active *cis*-α-, *cis*-β- and *trans*-dichloro complexes are obtained for each of L_1 and L_2. Interesting stereospecific geometrical isomerizations have also been observed in this work: each *trans*-dichloro complex of L_1 and L_2 is isomerized stereospecifically to the *cis*-α-dichloro complex in methanol, while each *cis*-α-dichloro complex of L_1 and L_2 isomerizes stereospecifically to the *trans*-diaqua complex in water.

EXPERIMENTAL

Preparations of the following compounds are described in this section.

N,N′-*Bis*(S-*phthaloylalanyl*)-S-*propylenediamine*

A solution of *S*-propylenediamine[7] (12.50 g, 0.1686 mol) and $NaHCO_3$ (29.46 g) in water (400 cm^3) was cooled in an ice-salt bath. To this ice-cold mixture was slowly added *S*-phthaloylalanyl chloride[8] (79.60 g, 0.3350 mol) dissolved in dry *p*-dioxane (100 cm^3). The reaction and formation of solid product was accompanied by much foaming. After the reaction was completed, HCl (2 M) was added to decompose the excess $NaHCO_3$. The precipitate was filtered off and recrystallized from methanol–water (1:2 by volume), yield 66.7 g (85%).

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N,N′-*bis*(S-*alanyl*)-S-*propylenediamine dichloride*

HCl (6 M, 400 cm^3) was added to *N,N′*-bis(*S*-phthaloylalanyl)-*S*-propylenediamine (65 g, 0.3164 mol) in a 1 dm^3 flask, and the mixture was refluxed for 4 h at 130–140°C with stirring. After cooling to room temperature, the reaction mixture was stored in a refrigerator for 1 day. The precipitate was filtered off, and the filterate was concentrated under reduced pressure to give a pale yellow oil. Water (30 cm^3) was added to the viscous oil, and the resulting solution was washed with three 10-cm^3 portions of chloroform. The aqueous phase was concentrated under reduced pressure and dried *in vacuo*. The pale yellow product was collected, yield 37.0 g (94%).

(2S,5S,9S)-*Trimethyltriethylenetetraamine* (L$_1$) *tetrahydrochloride*, $L_1 \cdot 4HCl$

A suspension of $LiAlH_4$ (19.0 g) and anhydrous THF (500 cm^3) was prepared in a 2 dm^3 three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel. This apparatus was flushed with dry nitrogen, and a dry nitrogen atmosphere was kept inside the apparatus throughout the reaction. The suspension was cooled in an ice-salt bath, and *N,N′*-bis(*S*-alanyl)-*S*-propylenediamine dihydrochloride (35.73 g, 0.1235 mol) dissolved in anhydrous THF (100 cm^3) was carefully added with vigorous stirring at ice-salt temperature. The reaction mixture was slowly refluxed and stirred for 24 h. It was then cooled, and water (45 cm^3) diluted with anhydrous THF (200 cm^3) was cautiously added with vigorous stirring in an ice-salt bath. The resultant slurry was filtered off and washed with a small volume of THF. The residue was extracted three times with boiling THF. The combined THF filterate and extracts were concentrated under reduced pressure to give a pale yellow oil. The oil was dissolved in absolute ethanol (100 cm^3), and HCl (12 M, 20 cm^3) was slowly added to this solution. It was then stored in a refrigerator for 2 days. The precipitated white crystals were collected and recrystallized from HCl (5 M) and ethanol, yield 8.6 g (20.8%). Found: C, 32.4; H, 8.5; N, 16.6. Calc. for $C_9H_{24}N_4 \cdot HCl$: C, 32.3; H, 8.5; N, 16.8%.

N,N′-*Bis*(S-*phthaloylalanyl*)-R-*propylenediamine*

This compound was prepared by the same method as that used for *N,N′*-bis(*S*-alanyl)-*S*-propylenediamine dihydrochloride using *N,N′*-bis(*S*-phthaloylalanyl)-*R*-propylenediamine (95.30 g, 0.2 mol) and HCl (6 M, 500 cm^3), yield 56.0 g (97%).

(2R,5R,9S)-*Trimethyltriethylenetetraamine* (L$_2$) *tetrahydrochloride*, $L_2 \cdot 4HCl$

This ligand was prepared by the same method as that used for $L_1 \cdot 4HCl$ using *N,N′*-bis(*S*-alanyl)-*R*-propylenediamine dihydrochloride (54.71 g, 0.1891 mol) and $LiAlH_4$ (30 g), yield 9.8 g (15.5%). Found: C, 32.3; H, 8.2; N, 16.9. Calc. for $C_9H_{24}N_4 \cdot 4HCl$: C, 32.3; H, 8.5; N, 16.8%.

Λ - Cis - α - (R,R) - *dichloro*((2S,5S,9S)-*trimethyltriethylenetetraamine*)*cobalt*(III) *chloride*, Λ-cis-α-(R,R)-$[CoL_1Cl_2]Cl$

To a solution of $L_1 \cdot 4HCl$ (1 g, 2.992 mmol) and $CoCl_2 \cdot 6H_2O$ (0.7119 g, 2.992 mmol) dissolved in water (50 cm^3) was added $LiOH \cdot H_2O$ (0.3766 g). The brown solution was aerated with CO_2-free air for 20 h. The resultant solution was filtered, and HCl (12 M, 6 cm^3) was added. It was then reduced in volume to *ca* 5 cm^3 under reduced pressure at room temperature. HCl (12 M, 0.5 cm^3) and acetone (80 cm^3) were added, and the solution was allowed to stand for 5 h in a refrigerator. The precipitated deep blue purple crystals were filtered off, washed with cold acetone and diethyl ether, and recrystallized from HCl (5 M) and acetone, yield 0.7 g (66.2%). Found: C, 31.1; H, 7.2; N, 15.6. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl$: C, 30.6; H, 6.9; N, 15.9%.

Λ-Cis-β-(R,R)-*dichloro*(L$_1$)*cobalt*(III) *chloride monohydrate*, Λ-cis-β-(R,R)-$[CoL_1Cl_2]Cl \cdot H_2O$

To a solution of $L_1 \cdot 4HCl$ (1.5 g, 4.488 mmol) and $CoCl_2 \cdot 6H_2O$ (1.0679 g, 4.488 mmol) dissolved in water (100 cm^3) was added $LiOH \cdot H_2O$ (0.5650 g). The brown solution was aerated with CO_2-free air for 10 h. The solution was filtered and reduced to half its volume under reduced pressure at room temperature. After addition of HCl (12 M, 4 cm^3) the evaporation was continued until the volume reached 5 cm^3. It was then extracted three times with acetone, and the resultant blue extracts were concentrated to a volume of *ca* 3 cm^3 under reduced pressure at room temperature. To the solution were successively added methanol (1 cm^3), acetone (150 cm^3) and diethyl ether (50 cm^3). This solution was allowed to stand for 5 days in a refrigerator to give a light purple precipitate. The precipitated crystals were filtered off, washed with cold diethyl ether, and recrystallized from methanol and acetone, yield 0.3 g (18.1%). Found: C, 28.9; H, 6.7; N, 15.2. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl \cdot H_2O$: C, 29.1; H, 7.1; N, 15.1%.

