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# Preparation and Characterization of Some Co(III) Complexes Containing (1*R*,2*R*)-Dimethyl-1,2-cyclohexanediamine. Crystal Structure of $(+)_{435}$-*trans*-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]$-$\mathrm{Cl\cdot HCl\cdot 2H_2O}$

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$(-)_{546}$-*trans*-$[\mathrm{Co(NO_2)_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$ and $(+)_{546}$-$\Lambda$-$[\mathrm{Co(CO_3)}(R,R\text{-}\mathrm{dmchxn})_2]^+$, which had been newly prepared, reacted with concentrated HCl to give, respectively, $(-)_{435}$-*trans*-(*SSSS*)-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$ and $(+)_{435}$-*trans*-(*SRRS*)-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$ stereospecifically, where *R*,*R*-dmchxn=(1*R*,2*R*)-*N*,*N′*-dimethyl-1,2-cyclohexanediamine. The stereospecific formation of $(+)_{546}$-$\Lambda$-$[\mathrm{Co(CO_3)}(R,R\text{-}\mathrm{dmchxn})_2]^+$ has been observed. The *trans*-dichloro complexes and their precursors have been characterized by elemental analysis and by electronic absorption, circular dichroism, $^1$H NMR, and $^{13}$C NMR spectroscopies. An X-ray crystal-structure determination was undertaken on one of the *trans*-dichloro isomers, $(+)_{435}$-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]\mathrm{Cl\cdot HCl\cdot 2H_2O}$, whose structure could not be characterized by usual spectroscopies. This complex forms triclinic crystals with $a=11.395(10)$ Å, $b=11.674(8)$ Å, $c=11.031(8)$ Å, $\alpha=98.62(6)$°, $\beta=102.48(8)$°, $\gamma=118.24(5)$°, and $Z=2$, in the space group P1. Least-squares refinements converged at an *R* value of 0.041 for 4870 independent reflections with $F_o>3[\sigma(F_o)]$. The complex cation has an approximately twofold symmetry. The conformations of the two five-membered chelate rings are both $\lambda$. The arrangements of the groups around the two secondary nitrogen atoms are *R* and *S* in each diamine. The isomerization from the $(+)_{435}$-*trans*-dichloro complex to the $(-)_{435}$ isomer has been observed under mild basic conditions.

It is an interesting subject to design ligands suitable for metal-assisted asymmetric synthesis where the orientation of the donor substituents can play a major role in the diastereotopic discrimination of the substrate. To examine the coordination behavior of the *N*-substituted polyamine from this point of view is an interesting subject, since the *N*-alkyl groups in the polyamines or diamines significantly affect the structures of metal complexes.[1,2]

As a part of a study to develop useful optical-active ligands for asymmetric synthesis, we have been investigated cobalt(III) complexes of the *N*-alkylated diamines. During this investigation, we have obtained two isomers of the *trans*-dichlorobis(diamine)cobalt(III) complex, where the diamine is (1*R*,2*R*)-*N*,*N′*-dimethyl-1,2-cyclohexanediamine (*R*,*R*-dmchxn), whose chelate ring would be fixed in the $\lambda$ gauche conformation with its rigid cyclohexane-ring skeleton. These *trans*-dichloro isomers, which are important precursors of the corresponding amino acidato complexes, $(-)_{435}$-*trans*-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$ and $(+)_{435}$-*trans*-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$, were derived from $(-)_{546}$-*trans*-$[\mathrm{Co(NO_2)_2}(R,R\text{-}\mathrm{dmchxn})_2]^+$ and $(+)_{546}$-$[\mathrm{Co(CO_3)}(R,R\text{-}\mathrm{dmchxn})_2]^+$ respectively.

In this paper we wish to report the syntheses and characterization of these four cobalt(III) complexes containing *R*,*R*-dmchxn, including an X-ray crystal-straucture determination of one of the *trans*-dichloro isomers, $(+)_{435}$-*trans*-$[\mathrm{CoCl_2}(R,R\text{-}\mathrm{dmchxn})_2]\mathrm{Cl\cdot HCl\cdot 2H_2O}$, whose structure could not be characterized by usual spectroscopies. In addition, the conversion reaction between the two *trans*-dichloro complexes has been investigated in order to elucidate the relationship between the two isomers.

## Experimental

*Measurement.* The visible absorption spectra were recorded on a Shimadzu UV-210 spectrophotometer. The circular dichroism spectra were measured with a JASCO J-500A recording spectropolarimeter. The spectra were obtained in methanol for the *trans*-dichloro complexes and in water for the dinitro and carbonato complexes. The $^1$H NMR spectra were measured on a HITACHI R-40 (90 MHz) spectrometer, with tetramethylsilane or sodium 3-trimethylsilyl-1-propanesulfonate as an internal standard. The $^{13}$C NMR spectra were obtained on a JEOL PS-100 (100 MHz) spectrometer, with tetramethylsilane as the external standard. Elemental analyses were performed by Shounan Bunseki Center Co., Ltd.

*Materials.* All the reagents were of the best commercial grade and were used without further purification. (1*R*,2*R*)-*N*,*N′*-Dimethyl-1,2-clohexanediamine (*R*,*R*-dmchxn) was prepared by the method of Kashiwabara *et al.*[3]

*Preparation of* $(-)_{546}$-trans-$[\mathrm{Co(NO_2)_2}(R,R\text{-}dmchxn)_2]\mathrm{ClO_4\cdot H_2O}$ *(**1a**).* A solution of *R*,*R*-dmchxn (4.4 g) in water (30 mL) was added, drop by drop, to an aqueous solution containing sodium hexanitrocobaltate(III) (7.7 g), after which the solution was heated at 70 °C for 1 h while being stirred. After cooling to room temperature, a solution of sodium perchlorate (2.5 g) in water (10 mL) was added to the reacted solution with stirring, and the solution was left to stand overnight at room temperature. The resulting yellow crystals were filtered, washed with

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ice-cold water, and air-dried. Recrystallization was performed from a minimum amount of water at 55 °C; yield, 6.5 g. Anal. Calcd for $C_{16}H_{38}N_6O_9ClCo$: C, 34.76; H, 6.93; N, 15.20. Found: C, 34.55; H, 6.87; N, 15.15. $^1$H NMR ($D_2O$) $\delta$=2.10 (*s*, N-C$H_3$). $^{13}$C NMR ($D_2O$) $\delta$= 25.5, 31.2, 38.2, and 69.3.

