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Metal Complexes Containing Six-membered Chelate Rings. IV. The Preparation and Structure of Dichlorocobalt(III) Complexes with Tetramines Derived from 2,4-Pentanediamine[1)]

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The tetramine ligands, 4,6-dimethyl-3,7-diaza-1,9-nonanediamine (2,3″, 2-tet), 6,8-dimethyl-2,5,9,12-tetraazatridecane (N,N'-Me_2-2,3″, 2-tet), and 4,9-dimethyl-5,8-diaza-2,11-dodecanediamine (3″,2,3″-tet), were prepared by using *RR*- and *RS*-2,4-pentanediamine as the starting material. Six kinds of *trans*-dichloro cobalt(III) complexes with these ligands were prepared and characterized. Among these complexes, three kinds of optically active complexes were obtained. The *RR*-2,4-pentanediamine and *RS*-2,4-pentanediamine parts in these complexes were considered to take a λ-skew-boat and a chair conformation respectively on the basis of molecular models, PMR, and the absorption and CD spectra.

Many cobalt(III) complexes with tetramine containing one or two β-diamine parts have been prepared in recent years.[2–9)] In these complexes, the most probable conformations for the β-diamine part have been considered to be the chair and skew-boat (or twist) conformations. Actually, two isomers in the *trans*-dichloro (3, 7-diaza-1,9-nonanediamine) cobalt(III) complex, *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$, have been isolated.[2–4)] One has been assigned to the *meso* structure, in which the six-membered chelate ring takes a chair form. The other has been assigned to the racemic structure, giving a skew-boat conformation. It is considered that the *meso* isomer is thermodynamically more stable than the racemic isomer, since the latter isomerizes to the former in a methanolic solution.

On the other hand, the *trans*-dichloro(4,7-diaza-1, 10-decanediamine)cobalt(III) complex, *trans*-$[CoCl_2(3,2,3\text{-tet})]^+$, which has also previously been isolated, is of only one kind and has been assigned a structure in which both the six-membered chelate rings take the chair conformation and both the secondary nitrogen atoms give the same configuration.[5–8)]

Previously, we have reported that, in the cobalt(III) complexes containing 2,4-pentanediamine (2,4-ptn), *RR*-, *SS*- and *RS*-2,4-pentanediamine give the λ- and δ-skew-boat and chair conformations respectively in six-membered chelate rings.[10,11)] Accordingly, it seemed that it would be interesting to prepare cobalt(III) complexes containing tetramines derived from 2,4-pentanediamines. Thus, in the present study, seven tetramines, *R*(4),*R*(6)- and *R*(4),*S*(6)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (*RR*-2,3″,2-tet and *RS*-2,3″, 2-tet), *R*(6),*S*(8)-6,8-dimethyl-2,5,9,12-tetraazatridecane (N,N'-Me_2-*RS*-2,3″,2-tet) and *R*(2),*R*(4),*R*(9), *R*(11), *R*(2),*S*(4),*S*(9),*R*(11)-, *S*(2),*R*(4),*R*(9),*S*(11)-, and *R*(2),*S*(4),*R*(9),*S*(11)-4,9-dimethyl-5,8-diaza-2,11-dodecanediamine (*RRRR*-, *RSSR*-, *SRRS*-, and *RSRS*-3″,2,3″-tet), were prepared.

This paper will deal with the preparation and structure of cobalt(III) complexes containing these tetramines on the basis of molecular models, PMR, and the absorption and CD spectra.

Experimental

Preparation of Ligands. The 4,6-dimethyl-3,7-diaza-1,9-nonanediamine (2,3″,2-tet) and 6,8-dimethyl-2,5,9,12-tetraazatridecane (N,N'-Me_2-2,3″,2-tet) were synthesized by a method similar to that used for *C*-substituted triethylenetetramine by Goto, Saburi and Yoshikawa.[12)] The 4,9-dimethyl-5,8-diaza-2,11-dodecanediamine (3″,2,3″-tet) was synthesized according to a method similar to that used for 4,7-diaza-1,10-decanediamine (3,2,3-tet) by Hamilton and Alexander.[2)] Thus, these ligands were prepared from 2,4-pentanediamines as shown in Schemes I, II, and III.