Trans-(S,S)-*dichloro*((2S,5S,9S) - *trimethyltriethylenetetraamine*)*cobalt*(III) *chloride*, trans-(S,S)-$[CoL_1Cl_2]Cl$

This complex was prepared by the same method as that used for Λ-*cis*-α-(*R*,*R*)-$[CoL_1Cl_2]Cl$. In this preparation the aeration with CO_2-free air was continued for 40 h to give green crystals. The crystals were filtered off, washed with acetone, and recrystallized from methanol and acetone, yield 0.8 g (75.6%). Another crop could be obtained from treating the concentrated solution of the filtrate of Λ-*cis*-α-(*R*,*R*)-$[CoL_1Cl_2]Cl$ with HCl (12 M, 0.5 cm^3) and acetone (100 cm^3). Found: C, 31.1; H, 6.7; N, 14.9. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl$: C, 30.6; H, 6.9; N, 15.9%.

Δ - Cis - α - (S,S) - *dichloro*((2S,5R,9S) - *trimethyltriethylenetetraamine*)*cobalt*(III) *chloride monohydrate*, Δ-cis-α-(S,S)-$[CoL_2Cl_2]Cl \cdot H_2O$

The deep red purple crystals were obtained using the same method as that used for Λ-*cis*-α-(*R*,*R*)-$[CoL_1Cl_2]Cl$ using $L_2 \cdot 4HCl$ (1 g, 2.992 mmol) and $CoCl_2 \cdot 6H_2O$ (0.7119 g, 2.992 mmol), yield 0.6 g (54.0%). Found: C, 29.0; H, 6.9; N, 14.9. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl \cdot H_2O$: C, 29.1; H, 7.1; N, 15.1%.

Δ - Cis - β - (R,S)-*dichloro*((2S,5R,9S)-*trimethyltriethylenetetraamine*)*cobalt*(III) *chloride hemihydrate*, Δ-cis-β-(R,S)-$[CoL_2Cl_2]Cl \cdot 1/2H_2O$

To a solution of $L_2 \cdot 4HCl$ (1.5 g, 4.488 mmol) and $CoCl_2 \cdot 6H_2O$ (1.0679 g, 4.488 mmol) dissolved in water (100 cm^3) was added $LiOH \cdot H_2O$ (0.5650 g). The brown solution was aerated with CO_2-free air for 10 h. The solution was then filtered and reduced to half its volume under reduced pressure at room temperature. After addition of HCl (12 M, 4 cm^3) the evaporation was continued until the volume reached 5 cm^3. It was extracted three times with acetone, and the resultant blue extracts were concentrated to a volume of *ca* 3 cm^3 under reduced pressure at room temperature. To the solution were added methanol (1 cm^3) and acetone (60 cm^3), and it was then allowed to stand for 1 day in a refrigerator to give an oily red residue. This residue was filtered off, and the filtrate was concentrated to a volume of *ca* 3 cm^3 under reduced pressure at room temperature. To this solution were added methanol (1 cm^3) and diethyl ether (50 cm^3). It was then allowed to stand for 2 days in a refrigerator to give a dark blue–purple precipitate. The crystals were filtered off, washed with cold acetone, and recrystallized from methanol and acetone, yield 0.3 g (18.0%). Found: C, 30.0; H, 7.1; N, 14.8. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl \cdot 1/2H_2O$: C, 29.8; H, 7.0; N, 15.5%.

Trans - (R,R) - *dichloro*((2S,5R,9S)-*trimethyltriethylenetetraamine*)*cobalt*(III) *chloride monohydrate*, trans-(R,R)-$[CoL_2Cl_2]Cl \cdot H_2O$

Green crystals were obtained using the same method as that used for *trans*-(*S*,*S*)-$[CoL_1Cl_2]Cl$ using $L_2 \cdot 4HCl$ (1 g, 2.992 mmol) and $CoCl_2 \cdot 6H_2O$ (0.7119 g, 2.992 mmol), yield 0.7 g (62.9%). Found: C, 29.6; H, 7.0; N, 14.8. Calc. for $[Co(C_9H_{24}N_4)Cl_2]Cl \cdot H_2O$: C, 29.1; H, 7.1; N, 15.1%.

Isomerization of Λ-cis-α-(R,R)-$[CoL_1Cl_2]^+$ *to* trans-(S,S)-$[CoL_1Cl_2]^+$ *in methanol*

A weighed sample (0.030 g, 0.0848 mmol) of Λ-*cis*-α-(*R*,*R*)-$[CoL_1Cl_2]Cl$ was dissolved in absolute methanol (5 cm^3). The electronic absorption and CD spectra were obtained immediately. When the solution was allowed to stand at room temperature, the colour of the solution changed gradually from purple to green. After the solution had stood for 24 h at room temperature, its electronic absorption and CD spectra were obtained.

Isomerization of trans-(S,S)-$[CoL_1Cl_2]^+$ *to* Λ-cis-α-(R,R)-$[CoL_1(H_2O)_2]^{3+}$ *in water*

A weighed sample (0.030 g, 0.0848 mmol) of *trans*-(*S*,*S*)-$[CoL_1Cl_2]Cl$ was dissolved in water (5 cm^3), and the electronic absorption and CD spectra of the solution were obtained immediately. The electronic absorption spectra were recorded every 10 min during the course of isomerization. The colour of the solution changed slowly from green to purplish red. When no futher change in the electronic absorption and CD spectra was observed (after 24 h), the final spectra of the purplish red solution were obtained. The isomerization was also detected by ^1H NMR. *Trans*-(*S*,*S*)-$[CoL_1Cl_2]Cl$ (0.01 g, 0.0283 mmol) was dissolved in D_2O (*ca* 0.2 cm^3) in a ^1H NMR tube, and the ^1H NMR spectrum of the green solution was obtained immediately. After the solution had stood for 10 h at room temperature, its ^1H NMR spectrum was obtained.