*Preparation of* (−)$_{435}$-trans-*[CoCl$_2$(*R,R*-dmchxn)$_2$]Cl·HCl·2H$_2$O (1b).* Slightly soluble perchlorate salt, (−)$_{546}$-*trans* $[Co(NO_2)_2(R,R\text{-dmchxn})_2]ClO_4\cdot H_2O$ (**1a**) (3.5 g) was converted to more soluble chloride salt by the vigorous stirring of the perchlorate salt with an anion-exchange resin (QAE-Sephadex, 100—200 mesh, 2 g) in the $Cl^-$ form for 6 h. Concentrated hydrochloric acid (50 mL) was then poured onto the chloride salt of the *trans*-$[Co(NO_2)_2(R,R\text{-dmchxn})_2]^+$, which had been obtained by the evaporation of the aqueous solution after the removal of the resin. The solution was heated on a water bath at 90 °C and concentrated at that temperature continuously. The original violet color turned to green, and green crystals gradually formed in the solution. Then the solution was cooled to room temperature and allowed to stand overnight. The resulting green crystals were filtered, washed with a small amount of hydrochloric acid (1 M (1 M=1 mol dm$^{-3}$)), and air-dried; yield, 2.1 g. Anal. Calcd for $C_{16}H_{41}N_4O_2Cl_4Co$: C, 36.84; H, 8.60; N, 10.62. Found: C, 37.18; H, 8.68; N, 10.38. $^1$H NMR ($CD_3OD$) $\delta$=2.43 (*d*, N-CH$_3$). $^{13}$C NMR ($D_2O$-DCl) $\delta$=24.4, 29.8, 37.8, and 69.5.

*Preparation of (+)$_{546}$-[Co(CO$_3$)(*R,R*-dmchxn)$_2$]Cl·2H$_2$O (2a).* *R,R*-Dmchxn (2.8 g) was added to a fresh solution (30 mL) containing sodium tricarbonatocobaltate(III) trihydrate (3.6 g). The solution was warmed on a water bath for 1 h at 50 °C. The original green color gradually turned to a reddish purple. After cooling to room temperature, an aqueous solution (30 mL) of sodium chloride (2.5 g) was stirred into the solution. Then, the solution was allowed to stand overnight. The resulting crystals were recrystallized from water at 60 °C. The reddish purple crystals which separated were filtered, washed with ethanol and ether, and air-dried; yield, 4.0 g. The formation of only one isomer has been observed. Anal. Calcd for $C_{17}H_{40}N_4O_5ClCo$: C, 42.99; H, 8.48; N, 11.80. Found: C, 43.01; H, 8.73; N, 11.89. $^1$H NMR ($D_2O$) $\delta$=2.02 and 2.05 (*s*, N-CH$_3$). $^{13}$C NMR ($D_2O$) $\delta$=24.6, 25.2, 29.2, 30.8, 31.4, 32.7, 63.3, 65.9, and 168.6.

*Preparation of (+)$_{435}$-*trans*-[CoCl$_2$(*R,R*-dmchxn)$_2$]Cl·HCl·2H$_2$O (2b).* 2.0 g of the (+)$_{546}$-$[Co(CO_3)(R,R\text{-dmchxn})_2]Cl\cdot 2H_2O$ (**2a**) obtained above was dissolved in a minimum volume of water. The solution was acidified with concentrated hydrochloric acid (50 mL), followed by foaming. The solution was heated on a water bath at 90 °C and then concentrated. The green crystals which separated were filtered, washed with ice-cold hydrochloric acid (1 M), and air-dried. Recrystallization was performed from 6 M hydrochloric acid; yield, 2.0 g. Anal. Calcd for $C_{16}H_{41}N_4O_2Cl_4Co$: C, 36.84; H, 8.60; N,10.62. Found: C, 36.80; H, 8.91; N, 10.73. $^1$H NMR ($CD_3OD$) $\delta$=2.25 and 2.34 (*d*, N-CH$_3$). $^{13}$C NMR ($D_2O$-DCl) $\delta$=25.1, 25.6, 29.6, 37.8, 38.2, 64.7, 65.2, and 68.0.

*Conversion Reaction from (+)$_{435}$-*trans*-[CoCl$_2$(*R,R*-dmchxn)$_2$]$^+$ Ion to (−)$_{435}$-*trans* Isomer.* A sample (100 mg) of either the (+)$_{435}$-*trans* or (−)$_{435}$-*trans* isomer was dissolved in methanol (60 mL). To the solutions we then added 1 mL of a methanol solution containing 2,6-lutidine (40 mg), after which the solutions were stored at 45 °C. The CD spectra were recorded every 30 min. After 1 d, the CD spectra of the (+)$_{435}$-*trans* isomer became identical with that of the (−)$_{435}$-*trans* isomer, which did not change under the same conditions. The same reaction was also followed by $^1$H NMR measurements. The results obtained by these two ways agreed with each other.

*X-Ray Analysis.* The crystal used in the data collection was a green prism with the approximate dimensions of 0.51×0.24×0.43 mm$^3$. The diffraction data were measured on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Within the range of $2\theta<65°$, 4870 independent reflections with $F_o>3[\sigma(F_o)]$ were obtained. The intensities were corrected for Lorentz and polarization factors and for absorption ($\mu$=11.7 cm$^{-1}$).

Crystal data are: Triclinic, P1, $a$=11.395(10), $b$=11.674 (8), $c$=11.031(8) Å, $\alpha$=98.62(6), $\beta$=102.48(8), $\gamma$=118.24(5)°, $Z$=2, $D_m$=1.435, $D_x$=1.438 gcm$^{-3}$.

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. A unit-weight weighting scheme was employed. All the hydrogen atoms except for those of the water and hydrochloride of crystallization were located by assuming a tetrahedral coordination; they are all included in the final refinement with the isotropic temperature factors. The atomic-scattering factors and values of $f'$ and $f''$ for Co, Cl, O, and C were taken from Ref 4. The final indicies were $R$=0.041 and $R'$=0.044.

All the calculations were performed on a FACOM M-380 computer at the Institute of Physical and Chemical Research with Universal Program System UNICS III.[5]

## Results and Discussion

*Preparations.* Two types of procedures were used for the preparation of *trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$-type complexes. In the methods, the resulting *trans*-dichloro complexes, **1b** and **2b**, were obtained from **1a** and **2a** respectively by treatment with concentrated hydrochloric acid.