Scheme I (*Method I*)

$$\mathrm{2ClCH_2COCl + NH_2CH(CH_3)CH_2CH(CH_3)NH_2 \xrightarrow{NaOH}}$$
$$\mathrm{ClCH_2CONHCH(CH_3)CH_2CH(CH_3)NHCOCH_2Cl \xrightarrow{NH_3\ aq.}}$$
$$\mathrm{NH_2CH_2CONHCH(CH_3)CH_2CH(CH_3)NHCONH_2 \cdot 2HCl \xrightarrow{LiAlH_4}}$$
$$\mathrm{NH_2CH_2CH_2NHCH(CH_3)CH_2CH(CH_3)NHCH_2CH_2NH_2}$$

(2,3″,2-tet)

Scheme II (*Method II*)

$$\mathrm{2ClCH_2COCl + NH_2CH(CH_3)CH_2CH(CH_3)NH_2 \xrightarrow{NaOH}}$$
$$\mathrm{ClCH_2CONHCH(CH_3)CH_2CH(CH_3)NHCOCH_2Cl \xrightarrow{CH_3NH_2\ aq.}}$$
$$\mathrm{CH_3NHCH_2CONHCH(CH_3)CH_2CH(CH_3)NHCOCH_2\text{-}}$$
$$\mathrm{NHCH_3 \cdot 2HCl \xrightarrow{LiAlH_4}}$$
$$\mathrm{CH_3NHCH_2CH_2NHCH(CH_3)CH_2CH(CH_3)\text{-}}$$
$$\mathrm{NHCH_2CH_2NHCH_3}$$

(N,N'-Me_2-2,3″,2-tet)

Scheme III (*Method III*)

$$\mathrm{2NH_2CH(CH_3)CH_2CH(CH_3)NH_2 + BrCH_2CH_2Br \xrightarrow{C_2H_5ONa}}$$
$$\mathrm{NH_2CH(CH_3)CH_2CH(CH_3)NHCH_2CH_2NHCH(CH_3)\text{-}}$$
$$\mathrm{CH_2CH(CH_3)NH_2}$$

(3″,2,3″-tet)

The optically active (*RR* and *SS*) and *meso* (*RS*) 2,4-pentanediamine (2,4-ptn) used as the starting materials in the preparation of the tetramines were synthesized according to a method reported previously.[10,13–15)]

R(4),R(6)-*4,6-Dimethyl-3,7-diaza-1,9-nonanediamine* (RR-*2, 3″,2-tet*): To 120 ml of a vigorously stirred aqueous

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sodium hydroxide solution (5 M NaOH), cooled in an ice-salt bath, was added 13.7 g of *RR*-2,4-pentanediamine (0.135 mol). A solution of chloroacetyl chloride (32 g, 0.28 mol) in 100 ml of benzene was then added dropwise over a period of 30 min. The solution was stirred and cooled throughout the addition. The reaction mixture was then allowed to stand at room temperature for another 3 hr. The resulting precipitate, *N,N′*-bis(chloroacetyl)-*RR*-2,4-pentanediamine, was filtered, washed with cold water, and dried under a vacuum. The product was purified by recrystallization from ethanol; yield, 25.3 g (74%); $[\alpha]^{28}_{D}$ +6.11. Found: C, 42.05; H, 6.46; N, 11.01%. Calcd for $C_9H_{16}N_2O_2Cl_2$: C, 42.37; H, 6.32; N, 10.98%.

The *N,N′*-bis(chloroacetyl)-*RR*-2,4-pentanediamine (11.2 g) and 100 g of ammonium carbonate were dissolved in 500 ml of a 28% ammonium hydroxyide solution. The solution was allowed to stand for 10 days and then evaporated to dryness at 60 °C on a rotary evaporator. The product, 4,6-dimethyl-3,7-diaza-1,9-diaminononane-2,8-dione dihydrochloride, which was a pale yellow oil, was dried in a vacumm desiccator over phosphorous pentoxide and used in the next step without further purification.

The product obtained above (14 g) was dissolved in 200 ml of dry tetrahydrofuran (THF). The solution was then placed into a 500-ml, four-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser with a soda lime tube. To the vigorously stirred solution was added 11 g of lithium aluminum hydride in small portions while the vessel was kept in an ice-cold bath. After the addition was complete, the mixture was allowed to stand at room temperature for another 30 min and then refluxed overnight. The reaction mixture was cooled in an ice-cold bath and carefully quenched by the dropwise addition of 30 ml of water. The white precipitate was filtered off. The filtered solid was then washed twice with 200 ml of boiling THF. The combined filtrate and washing were evaporated on a rotary evaporator. The oily residue, the crude *R*(4),*R*(6)-dimethyl-3,7-diaza-1,9-nonanediamine (*RR*-2,3″,2-tet), was used in the synthesis of the cobalt(III) complex without further purification. However, the cobalt(III) complex of this tetramine gave very satisfactory analytical results as stated in the preparation of complexes. Therefore, the oily residue is the desired product (*RR*-2,3″,2-tet).