Isomerization of Δ-cis-α-(S,S)-$[CoL_2Cl_2]^+$ *to* trans-(R,R)-$[CoL_2Cl_2]^+$ *in methanol*

The electronic absorption and CD spectra were measured according to the same procedure as that for the isomerization of Δ-*cis*-α-(*R*,*R*)-$[CoL_1Cl_2]^+$ to *trans*-(*S*,*S*)-$[CoL_1Cl_2]^+$. The colour of the solution changed from purplish red to green during the isomerization.

Isomerization of trans-(R,R)-$[CoL_2Cl_2]^+$ *to* Δ-cis-α-(S,S)-$[CoL_2(H_2O)]^{3+}$ *in water*

The electronic absorption, CD and ^1H NMR spectra were measured according to the same procedure as that used for the isomerization of *trans*-(*S*,*S*)-$[CoL_2Cl_2]^+$ to Λ-*cis*-(*R*,*R*)-$[CoL_1C(H_2O)_2]^{3+}$. The colour of the solution changed from green to purplish red during the isomerization.

RESULTS AND DISCUSSION

All the *cis*-α, *cis*-β and *trans* geometrical isomers were obtained for complexes containing both L_1 and L_2. The *cis*-α- and *cis*-β-dichloro complexes of these ligands were obtained as purple and red crystals, respectively, while the *trans*-dichloro complexes of these ligands were obtained as green precipitates. In the absorption spectra of the $[CoL_1Cl_2]^+$ complexes (Fig. 1), the *cis*-α isomer shows a broad first absorption band at 537 nm with a shoulder at the longer wavelength side at *ca* 600 nm, which is characteristic of the *cis*-α-dichloro cobalt(III) isomer with trien derivatives.[9] The *cis*-β isomer shows the first absorption band at 527 nm with no indication of a shoulder on the longer wavelength side, while the splitting of the lower energy band at 605 and 455 nm was observed for the *trans* isomer, as expected for these kinds of complexes. The three isomers of the $[CoL_2Cl_2]^+$ complexes show very similar absorption spectra to those of the $[CoL_1Cl_2]^+$ isomers.

The *cis*-α-$[CoL_1Cl_2]^+$ isomer shows a long-wavelength negative Cotton effect followed by a positive Cotton effect in its first absorption region (Fig. 1), showing the Λ absolute configuration,[9–11] while the CD curve of *cis*-α-$[CoL_2Cl_2]^+$ is opposite to that of Λ-*cis*-α-$[CoL_1Cl_2]^+$, indicating the Δ absolute configuration.

For *cis*-β-$[Co(L_1 \text{ or } L_2)Cl_2]^+$, the CD spectra show the Δ absolute configuration. The electronic absorption and CD spectra (Fig. 1) of *trans*-$[CoL_1Cl_2]^+$ are similar to those of *trans*-$[Co(S\text{-}pn)_2Cl_2]^+$:[12–14] a positive CD band at 456 nm $[^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ component) and a negative CD band at 596 nm $[^1A_{1g} \rightarrow {}^1E_g(D_{4h})$ component]. For the *trans*-dichlorotetraaminecobalt(III) complexes, the sign of the Cotton effects depends on the conformation of the chelate ring, and the asymmetric C-methyl group exhibits very little CD activity of the *d*–*d* transition region.[14] The positive Cotton

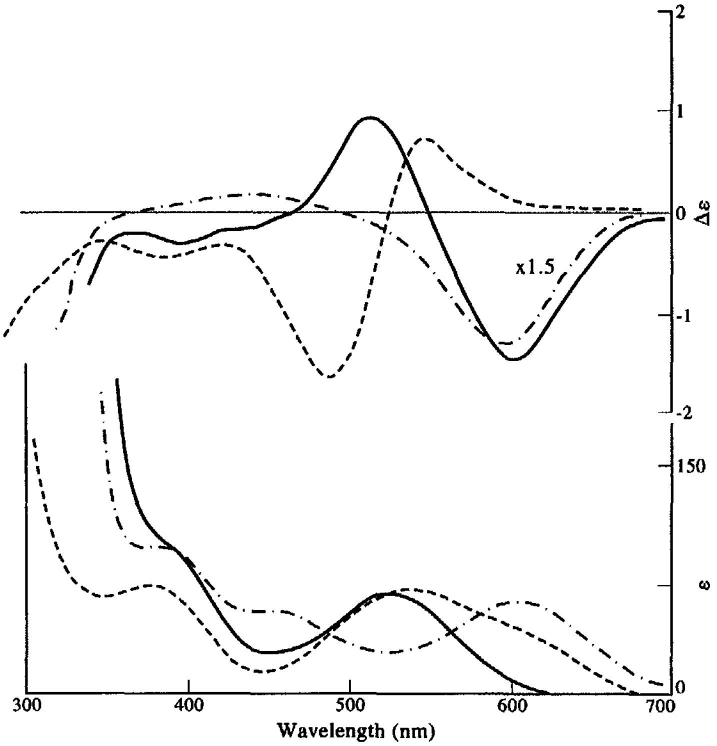

Fig. 1. CD and absorption spectra of Λ-*cis*-α-(*R*,*R*) (——), Δ-*cis*-β-(*R*,*R*) (– – –) and *trans*-(*S*,*S*) (—·—·—) dichlorocobalt(III) complexes with 2*S*,5*S*,9*S*-me_3trien in CH_3OH.

effect of the ${}^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ component in the CD curve of *trans*-$[CoL_1Cl_2]^+$ indicates that this complex takes the *trans*-($\delta\ \lambda\ \delta$) chelate ring conformation. The electronic absorption and CD spectra of the *trans*-$[CoL_2Cl_2]^+$ (Fig. 3) are apparently similar to those of *trans*-$[Co(R\text{-pn})_2Cl_2]^+$ [15] and *trans*-$[Co(R\text{-pn})(NH_3)_2Cl_2]^+$,[16] and the CD curve of the *trans*-$[CoL_2Cl_2]^+$ complex shows the *trans*-($\lambda\ \delta\ \lambda$) chelate ring conformation.