*Method 1.* The (−)$_{546}$-*trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$ complex (**1b**) was obtained by the usual substitution reaction, using hexanitrocobaltate(III) as the starting material.[6] The reaction scheme is:

$$[Co(NO_2)_6]^{3-} + 2R,R\text{-dmchxn} \longrightarrow \textit{trans}\text{-}[Co(NO_2)_2(R,R\text{-dmchxn})_2]^+ \quad (\mathbf{1a}).$$

$$(\mathbf{1a}) + \text{concd HCl} \longrightarrow \textit{trans}\text{-}[CoCl_2(R,R\text{-dmchxn})_2]^+ \quad (\mathbf{1b}).$$

*Method 2.* The (+)$_{435}$-*trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$ complex (**2b**) was also obtained by the usual substitution reaction, using tricarbonatocobaltate(III) as the starting material.[7] The reaction scheme is:

$$[Co(CO_3)_3]^{3-} + 2R,R\text{-dmchxn} \longrightarrow \Lambda\text{-}[Co(CO_3)(R,R\text{-dmchxn})_2]^+ \quad (\mathbf{2a}).$$

$$(\mathbf{2a}) + \text{concd HCl} \longrightarrow \textit{trans}\text{-}[CoCl_2(R,R\text{-dmchxn})_2]^+ \quad (\mathbf{2b}).$$

For each complex, **1a**, **1b**, **2a**, or **2b**, only one isomer was obtained stereospecifically. The structural assignments of the geometries of the present complexes are based on (a) the $^1$H NMR signals of the *N*-methyl groups, (b) the $^{13}$C NMR signals of the complexes, and (c) the electronic absorption and the circular dichroism spectra. The data on the electronic spectra and circular dichroism curves for the dinitro, carbonato, and the dichloro complexes are given in Fig. 1 and Table 1. The results of the $^1$H and $^{13}$C NMR spectra of the four complexes are presented in the Experimental section.

*Structures of Two* trans-*Dichloro Complexes.* The dichloro complexes **1b** and **2b** obtained are green, which is characteristic of the *trans*-$[CoCl_2N_4]^+$ type. The visible absorption spectra of **1b** and **2b** are very similar to each other and give typical *trans*-$[CoCl_2N_4]^+$ absorptions (Fig. 1b). On the other hand, the CD spectra of **1b** and **2b** are significantly different from each other. The changes in the CD spectrum of $(+)_{435}$-*trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$ during the conversion reaction are shown in Fig. 2. In the CD spectra of the $(-)_{435}$-*trans*-dichloro complex **1b**, no change has been observed during the same treatment. The reaction scheme is:

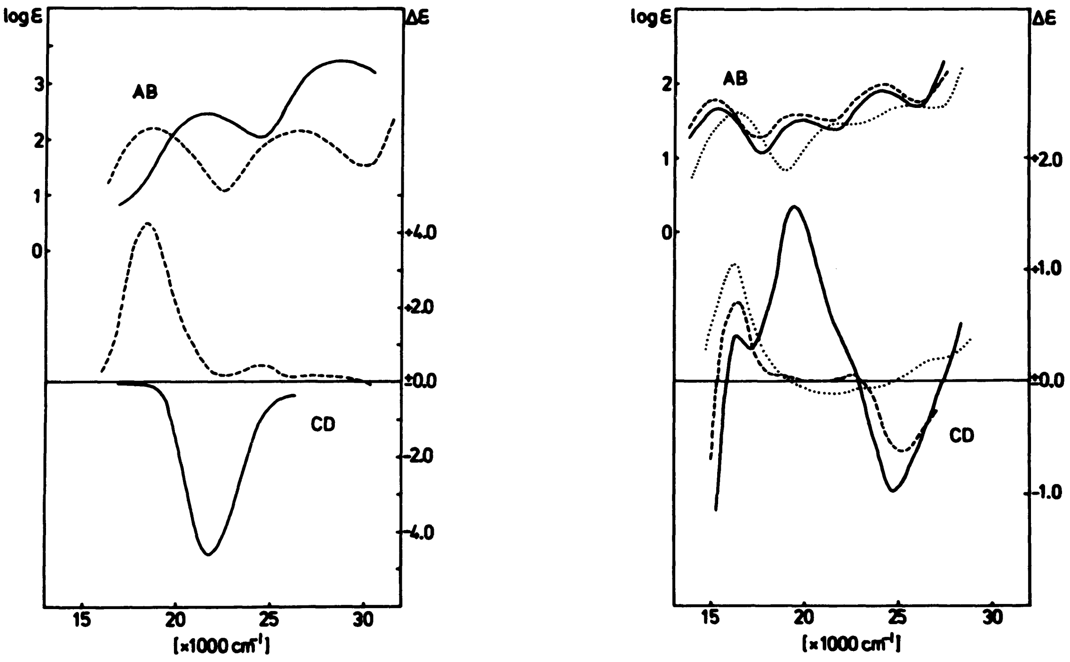
$$(+)_{435}\text{-}trans\text{-}[CoCl_2(R,R\text{-dmchxn})_2]^+\ (\mathbf{2b}) \xrightarrow{\text{2,6-lutidine}} (-)_{435}\text{-}trans\text{-}[CoCl_2(R,R\text{-dmchxn})_2]^+\ (\mathbf{1b}).$$

It is generally accepted that the absolute configuration of the asymmetric nitrogen atoms coor-

TABLE 1. NUMERICAL DATA OF ABSORPTION (AB) AND CIRCULAR DICHROISM (CD)

| | AB$\tilde{\nu}$, $10^3$ cm$^{-1}$ (log ε) | CD$\tilde{\nu}$, $10^3$ cm$^{-1}$ ($\varepsilon_l-\varepsilon_r$) |
|---|---|---|
| $(-)_{546}$-*trans*-$[Co(NO_2)_2$- | 21.6(2.45) | 21.7(−4.60) |
| $(R,R\text{-dmchxn})_2]^+$ (**1a**) | 28.5(3.40) | |
| $(+)_{546}$-$[Co(CO_3)$- | 18.7(2.21) | 18.4(+4.26) |
| $(R,R\text{-dmchxn})_2]^+$ (**2a**) | 26.5(2.16) | 24.5(+0.46) |
| | | 27.8(+0.19) |
| $(-)_{435}$-*trans*-$[CoCl_2$- | 15.3(1.67) | 16.3(+0.41) |
| $(R,R\text{-dmchxn})_2]^+$ (**1b**) | 19.8(1.52) | 19.4(+1.57) |
| | 24.1(1.90) | 24.8(−0.97) |
| $(+)_{435}$-*trans*-$[CoCl_2$- | 15.2(1.79) | 16.1(+0.87) |
| $(R,R\text{-dmchxn})_2]^+$ (**2b**) | 19.8(1.58) | 22.5(+0.06) |
| | 24.1(1.98) | 25.0(−0.62) |
| *trans*-$[CoCl_2$- | 16.3(1.62) | 16.1(+1.05) |
| $(R,R\text{-chxn})_2]^+$ [a] | 21.7(1.47) | 21.3(−0.10) |
| | 25.8(1.70) | |

a) Ref. 27).