R(4),S(6)-*Dimethyl-3,7-diaza-1,9-nonanediamine* (RS-*2,3″,2-tet*): *N,N′*-Bis(chloroacetyl)-*RS*-2,4-pentanediamine was prepared from *RS*-2,4-pentanediamine and chloroacetyl chloride by a method similar to that used for the corresponding *RR*-2,3″,2-tet described above. Found: C, 42.46; H, 6.34; N, 10.98%. Calcd for $C_9H_{16}N_2O_2Cl$: C, 42.37; H, 6.32; N, 10.98%.

The remainder of the procedure used to obtain *RS*-2,3″,2-tet is identical with the method for the corresponding *RR*-2,3″,2-tet described above. The elemental analysis of *RS*-2,3″,2-tet was achieved by the formation of the cobalt(III) complex as well as the *RR*-2,3″,2-tet described above.

R(6), S(8)-*6,8-Dimethyl-2,5,9,12-tetraazatridecane* (N,N′-*Me*$_2$-RS-*2,3″,2*-tet): According to Method II, *N,N′*-bis-(chloroacetyl)-*RS*-2,4-pentanediamine (11.2 g) wasdissolved in an aqueous solution of 30% methylamine. The solution was allowed to stand for 10 days and then evaporated to dryness on a rotary evaporator. The product, *R*(6), *S*(8)-6, 8-dimethyl-2,5,9,12-tetraazatridecane-4,10-dione, was used in the next step without further purification. The remainder of the procedure was identical with that of the method for the corresponding *RR*-2,3″,2-tet described above. The elemental analysis of *N,N′*-Me$_2$-*RS*-2,3″,2-tet was achieved by the formation of the cobalt(III) complex as well as the *RR*-2,3″,2-tet described above.

R(2),S(4),S(9),R(11)-, S(2),R(4),R(9),S(11)-, *and* R-(2), S(4),R(9),S(11)-*4,9-Dimethyl-5,8-diaza-2,11-dodecanediamine* (RSSR-, SRRS-, *and* RSRS-*3″,2,3,″-tet*): The procedure reported by Hamilton and Alexander[3] was modified. To a vigorously stirred solution of *RS*-2,4-pentanediamine (26.7 g) in 100 ml of ethanol was added 10 g of 1,2-dibromoethane in small portions. The solution was stirred and the temperature kept at about 50 °C in a water bath throughout the addition. The reaction mixture was stirred at 50 °C for another 1.5 hr and then refluxed for 12 hr. The reaction mixture was subsequently cooled to room temperature. To the vigorously stirred solution was added 2.5 g of metallic sodium in small portions. The reaction mixture was stirred at 50 °C for another 2 hr and cooled to 0 °C. After filtration, the ethanol was removed by distillation. The product, a mixture of *RSSR*-, *SRRS*- and *RSRS*-3″,2,3″-tet, was then collected by vacuum distillation at 140—160 °C (3 mmHg). Found: C, 63.15; H, 13.18; N, 23.71%. Calcd for $C_{12}H_{30}N_4$: C, 62.56; H, 13.13; N, 24.32%. A mixture of *RSSR*-, *SRRS*-, and *RSRS*-3″,2,3″-tet was separated by complexing with cobalt(III) ions as described below.

R(2),R(4),R(9),R(11)-*4,9-Dimethyl-5,8-diaza-2,11-dodecanediamine* (RRRR-*3″,2,3″-tet*): This was prepared from *RR*-2,4-pentanediamine and 1,2-dibromoethane by a method similar to that used for the corresponding *RSSR*-, *SRRS*-, and *RSRS*-3″,2,3″-tet described above. The rotation of *RRRR*-3″,2,3″-tet in water showed a plus sign at the Na D line. This tetramine gave only an approximate coincidence between the found and calculated analytical results, but its cobalt(III) complex gave very satisfactory analytical results.