There are four possible chelate ring conformations for each of the Λ- and Δ-*cis*-α-$[Co(L_1$ or $L_2)Cl_2]^+$ complexes: ($\delta\ \delta\ \delta$), ($\delta\ \lambda\ \delta$), ($\lambda\ \delta\ \lambda$) and ($\lambda\ \lambda\ \lambda$). The Λ-*cis*-α-$[CoL_1Cl_2]^+$ isomer obtained in this work will have the ($\delta\ \delta\ \delta$) configuration with all three methyl groups equatorial. The Δ-*cis*-α-$[CoL_2Cl_2]^+$ isomer prepared in this study, the first complex known to have such a structure in which a trien derivative ligand coordinates to the cobalt(III) ion to give the Δ-*cis*-α configuration, should take the ($\delta\ \lambda\ \delta$) chelate ring conformation, where all the substituted methyl groups are equatorially oriented. Between the two possible conformations ($\delta\ \lambda\ \delta$) and ($\delta\ \delta\ \lambda$), for the *cis*-β isomer, the ($\delta\ \delta\ \lambda$) conformation is more probable for the Δ-*cis*-β-$[CoL_1Cl_2]^+$ complex, as the ($\delta\ \lambda\ \delta$) conformation increases the non-bonded interaction between its central chelate ring having an axial methyl group and its terminal chelate ring. On the other hand, the Δ-*cis*-β-$[CoL_2Cl_2]^+$ complex takes the ($\delta\ \lambda\ \delta$) configuration, in which all the substituted methyl groups are equatorially oriented and the non-bonded interaction between its chelate ring is minimized. In the *trans*-($\delta\ \lambda\ \delta$)-$[CoL_1Cl_2]^+$ complex, the methyl group in each of the two outside chelate rings adopts the equatorial position, while that in the central chelate ring is axial. The *trans*-($\lambda\ \delta\ \lambda$)-$[CoL_2Cl_2]^+$ complex has a very peculiar structure where all the substituted methyl groups in its three chelate rings are axially oriented.

The ${}^1H$ NMR spectra of the ligand and complexes are shown in Fig. 2. The methyl signal appears as a doublet in the complexes with the Λ-*cis*-α-($\delta\ \delta\ \delta$), Δ-*cis*-α-($\delta\ \lambda\ \delta$) and Δ-*cis*-β-($\delta\ \lambda\ \delta$) configurations, where all the methyl groups of the three chelate ring are equatorially oriented. In the ${}^1H$ NMR spectrum of the Δ-*cis*-β-($\delta\ \delta\ \lambda$)-$[CoL_1Cl_2]^+$ complex, the doublet at 1.14 ppm due to the protons of the two equatorial methyl groups is broadened to higher field by the signal due to the axial methyl protons. The methyl protons appears as two doublets in the *trans* complexes. For the *trans*-($\delta\ \lambda\ \delta$)-$[CoL_1Cl_2]^+$ complex, the axial protons in its central chelate ring appear as a doublet at 1.43 ppm, and the protons of the two equatorial methyl groups at 1.38 ppm. For the *trans*-($\lambda\ \delta\ \lambda$)-$[CoL_2Cl_2]^+$ complex, two doublets due to the axial methyl protons in its outside chelate rings and in its central chelate rings were observed at 1.40 and 1.38 ppm, respectively.

Isomerization reactions were followed by the electronic absorption and CD spectral change under neutral conditions such as in methanol or water. The following isomerizations were observed in this work:

$$\Lambda\text{-}cis\text{-}\alpha\text{-}[CoL_1Cl_2]^+ \text{ or } \Delta\text{-}cis\text{-}\alpha\text{-}[CoL_2Cl_2]^+ \xrightarrow{CH_3OH} trans\text{-}[Co(L_1 \text{ or } L_2)Cl_2]^+$$

$$trans\text{-}[Co(L_1 \text{ or } L_2)Cl_2]^+ \xrightarrow{H_2O} \Lambda\text{-}cis\text{-}\alpha\text{-}[CoL_1(H_2O)_2]^{3+} \text{ or } \Delta\text{-}cis\text{-}\alpha\text{-}[CoL_2(H_2O)_2]^{3+}.$$

Dissolution of Λ-*cis*-α-$[CoL_1Cl_2]^+$ in methanol gives not only the colour change from purple to green, but also the electronic absorption and CD spectral changes. These spectra of the isomerized species are very similar in shape to those of *trans*-$[CoL_1Cl_2]^+$, as shown in Fig. 3. When *trans*-$[CoL_1Cl_2]^+$ is dissolved in water, on the other hand, the colour of the solution changes from green to purplish red. Examinations of the electronic absorption and CD spectra show that the spectra of the isomerized species are very similar in shape to those of the Λ-*cis*-α-$[CoL_1(H_2O)_2]^{3+}$ complex, which is obtained from the corresponding Λ-*cis*-α-$[CoL_1Cl_2]^+$ complex (Fig. 4). The absorption spectral change during this isomerization shows two consecutive stages in which the isosbestic points are observed at 364, 385, 450 and 560 nm for the first stage, and at 358, 404, 457 and 587 nm for the second stage, as shown in Fig. 5. The ${}^1H$ NMR spectra also provide strong support for this isomerization (Fig. 6).

Dissolution of the Δ-*cis*-α-$[CoL_2Cl_2]^+$ in methanol gives a colour change from purple to green, as well as the electronic absorption and CD spectral changes. These spectra of the isomerized species are very similar in shape to those of *trans*-$[CoL_2Cl_2]^+$ (Fig. 7). On the other hand, when *trans*-$[CoL_2Cl_2]^+$ is dissolved in water, the colour of the solution changes from green to purplish red. The absorption and CD spectra of the isomerized species are very similar to those of Δ-*cis*-α-$[CoL_2(H_2O)_2]^{3+}$, which is obtained from the corresponding Δ-*cis*-α-$[CoL_2Cl_2]^+$ complex (Fig. 8). The electronic absorption spectral change during this isomerization shows three consecutive stages in which the isosbestic points are observed, at 385, 466 and 543 nm for the first stage, at 359, 392, 455 and 580