(a) (b)

Fig. 1. (a) The AB and CD spectra of $(-)_{546}$-*trans*-$[Co(NO_2)_2(R,R\text{-dmchxn})_2]^+$ (**1a**) and $(+)_{546}$-$\Lambda$-$[Co(CO_3)(R,R\text{-dmchxn})_2]^+$ (**2a**) complexes. The solid line indicates the former complex ion. (b) The AB and CD spectra of *trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$ complexes in methanol. The solid line and the broken line indicate the $(-)_{435}$-isomer (**1b**) and the $(+)_{435}$-isomer (**2b**), respectively. The AB and CD spectra of *trans*-$[CoCl_2(R,R\text{-chxn})_2]^+$ in methanol is presented by the dotted line.

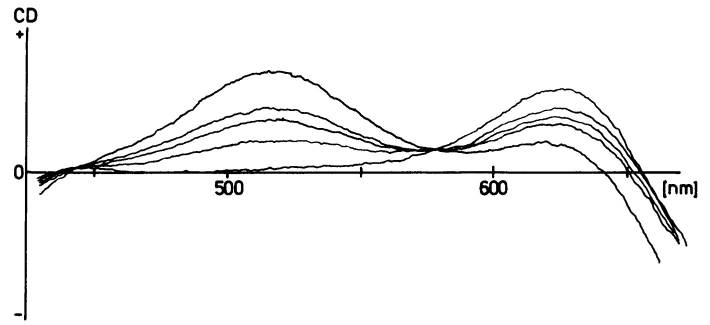


Fig. 2. The changes in the CD spectrum of $(-)_{435}$-*trans*-[CoCl$_2$(*R*,*R*-dmchxn)$_2$]$^+$ during the conversion reaction.

dinated to a Co(III) can be changed under mild basic conditions without any change in the absorption spectrum, which is generally sensitive to any change in the structure of the complex.[8] The present conversion reaction using 2,6-lutidine proceeded from **2b** to **1b** without any color change, and the CD curves of **2b** during the reaction passed through the isodichroic points (439 and 578 nm, Fig. 2). Accordingly, these results indicate that the two dichloro complexes obtained differ in the absolute configurations of the coordinated secondary nitrogen centers, and that the isomeric mixtures produced during the reaction are composed of **2b** and **1b**.

The $^1$H NMR spectrum of **1b** shows and *N*-methyl doublet at δ 2.43. The $^{13}$C NMR spectrum of **1b** gives only four signals, though this complex contains 16 carbon atoms as its components. These NMR results prove that the four methyl groups on the nitrogen atoms are in the same chemical environment.

The X-ray structure analysis and circular dichroism studies of *trans*-[CoCl$_2$(*N*-methyl-substituted diamine)$_2$]$^+$ suggest the following empirical rule: the sign of the CD band near 22000 cm$^{-1}$ ($A_{1g} \rightarrow A_{2g}$-($D_{4h}$) CD band ) can be closely related to the configuration of the asymmetric nitrogen centers, as has been shown for *trans*-dichlorobis(diamine)-cobalt(III) complexes of *N*-methyl and *C*-methylethylenediamine.[9–11] When a complex involving five-membered chelate rings of λ-gauche conformations gives a positive Cotton effect in this region, it should be assigned to the *S* configuration around the asymmetric nitrogen center. According to this rule and the NMR results of **1b**, the absolute configurations around the four asymmetric nitrogen centers of the $(-)_{435}$-*trans*-dichloro complex **1b** might be concluded to be all *S*, since a large positive Cotton effect has been observed in the corresponding region (Fig. 1b) and since (1*R*,2*R*)-1,2-cyclohexanediamine adopts the λ-gauche conformation toward the Co(III) ion. Consequently, the structure of the $(-)_{435}$-isomer **1b** can be identified as the *trans*-*SSSS* structure (Fig. 3b, X=Cl$^-$), which is thought to be most stable of the combinations of asymmetric nitrogen atoms.

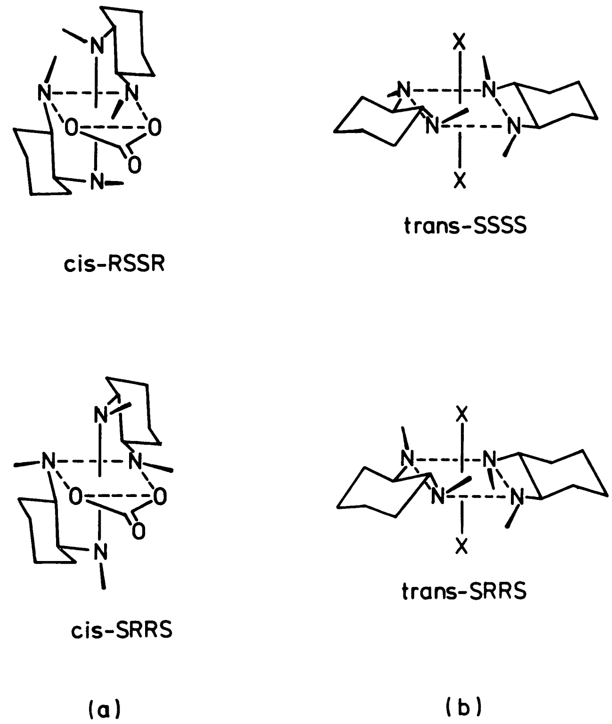


Fig. 3. (a) Two possible isomers of Δ-[Co(CO$_3$)(*R*,*R*-dmchxn)$_2$]$^+$, and (b) structures of *trans*-type complexes, *trans*-[CoX$_2$(*R*,*R*-dmchxn)$_2$]$^+$ (X=NO$_2^-$ or Cl$^-$).