Preparation of Cobalt(III) Complexes. (+)$_{600}$-trans-[*CoCl*$_2$(RR-*2,3″,2-tet*)]*ClO*$_4$: The ligand, *RR*-2,3″,2-tet (1 g), was added to 60 ml of an aqueous solution containing 1.2 g of cobalt(II) chloride hexahydrate and the solution was aerated with carbon dioxide-free air for 10 hr at room temperature. The solution was then filtered off, and the insoluble material was washed with a small amount of water. The filtrate and the washing were combined. To the solution was added 20 ml of concd HCl. The solution was warmed at 60 °C for 30 min to give a green solution. This solution was concentrated to 50 ml at 50 °C on a water bath and cooled to room temperature. To the solution was added 15 ml of 60% perchloric acid. The solution was allowed to stand overnight in a refrigerator. The green crystals were then filtered off, washed with a small amount of cold ethanol and ether, and air-dried. Yield: 60%. Found: C, 25.87; H, 5.92; N, 13.09%. Calcd for $C_9H_{24}N_4Cl_3CoO_4$: C, 25.89; H, 5.79; N, 13.42%.

trans-[*CoCl*$_2$(RS-*2,3″,2-tet*)]*ClO*$_4$, trans-[*CoCl*$_2$(*N,N′-Me*$_2$-RS-*2,3″,2-tet*)]*ClO*$_4$: These complexes were prepared from $CoCl_2 \cdot 6H_2O$ and *RS*-2,3″,2-tet or *N,N′*-Me$_2$-*RS*-2,3″,2-tet by a method similar to that used for the corresponding *RR*-2,3″,2-tet complex described above. *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]ClO$_4$ is soluble in water, but *trans*-[CoCl$_2$(*N,N′*-Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$ is only slightly soluble. The yields of the former and the latter: 50% and 80% respectively. Found: C, 25.92 H, 6.03; N, 13.15%. Calcd for $C_9H_{24}N_4Cl_3CoO_4$: C, 25.89; H, 5.79; N, 13.42%. Found: C, 29.48; H, 6.70; N, 12.52%. Calcd for $C_{11}H_{28}N_4Cl_3CoO_4$: C, 29.64; H, 6.33; N, 12.57%.

trans-[*CoCl*$_2$(RSSR- *and* SRRS-3″,2,3″-*tet*)]*Cl*·*H*$_2$*O*: A mixed tetramine containing a racemic pair (*RSSR* and *SRRS*) and *meso* (*RSRS*) 3″,2,3″-tet (11 g) was dissolved in 120 ml of water. To the solution was added 11.4 g of $CoCl_2 \cdot 6H_2O$. The solution was aerated with carbon dioxide-free air for

14 hr at room temperature. The deposited green powder was filtered off and washed with a small amount of water. The filtrate and the washing were then combined. To this solution was added 100 ml of concd HCl. The resulting green precipitate was filtered off and washed with a small amount of cold water. The powder and the precipitate were combined and recrystallized from water by adding concd HCl. Yield: 7.6 g. Found: C, 34.50; H, 7.96; N, 13.55%. Calcd for $C_{12}H_{32}N_4Cl_3CoO$: C, 34.84; H, 7.80; N, 13.54%.

trans-[*CoCl*$_2$(RSRS-*3″,2,3″-tet*)]*ClO*$_4$: To the blue filtrate from which the green crystals of *trans*-[$CoCl_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O had been removed, was added 60 ml of 60% perchloric acid. The solution was then concentrated on a water bath at 60 °C to yield green crystals, though the color of the solution remained blue. The green crystals were recrystallized from hot methanol. Yield 8 g. Found C, 31.58; H, 6.56; N, 11.89%. Calcd for $C_{12}H_{30}N_4Cl_3CoO_4$: C, 31.35; H, 6.58; N, 12.19%.

This complex showed a green color in the methanol solution, but a blue-violet in a concd HCl solution. This shows that the complex takes the *trans* (Cl–Cl) configuration in the methanol and the *cis* (Cl–Cl) configuration in the concd HCl solution.

cis-[*CoCl*$_2$(RSRS-*3″,2,3″-tet*)]*Cl*: The blue filtrate from which the green crystals of *trans*-[$CoCl_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O had been removed was concentrated on a water bath at 60 °C. The deposited blue-violet powder was filtered off and dried over sodium hydroxide under reduced pressure. The complex was recrystallized from concd HCl by evaporating on a water bath at 60 °C. Found: C, 36.00; H, 7.85; N, 13.84%. Calcd for $C_{12}H_{30}N_4Cl_3Co$: C, 36.43; H, 7.64; N, 14.16%.

This complex showed a blue-violet color (*cis* (Cl–Cl)) in a concd HCl solution, but a green color (*trans* (Cl–Cl)) in the methanol solution.