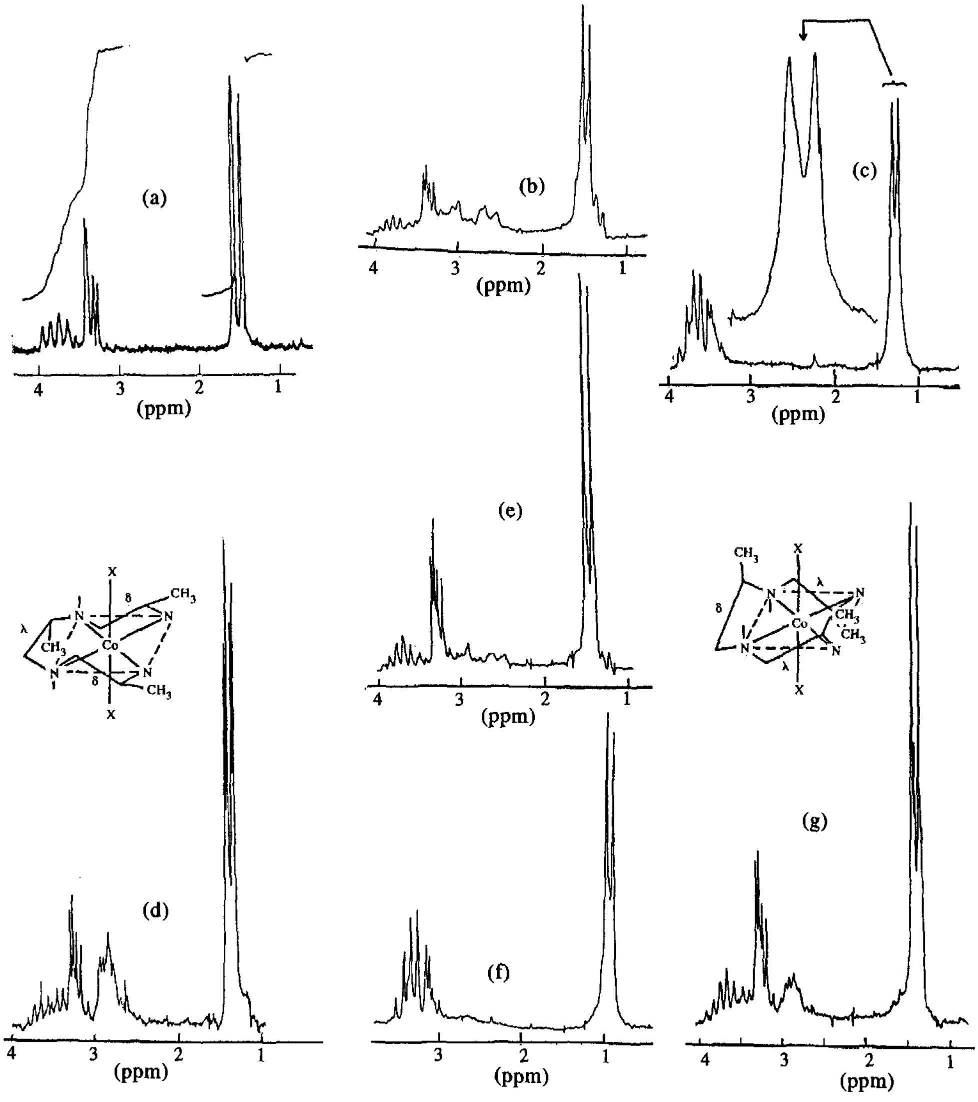

Fig. 2. ^{1}H NMR spectra of ligand (a) and complexes: Λ-*cis*-α (b), Δ-*cis*-β (c) and *trans* (d) isomers of $[Co(L_1)Cl_2]^+$, and Δ-*cis*-α (e), Δ-*cis*-β (f) and *trans* (g) isomers of $[Co(L_2)Cl_2]^+$.

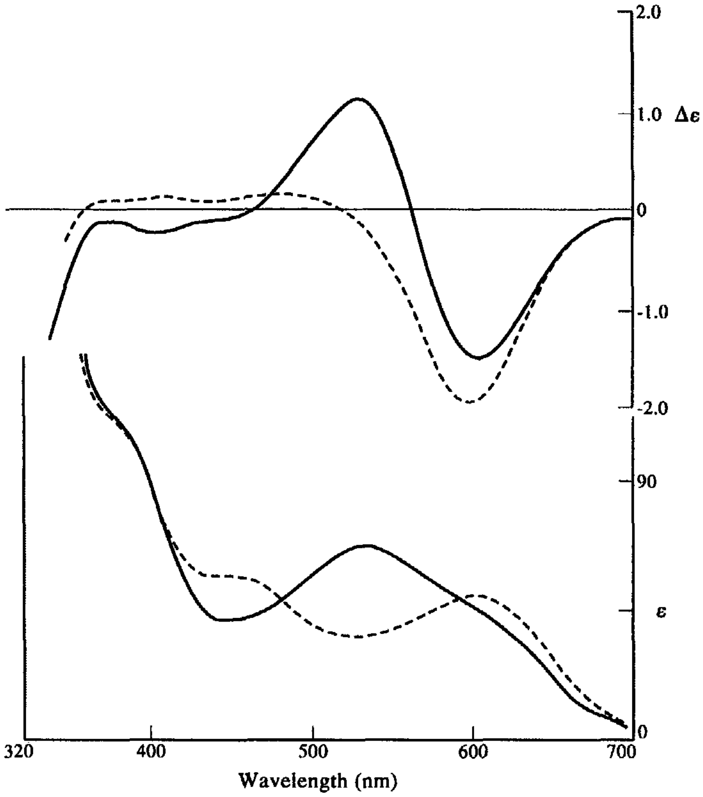

Fig. 3. CD and absorption spectral change for the isomerization of Λ-*cis*-α-(R,R)-$[Co(L)Cl_2]^+$ (——, 0 h) to *trans*-(S,S)-$[Co(L)Cl_2]^+$ (– – – –, after 24 h) in CH_3OH (L = 2S,5S,9S-me$_3$trien).

nm for the second stage, and at 359, 396, 453 and 585 for the third stage, as shown in Fig. 9. This isomerization is also supported by the ^1H NMR spectral change (Fig. 6).

Two general routes are available for the stereochemical change, intramolecular rearrangement and substitution, but neither can account for the inversion in simple terms. Trigonal or rhombic twists[9a] are excluded by the restrictions enforced by the multidentate ligand. In each of the four observed stereospecific isomerizations, the geometrical and optical inversions took place at the same time. Therefore, it is quite likely that these isomerizations proceed via a dissociative mechanism with a five-coordinated intermediate, as proposed for the trien[17,18] or trien derivative[19] cobalt(III) complexes. The dissociation of one ligand (Cl^-) from the octahedron leaves a square-pyramidal (SP) C_{4v} structure. An isomerization is only possible if this five-coordinated fragment is reorganized into another geometry, which must be close to trigonal bipyramidal (TBP, D_{3h}). Therefore, the isomerization of the cobalt(III) complex with a trien skeleton may proceed via the following route:[20] Λ-*cis*-$\alpha \leftrightarrow \Delta$-*cis*-$\beta \leftrightarrow$ *trans* $\leftrightarrow \Lambda$-*cis*-$\beta \leftrightarrow \Delta$-*cis*-$\alpha$. Considering all the isomers which can exist during the isomerization, the observed stereochemical inversions can proceed via the routes shown in Fig. 10. These possible routes are very intricate, which is supported by the electronic absorption spectral changes, composed of several stages during the isomerization (Figs 5 and 9).

Methanol frequently induces isomerizations in the dichlorotetraamine cobalt(III) complexes, which are usually *cis* → *trans* inversion with bis(ethylenediamine)-type complexes[21] or *cis*-$\beta \rightarrow$ *trans* inversion with trien[9b] and some trien derivatives.[22–24] However, in water isomerization from *trans* to *cis* isomer is usually observed.[18] The solvation properties of methanol and water are therefore likely that methanol and water stabilize the *trans* and *cis* configurations, respectively, in the dichlorocobalt(III) complexes with a trien skeleton, which has been the case in the isomerization reactions observed in this study.