On the other hand, the $^1$H NMR spectrum of **2b** gives two kinds of *N*-methyl doublets, showing the presence of two pairs of *N*-methyl groups in different chemical environments. The $^{13}$C NMR spectrum of **2b**, moreover, suggests that one twofold axis through the Co(III) ion exists, as eight signals were observed. The CD spectrum of the complex **2b** is very similar to that of the complex *trans*-[CoCl$_2$(1*R*,2*R*)-chxn)$_2$]$^+$[12], which has four coordinated primary nitrogen atoms and no asymmetric center except for the asymmetric carbon atoms belonging to the (1*R*,2*R*)-1,2-cyclohexanediamine. Since no contribution from the asymmetric nitrogen centers appears in the CD spectrum,

Table 2. Atomic parameters for non-hydrogen atoms, with their standard deviations in parentheses[a)]

| Atom | $x$ | $y$ | $z$ | $B_{eqv}$ |
|---|---|---|---|---|
| Co(1) | 1(1) | 0(1) | −1(1) | 1.7 |
| Co(2) | −204(1) | 4864(1) | 4945(1) | 1.5 |
| Cl(1) | 611(2) | −106(2) | −1814(2) | 2.7 |
| Cl(2) | −647(2) | 112(2) | 1749(2) | 2.8 |
| Cl(3) | −246(2) | 5149(2) | 6983(2) | 2.4 |
| Cl(4) | −160(2) | 4537(2) | 2884(2) | 2.4 |
| Cl(5) | 2496(2) | 9072(2) | 3686(2) | 3.8 |
| Cl(6) | 7060(3) | 10527(3) | 5977(3) | 4.9 |
| Cl(7) | −5716(3) | 7838(2) | 8635(2) | 4.8 |
| Cl(8) | −4784(2) | 2001(2) | 1076(2) | 4.0 |
| O(1) | −5209(7) | 964(7) | 6306(7) | 4.7 |
| O(2) | −5134(8) | 8758(8) | 3237(7) | 5.1 |
| O(3) | −4583(7) | 9584(7) | 1395(6) | 4.8 |
| O(4) | −5699(8) | 356(8) | 8243(7) | 5.5 |
| N(1) | −538(6) | 1309(5) | −486(5) | 2.0 |
| N(2) | 1970(6) | 1619(5) | 868(5) | 2.2 |
| N(3) | −1884(6) | −1665(6) | −1004(5) | 2.1 |
| N(4) | 582(5) | −1258(5) | 570(5) | 1.9 |
| N(5) | −2212(5) | 4350(5) | 4335(5) | 1.8 |
| N(6) | 280(6) | 6737(5) | 4905(5) | 2.0 |
| N(7) | −632(5) | 2977(5) | 4800(5) | 1.8 |
| N(8) | 1835(6) | 5446(5) | 5690(5) | 2.0 |
| C(1) | 697(7) | 2740(6) | 245(7) | 2.2 |
| C(2) | 2016(7) | 2732(6) | 316(7) | 2.1 |
| C(3) | 3346(8) | 4142(7) | 1027(8) | 3.0 |
| C(4) | 3286(9) | 5173(7) | 350(8) | 3.2 |
| C(5) | 1964(9) | 5206(8) | 253(9) | 3.6 |
| C(6) | 628(9) | 3779(8) | −420(9) | 3.3 |
| C(7) | −1880(8) | 1173(8) | −374(8) | 3.2 |
| C(8) | 2547(9) | 2025(8) | 2292(8) | 3.2 |
| C(9) | −1774(7) | −2883(6) | −970(7) | 2.2 |
| C(10) | −766(6) | −2596(6) | 327(6) | 1.9 |
| C(11) | −609(7) | −3786(7) | 474(7) | 2.4 |
| C(12) | −2046(8) | −5040(7) | 241(8) | 3.0 |
| C(13) | −3045(8) | −5368(8) | −1083(8) | 3.4 |
| C(14) | −3190(8) | −4182(8) | −1276(9) | 3.5 |
| C(15) | −2655(9) | −1790(8) | −2331(7) | 3.3 |
| C(16) | 1615(7) | −1452(7) | 86(8) | 2.6 |
| C(17) | −2230(7) | 5636(6) | 4543(6) | 2.0 |
| C(18) | −1029(7) | 6645(6) | 4159(6) | 2.0 |
| C(19) | −996(8) | 7978(7) | 4252(8) | 2.8 |
| C(20) | −2411(9) | 7724(8) | 3461(8) | 3.2 |
| C(21) | −3589(8) | 6765(8) | 3893(8) | 2.9 |
| C(22) | −3641(7) | 5437(7) | 3815(8) | 2.7 |
| C(23) | −3252(8) | 3354(8) | 4832(8) | 3.0 |
| C(24) | 1092(8) | 7832(7) | 6144(7) | 2.8 |
| C(25) | 694(7) | 2963(6) | 5029(6) | 1.9 |
| C(26) | 1858(7) | 4272(6) | 6071(6) | 2.1 |
| C(27) | 3256(8) | 4351(8) | 6365(8) | 3.1 |
| C(28) | 3154(8) | 3111(8) | 6750(9) | 3.4 |
| C(29) | 1994(9) | 1807(8) | 5727(8) | 3.1 |
| C(30) | 600(7) | 1734(7) | 5410(7) | 2.6 |
| C(31) | −1740(7) | 1874(7) | 3606(7) | 2.5 |
| C(32) | 2829(8) | 6112(8) | 4993(8) | 3.3 |

a) Positional parameters are multiplied by $10^4$.

the complex **2b** may have the same numbers of secondary nitrogen centers in opposite configurations, two *R* and two *S*. From these spectral results, three geometrical isomers (*trans-SRRS, trans-RSSR*, and *trans-SSRR*) are possible for the *trans*-dichloro complex with one $C_2$ symmetry. Accordingly, it is difficult to assign the geometry of **2b** by means of the AB, CD, and NMR spectroscopies. The following section will deal with the detailed structural results concerning the **2b** complex obtained from X-ray diffraction.

*Crystal and Molecular Structure of **2b**.* The final atomic coordinates of non-hydrogen atoms are listed in Table 2. The thermal parameters, the parameters for the hydrogen atoms, and the lists of structure factor amplitudes are available as supplementary material.[13)] Selected bond lengths and angles are presented in Tables 3 and 4. Perspective drawings of the complex cations showing ellipsoids of thermal

Table 3. Bond distances ($l$/Å)[a)]

| | | | |
|---|---|---|---|
| Co(1)-Cl(1) | 2.260(3) | Co(2)-Cl(3) | 2.237(2) |
| Co(1)-Cl(2) | 2.218(3) | Co(2)-Cl(4) | 2.263(3) |
| Co(1)-N(1) | 1.998(7) | Co(2)-N(5) | 1.990(6) |
| Co(1)-N(2) | 2.010(7) | Co(2)-N(6) | 1.996(7) |
| Co(1)-N(3) | 1.998(7) | Co(2)-N(7) | 1.996(7) |
| Co(1)-N(4) | 2.002(6) | Co(2)-N(8) | 2.013(6) |
| N(1)-C(1) | 1.517(10) | N(5)-C(17) | 1.495(10) |
| N(2)-C(2) | 1.500(10) | N(6)-C(18) | 1.486(10) |
| N(3)-C(9) | 1.491(10) | N(7)-C(25) | 1.486(10) |
| N(4)-C(10) | 1.516(10) | N(8)-C(26) | 1.501(10) |
| N(1)-C(7) | 1.495(11) | N(5)-C(23) | 1.491(11) |
| N(2)-C(8) | 1.469(12) | N(6)-C(24) | 1.473(11) |
| N(3)-C(15) | 1.482(12) | N(7)-C(31) | 1.490(10) |
| N(4)-C(16) | 1.486(11) | N(8)-C(32) | 1.484(12) |
| C(1)-C(2) | 1.492(11) | C(17)-C(18) | 1.521(11) |
| C(9)-C(10) | 1.503(11) | C(25)-C(26) | 1.521(11) |

a) Estimated standard deviations in parentheses.

Table 4. Bond angles (degree $\phi$/°)[a)]

| | | | |
|---|---|---|---|
| Cl(1)-Co(1)-Cl(2) | 178.4(1) | Cl(3)-Co(2)-Cl(4) | 178.8(1) |
| N(1)-Co(1)-N(2) | 86.5(3) | N(5)-Co(2)-N(6) | 86.3(3) |
| N(3)-Co(2)-N(4) | 86.5(3) | N(7)-Co(2)-N(8) | 86.1(3) |
| Co(1)-N(1)-C(1) | 108.1(5) | Co(2)-N(5)-C(17) | 107.5(5) |
| Co(1)-N(2)-C(2) | 106.0(5) | Co(2)-N(6)-C(18) | 107.7(5) |
| Co(1)-N(3)-C(9) | 108.5(5) | Co(2)-N(7)-C(25) | 109.6(5) |
| Co(1)-N(4)-C(10) | 106.6(4) | Co(2)-N(8)-C(26) | 107.0(5) |
| Co(1)-N(1)-C(7) | 119.9(5) | Co(2)-N(5)-C(23) | 119.8(5) |
| Co(1)-N(2)-C(8) | 118.4(4) | Co(2)-N(6)-C(24) | 117.6(5) |
| Co(1)-N(3)-C(15) | 120.3(5) | Co(2)-N(7)-C(31) | 118.2(5) |
| Co(1)-N(4)-C(16) | 119.9(5) | Co(2)-N(8)-C(32) | 119.6(5) |
| C(1)-N(1)-C(7) | 110.3(6) | C(17)-N(5)-C(23) | 110.6(6) |
| C(2)-N(2)-C(8) | 114.6(7) | C(18)-N(6)-C(24) | 114.5(6) |
| C(9)-N(3)-C(15) | 111.3(6) | C(25)-N(7)-C(31) | 110.2(6) |
| C(10)-N(4)-C(16) | 112.2(6) | C(26)-N(8)-C(32) | 115.0(6) |

a) Estimated standard deviations in parentheses.

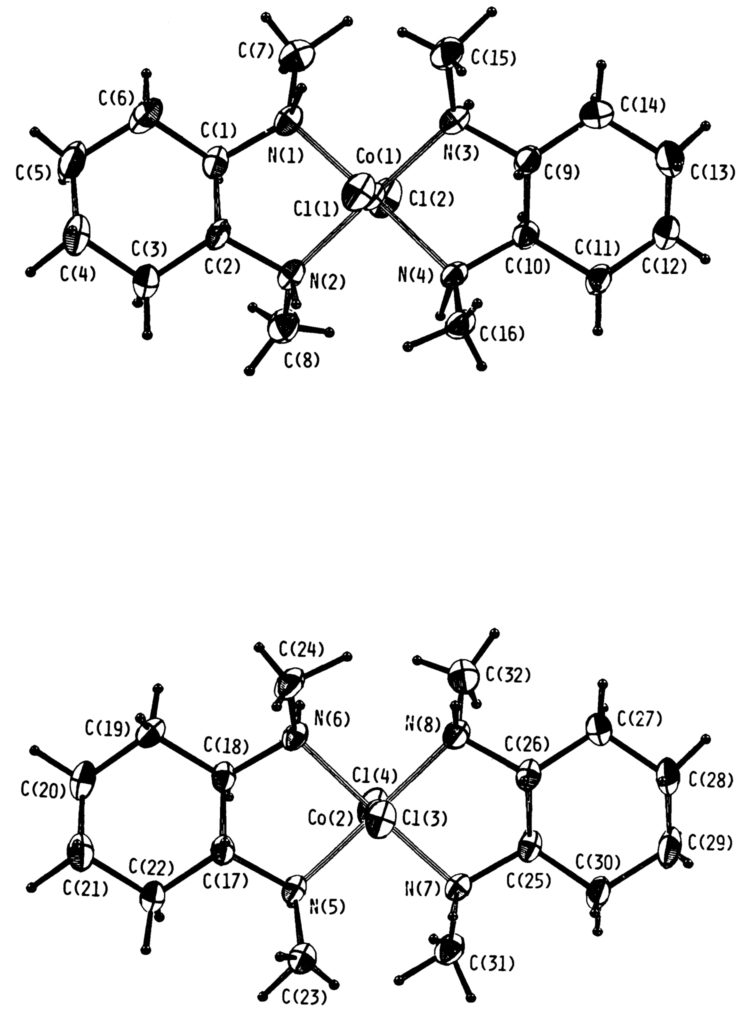


Fig. 4. Perspective drawings of the complex cations $(-)_{435}$-*trans*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$ and the numbering scheme for the atoms.

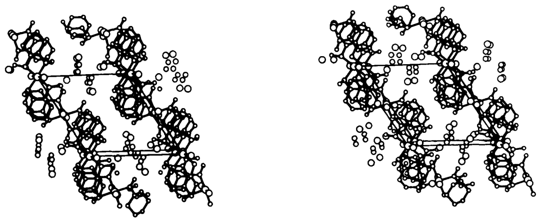


Fig. 5. A stereoscopic illustration of one unit cell, viewed down the c axis with the a axis vertical.

motion are given in Fig. 4. A stereoview of the contents of one unit cell and each conformation of the diamine-chelate rings are shown in Fig. 5 and 6 respectively.