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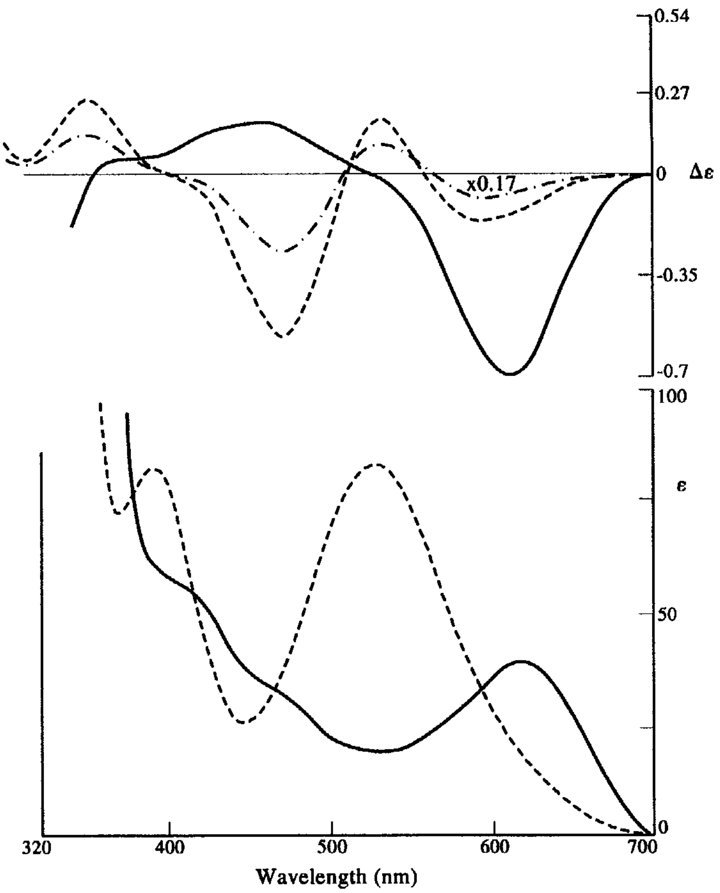
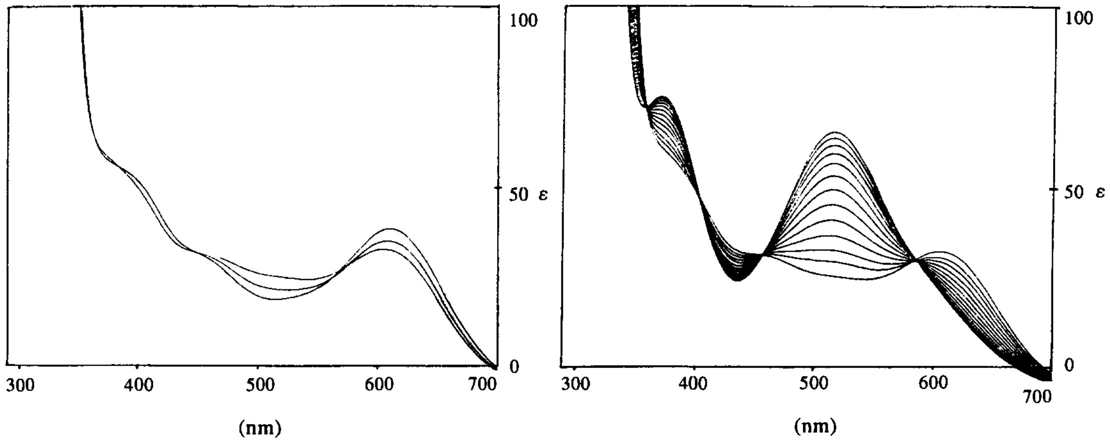


Fig. 4. CD and absorption spectral change for the isomerization of *trans*-(*S*,*S*)-$[Co(L)Cl_2]^+$ (——, 0 h) to Λ-*cis*-α-(*R*,*R*)-$[Co(L)(H_2O)_2]^{3+}$ (— — —, after 24 h) in H_2O (L = 2*S*,5*S*,9*S*-me_3trien).



1st stage

2nd stage

Fig. 5. Two stages of the electronic absorption spectral changes during the course of isomerization of *trans*-(*S*,*S*)-$[Co(L)Cl_2]^+$ to Λ-*cis*-α-(*R*,*R*)-$[Co(L)(H_2O)_2]^{3+}$ in H_2O (L = 2*S*,5*S*,9*S*-me_3trien).