The unit cell consists of 2 complex cations, chloride counterions, hydrochloride molecules, and the 4 waters of crystallization. The two complex cations in one unit cell have almost identical structures. The complex cations have an approximately $C_2$ symmetry. Each cobalt atom is surrounded by four nitrogen atoms and two chlorine atoms at the apices of a slightly distorted octahedron. The chloro groups are in the trans positions. The absolute configurations around the asymmetric carbon centers are both *R* for each cyclohexanediamine. The conformations of the two five-membered chelate rings are both $\lambda$ in each complex ion. The four cyclohexane rings adopt the chair conformation, and all the *C*-methylene groups have equatorial orientation with respect to the chelate rings. The structure of (1*R*,2*R*)-1,2-cyclohexanediamine, used in the syntheses, agrees with the known absolute configurations.[14,15] The arrangements around the secondary nitrogen atoms are the pair of the *R* and *S* configurations in the notation of Cahn, Ingold, and Prelog.[16] In each complex ion, two *N*-methyl groups have equatorial orientations, while the other groups have axial orientations, with respect to the chelate rings. The *N*-methyl group bonded to the nitrogen atom of the *R* or *S* configuration in each diamine is neighboring with the group linked to that of the same configuration of the other respective diamine. This findings as to the structure around the asymmetric nitrogen centers, which involves the asymmetric nitrogen atoms of two *R* and two *S* configurations in each complex ion, agrees with the spectral assignment of **2b** (*vide supra*).

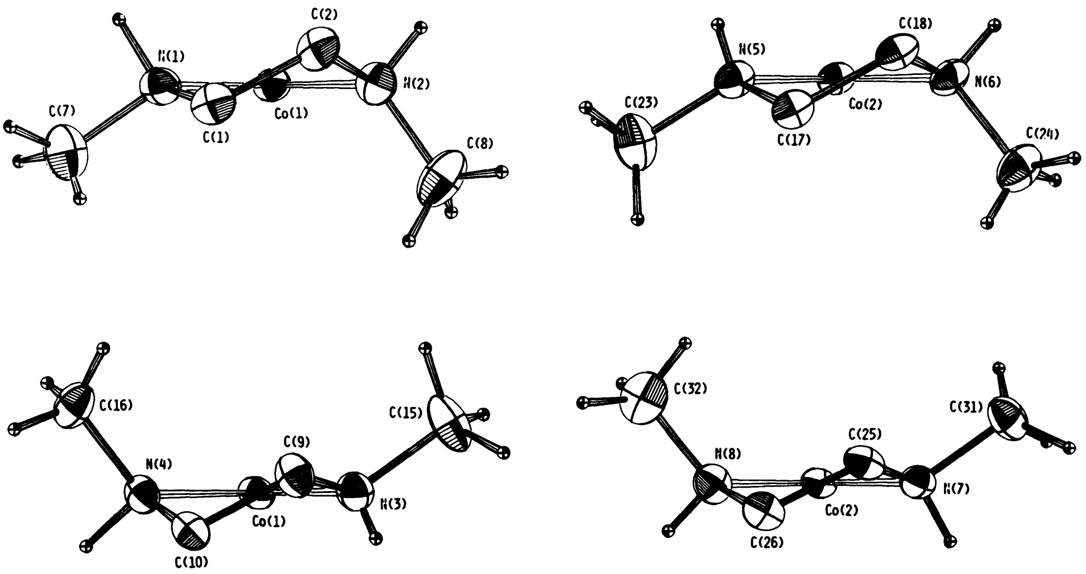


Fig. 6. Each conformation of the four diamine-chelate rings.

The average Co-N bond distance is 1.998(6) Å, slightly longer than the recent values reported for *trans*-[CoCl$_2$(en)$_2$]$^+$; the average Co–N(ethylenediamine) lengths are 1.960(5), 1.960(10), and 1.950(3) Å.[17] Moreover, the present Co-N value is slightly long as compared with the average distances reported for the Co-N bond in *tris*-type complexes involving *trans*-1,2-cyclohexanediamine, 1.972(5) and 1.984(4) Å for (−)$_{589}$-[Co((+)-chxn)$_2$((−)-chxn)]$^{3+}$ and (−)$_{589}$-[Co((−)-chxn)$_3$]$^{3+}$ respectively.[14,15] Such as elongation of the chelate bond Co-N is also occasionally observed in the complexes involving *N*-alkylated diamines, for example, (−)$_{546}$-*trans*-[Co(NO$_2$)$_2$((−)$_{589}$-2,2′-bpp)$_2$]$^+$,[18] *trans*-[Co(pip)$_2$(tpp)]$^+$,[19] and (−)$_{589}$-*cis*-[Co(NO$_2$)$_2$(N$^1$-me-(S)-pn)$_2$]$^+$,[20] where 2,2′-bpp, pip, tpp, and N$^1$-me-(*S*)-pn represent 2,2′-bipiperidine, piperidine, the 5,10,15,20-tetraphenylporphinate anion, and (2*S*)-N$^1$-methyl-1,2-propanediamine respectively, the average Co–N(2,2′-bpp), Co–N(pip), and Co–N(N$^1$-me-(*S*)-pn) distances being 2.004(5), 2.060(3), and 2.015(5) Å respectively. The ring angles at the cobalt atom for the five-membered chelate rings, N(1)–Co(1)–N(2), N(3)–Co(1)–N(4), N(5)–Co(2)–N(6), and N(7)–Co(2)–N(8), are 86.3(2), 86.2(2), 86.7(2), and 86.4(2)° respectively, the average being 86.4(2)°. These angles appear normal for Co(III) five-membered chelate rings, which are usually less than 90°, though the angles of the present complex are slightly larger than those observed in the complexes coordinating the bidentate ligands *trans*-1,2-cyclohexanediamine and 2,2′-bipiperidine described above, which range from 84.1(2) to 84.7(2)°. The Co–Cl bond lengths of Co(1)–Cl(1) and Co(2)–Cl(4) are 2.261(3) and 2.264(3) Å, which can be compared with the mean values of 2.253(2), 2.254(3), 2.244(1), and 2.26 Å in *trans*-[CoCl$_2$(en)$_2$]$^+$,[17] 2.26 Å in *trans*-[CoCl$_2$(1,3-propanediamine$_2$]$^+$,[21] and 2.257(2) Å in *trans*-[CoCl$_2$((−)-1,2-cyclopentanediamine)$_2$]$^+$,[22] where as the bond lengths of Co(1)–Cl(2) and Co(2)–Cl(3) are 2.217(3) and 2.236(3) Å respectively, slightly shorter than the other values. The average N–C and C–C distances, 1.491(11) and 1.518(12) Å respectively, are comparable with the reported values in (−)$_{589}$-[Co((+)-chxn)$_2$((−)-chxn)]$^{3+}$ (1.486(7) and 1.498(8) Å) and (−)$_{589}$-[Co((−)-chxn)$_3$]$^{3+}$ (1.494(7) and 1.516(8) Å), for the mean N–C and C–C distances respectively of the cyclohexanediamine. The average C–C bond distance of the chelate-ring carbon atoms is 1.509(11) Å, which is quite normal for Co(III) five-membered chelate rings. The average bond angle at the carbon and nitrogen atoms for the (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine is 111.6°, which is slightly large as compared with the idealized tetrahedral values of 109.5°. This enlargement of the average bond angle of the ligand is mainly due to the larger angles at the carbon and nitrogen atoms belonging to the asymmetric nitrogen atoms whose absolute configurations are *R* around them; for example, the bond angles of N(2)–C(2)–C(3), N(4)–C(10)–C(11), N(6)–C(18)–C(19), and N(8)–C(26)–C(27) are 114.5(7), 116.5(6), 116.9(7), and 115.8(5)° respectively.

Thus, the exact structure of the (+)$_{435}$-*trans*-dichloro complex **2b**, which could not be determined by usual spectroscopy, has been elucidated as the isomer *trans-SRRS* (Fig. 3b, X=Cl$^-$). On the basis of the spectral evidence and the crystal structure of these two *trans*-dichloro complexes **1b** and **2b**, the structures of their precursors, **1a** and **2a**, will be discussed in the following section.

*Structural Assignment of the Precursors.* It is generally acknowledged that the AB spectral patterns of Co(III) diacidobis(diamine) complexes are characteristic of their geometry.[23] It is recognized that *cis*- and *trans*-dinitro complexes of Co(III) show

$\lambda_{max}$ at ≈330 nm and ≈350 nm respectively. The present dinitro complex **1a** shows $\lambda_{max}$ at 351 nm (Fig. 1a), showing that it has the *trans* configuration with respect to the two nitro groups. The $^1H$ NMR spectrum of Ia shows an *N*-methyl signal at $\delta$ 2.10, indicating that the four methyl groups in the complex ion are in the same chemical environment. In the $^{13}C$ NMR spectrum of **1a**, moreover, four signals were observed when irradiating all of the hydrogen nuclei. Because the dinitro complex **1a** contains 16 carbon atoms, this result means that **1a** has a triple twofold symmetry, like the derived dichloro complex **1b**. Generally, the absolute configuration of the coordinated asymmetric nitrogen centers can be effected to fit in with *S* arrangements when the five-membered chelates adopt the $\lambda$-gauche conformations, as has been indicated in the case of the Co(III) complex containing *N*-methylethylenediamine.[24] The absolute configurations around the four asymmetric nitrogen atoms of **1a**, therefore, can be concluded to all be *S*, and the four methyl groups can be concluded to have an equatorial orientation with respect to the chelate rings (Fig. 3b, *trans-SSSS*, $X=NO_2^-$).

The visible absorption spectrum of **2a** is very similar to that of *cis*-$[Co(CO_3)(en)_2]^+$,[25] and it gives the typical *cis*-$[CoN_4O_2]^+$ absorption (Fig. 1a). In the CD spectrum of **2a**, a large positive Cotton effect has been observed in the first absorption region, comparable with that of $\Lambda$-$[Co(CO_3)((2R)\text{-}1,2\text{-propanediamine})_2]^+$.[26] The absolute configuration around Co(III) can be assigned to $\Lambda$ on the basis of this observaton. The $^1H$ NMR spectrum of **2a** shows two kinds of *N*-methyl signals, like the derived dichloro complex **2b**. Moreover, nine signals were observed in the $^{13}C$ NMR spectrum of **2a**, though the carbonato complex contains 17 carbon atoms. It has been elucidated by the present X-ray study that the *trans*-dichloro complex **2b** derived from this carbonato complex **2a** has two secondary nitrogen atoms of the *R* configuration and two of those of the *S* arrangement in each diamine. It can be expected that the carbonato complex reacts with hydrochloric acid to yield the *trans*-dichloro complex, with a retention of the absolute configuration of the asymmetric nitrogen centers. From these considerations, the structure of the carbonato complex **2a** may be restricted to either the *cis-SRRS* or *cis-RSSR* isomer (Fig. 3a), though ten structures are theoretically possible. According to the molecular model study, the *cis-SRRS* isomer seems to be more stable than the latter, since the *N*-methyl groups bonded to the asymmetric nitrogen atom of the *R* configuration in the isomer is distant from the neighboring diamine chelate ring, while those of the *S* configuration in the *cis-RSSR* are close to the corresponding chelate ring. Thus, the present carbonato complex **2a** can be tentatively assigned to the *cis-SRRS* isomer.

Thus, the new complexes, $(-)_{546}$-*trans-(SSSS)*-$[Co(NO_2)_2(R,R\text{-dmchxn})_2]^+$, $(+)_{546}$-$\Lambda$-$[Co(CO_3)(R,R\text{-dmchxn})_2]^+$, $(-)_{435}$-*trans-(SSSS)*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$, and $(+)_{435}$-*trans-(SRRS)*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$, were prepared and characterized. It is evident that $(+)_{546}$-$\Lambda$-$[Co(CO_3)(R,R\text{-dmchxn})_2]^+$ was converted by concentrated HCl to $(+)_{435}$-*trans-(SRRS)*-$[CoCl_2(R,R\text{-dmchxn})_2]^+$, with a retention of the configuration of the secondary nitrogen atoms. This observation will be very important in discussing the mechanism of the *cis-trans* conversion reaction when the exact structure of the starting carbonato complex can be determined by means of X-ray crystallography.

For all four complexes investigated in this study, the stereospecific formation has been observed. For the $[Co(CO_3)(R,R\text{-dmchxn})_2]^+$ complex, only the $\Lambda$ isomer has been detected. This result indicates that suitably designed diamines could govern the overall geometry of the complexes and afford useful coordination sites for the asymmetric reactions, as is observed in the case of the linear tetradentate tetraamines.[1,2,27]

Studies are now in progress to establish the stereochemistry of this system in hoping to clarify the mechanism for the *cis-trans* conversion reaction and to develop suitable ligands for metal-assisted asymmetric reactions.

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