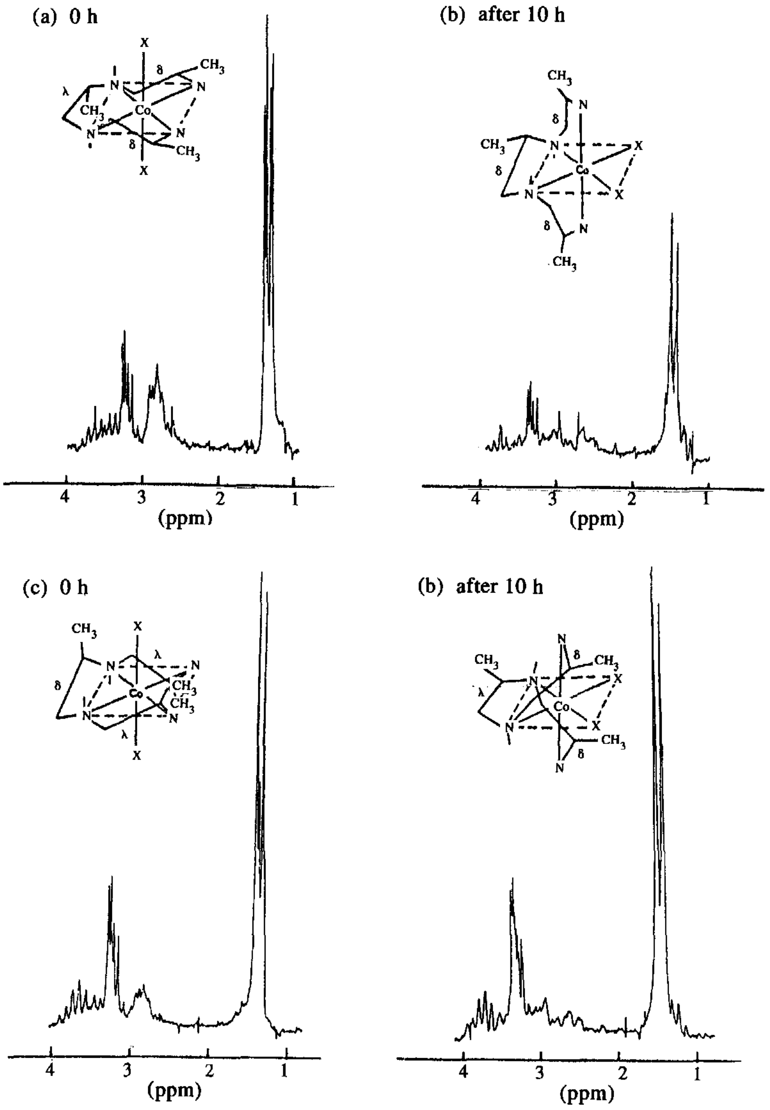


Fig. 6. The ^{1}H NMR spectral change for the isomerization of *trans*-(*S*,*S*)-$[Co(L)Cl_2]^+$ (A) to Λ-*cis*-α-(*R*,*R*)-$[Co(L)(D_2O)_2]^{3+}$ (B) in D_2O (L = 2*S*,5*S*,9*S*-me$_3$trien). The ^{1}H NMR spectral change for the isomerization of *trans*-(*R*,*R*)-$[Co(L)Cl_2]^+$ (C) to Δ-*cis*-α-(*S*,*S*)-$[Co(L)(D_2O)_2]^{3+}$ (D) in D_2O (L = 2*S*,5*R*,9*S*-me$_3$trien).

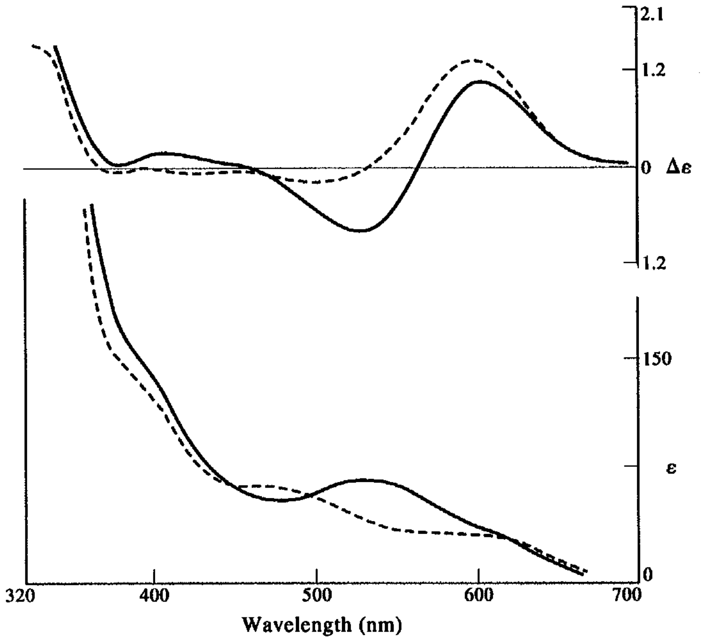


Fig. 7. CD and absorption spectral changes for the isomerization of Δ-*cis*-α-(*S*,*S*)-$[Co(L)Cl_2]^+$ (– 0 h) to *trans*-(*R*,*R*)-$[Co(L)Cl_2]^+$ (– – –, after 24 h) in CH_3OH (L = 2*S*,5*R*,9*S*-me$_3$trien).

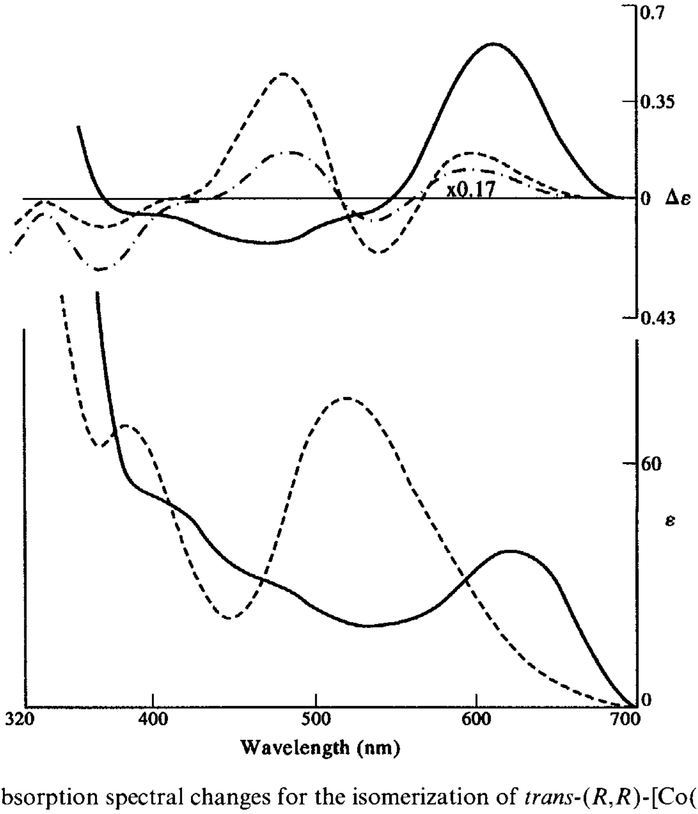
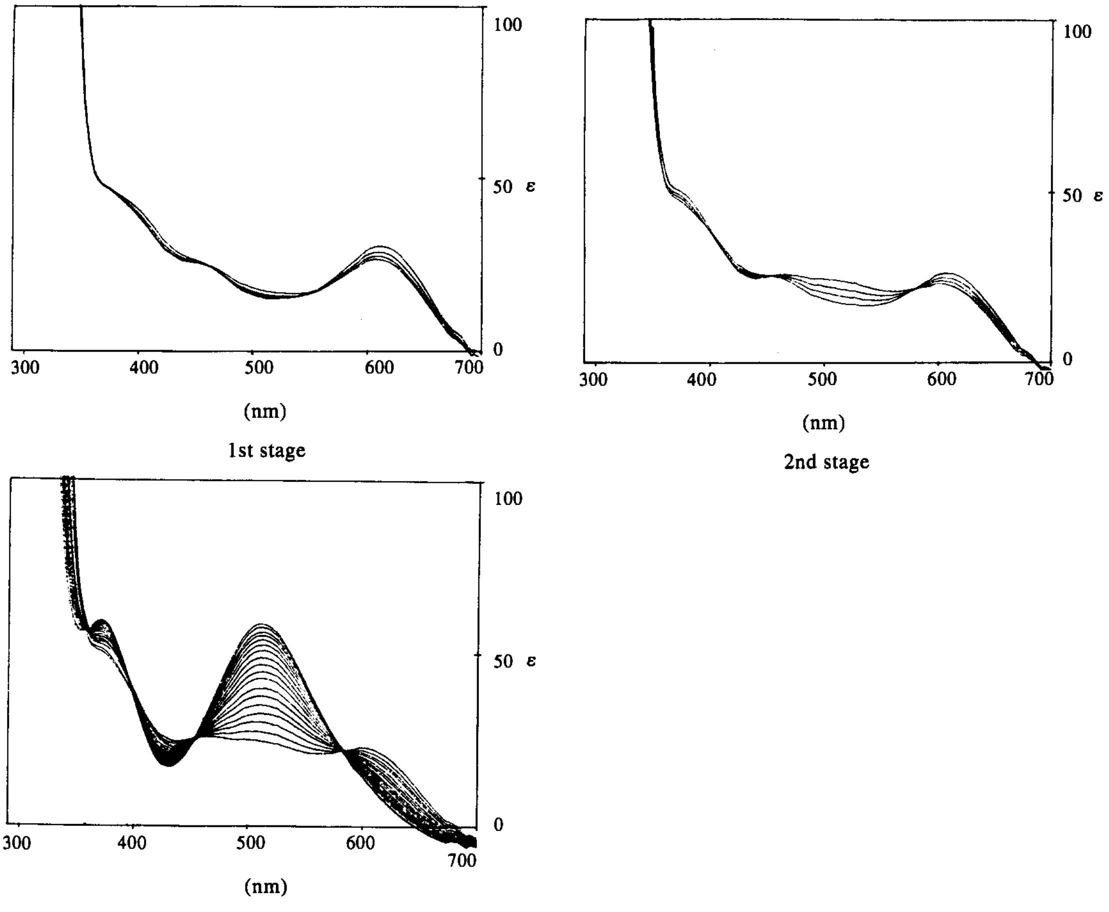


Fig. 8. CD and absorption spectral changes for the isomerization of *trans*-(*R*,*R*)-$[Co(L)Cl_2]^+$ (– 0 h) to Δ-*cis*-α-(*S*,*S*)-$[Co(L)(H_2O)_2]^{3+}$ (– – –, after 24 h) in H_2O (L = 2*S*,5*R*,9*S*-me$_3$trien).



1st stage

2nd stage

3 rd stage

Fig. 9. Three stages of the electronic absorption spectral changes during the course of isomerization of *trans*-(*R*,*R*)-$[Co(L)Cl_2]^+$ to Δ-*cis*-α-(*S*,*S*)-$[Co(L)(H_2O)_2]^{3+}$ in H_2O (L = 2*S*,5*R*,9*S*-me$_3$trien).

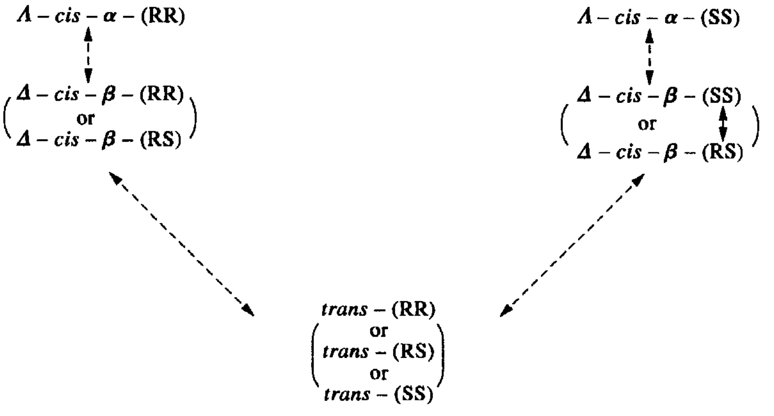


Fig. 10. Possible routes for the observed stereochemical inversion reactions.

REFERENCES

1. G. R. Brubaker, D. P. Schaefer, J. H. Worrel and J. I. Legg, *Coord. Chem. Rev.* 1971, **7**, 161.
2. D. J. Radanovic, *Coord. Chem. Rev.* 1984, **54**, 159.
3. G. R. Asperger and C. F. Liu, *Inorg. Chem.* 1967, **6**, 796; M. J. Jun, J. W. Cheon, S. Lee and S. Choi, *Polyhedron* 1989, **8**, 2889, 1205.
4. M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Japan* 1972, **45**, 806; G. R. Asperger, *Inorg. Chem.* 1969, **8**, 2127.
5. M. J. Jun and C. F. Liu, *J. Chem. Soc., Dalton Trans.* 1976, 1031; J. W. Turley and R. G. Asperger, *Inorg. Chem.* 1971, **10**, 558.
6. M. Saburi, T. Sawai and S. Yoshikawa, *Bull. Chem. Soc. Japan* 1972, **45**, 1086.
7. F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.* 1959, **81**, 290.
8. G. R. Asperger and C. F. Liu, *Inorg. Chem.* 1965, **4**, 1395.
9. (a) A. M. Sargeson and G. H. Searle, *Inorg. Chem.* 1965, **4**, 45; (b) 1967, **6**, 787.
10. A. J. MacCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.* 1965, 5094.
11. T. E. MacDermott and A. J. Sargeson, *Aust. J. Chem.* 1963, **16**, 334.
12. C. J. Hawkins, *J. Chem. Soc., Chem. Commun.* 1969, 777.
13. C. J. Hawkins and E. Larsen, *Acta Chem. Scand.* 1965, **19**, 185.
14. C. J. Hawkins, E. Larsen and I. Olsen, *Acta Chem. Scand.* 1965, **19**, 1915.
15. R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.* 1965, **4**, 202.
16. B. Bosnich and J. Harrowsfield, *J. Am. Chem. Soc.* 1972, **94**, 3425.
17. R. Nithyananthan and M. L. Tobe, *Inorg. Chem.* 1969, **8**, 1589.
18. D. A. Buckingham, P. A. Marzill and A. M. Sargeson, *Inorg. Chem.* 1967, **6**, 1032.
19. E. Ahmed and M. L. Tobe, *Inorg. Chem.* 1974, **13**, 2956.
20. E. Kyuno and J. C. Bailar, *J. Am. Chem. Soc.* 1966, **88**, 1120.
21. B. Bosnich, C. K. Ingold and M. L. Tobe, *J. Chem. Soc.* 1965, 4074.
22. M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Japan* 1972, **45**, 1443.
23. M. Goto, M. Saburi and S. Yoshikawa, *Inorg. Chem.* 1969, **8**, 358.
24. G. H. Searle and A. M. Sargeson, *Inorg. Chem.* 1973, **12**, 1014.