$(+)_{600}$-trans-[*CoCl*$_2$(RSSR-*3″,2,3″-tet*)]*Cl*·H_2O: The *trans*-[$CoCl_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O complex (5 g) was dissolved in 100 ml of water. To the solution was added 2.4 g of potassium oxalate monohydrate, and the solution was warmed at 70 °C for 4 hr. The reaction mixture was evaporated to dryness at 60 °C under reduced pressure. The residue was dissolved in 95% ethanol, and the potassium chloride was removed by filtration. The product was crystallized by gradually evaporating the filtrate. This product was assigned to *cisβ*-[Co(ox)(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O, because its PMR spectrum showed four kinds of methyl signals.

The *cisβ*-[Co(ox)(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O complex (3.1 g) was dissolved in 200 ml of water at 60 °C. To the solution was added a solution of sodium hydrogen dibenzoyl-*d*-tartrate (3.3 g) in 200 ml of hot water. The solution was stirred at 60 °C for 6 hr. The solution was subsequently cooled to room temperature, and the deposited powder was filtered off. The filtrate was concentrated to 250 ml, and the precipitated second powder was filtered off. To the second filtrate was added an appropriate amount of concd HCl slowly. The solution was stirred throughout the addition. The deposited white precipitate was filtered off. The third filtrate was evaporated in a vacuum desiccator over potassium hydroxide, and the resulting red crystals were filtered off. Red crystals were recrystallized fractionally from water until the CD spectra exhibited a constant curve.

This optically pure complex of oxalatotetramine was dissolved in concd HCl and warmed at 70 °C for 3 hr. The resulting green crystals were filtered off, washed with a small amount of cold water and ethanol, and air-dried. It was found that the optically active complex of oxalatotetramine was almost quantitatively converted to the $(+)_{600}$-*trans*-dichloro complex by this procedure. Found: C, 34.84; H, 7.62; N, 13.14%. Calcd for $C_{12}H_{32}N_4Cl_3CoO$: C, 34.84; H, 7.80; N, 13.54%.

The $(+)_{600}$-*trans*[$CoCl_2$(*RSSR*-3″,2,3″-tet)]Cl·H_2O complex was also obtained by the optical resolution of *trans*-[$CoCl_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H_2O in water using sodium hydrogen dibenzoyl-*d*-tartrate as the resolving agent. This procedure was not very good, however, because the *trans*-[$CoCl_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]$^+$ aquated slowly in water.

$(-)_{600}$-trans-[*CoCl*$_2$(*RRRR-3″,2,3″-tet*)]*ClO*$_4$·*H*$_2$*O*: This complex was prepared from $CoCl_2·6H_2O$ and *RRRR*-3″,2,3″-tet by a method similar to that used for the corresponding *RR*-2,3″,2-tet described above. *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$ClO_4·H_2O$ aquated slowly in water at room temperature, as did the other *trans*-2,3″,2-tet and 3″,2,3″-tet complexes of cobalt(III) except for *trans*-[($CoCl_2$(*RSRS*-3″,2,3″-tet)]ClO_4. Found: C, 30.61; H, 6.78; N, 12.15%. Calcd for $C_{12}H_{32}N_4Cl_3CoO_5$: C, 30.17, H, 6.75; N, 11.73%.

Measurements. The visible and ultraviolet absorption spectra were recorded with a Hitachi 124 recording spectrophotometer. The CD curves were recorded with Model ORD/UV-5 spectrophotometer of the Japan Spectroscopic Co., with a CD attachment. The spectra of the *trans*-dichloro complexes were recorded in a methanol solution, while the spectrum of the *cis*-dichloro complex was recorded in a concd HCl solution. The PMR spectra were obtained with Varian T-60 and HA-100 spectrophotometers, using Na-TMS as the internal standard. The perchlorate salts of three *trans*-dichloro complexes, *trans*-[$CoCl_2$(*RR*-2,3″,2-tet)]ClO_4, *trans*-[$CoCl_2$(*RS*-2,3″,2-tet)]ClO_4, and *trans*-[$CoCl_2$(*N,N′*-Me_2-*RS*-2,3″,2-tet)]ClO_4, were converted into chloride salts by the use of an anion exchanger, Dowex 1-X4, because the perchlorate salts were not sufficiently soluble in D_2O. The PMR spectra of the corresponding *RSSR*-, *SRRS*-, and *RSRS*-3″,2,3″-tet complexes could not be obtained, because these complexes were not sufficiently soluble in D_2O. All the measurements were made at room temperature.

Results and Discussion

Geometrical Isomers of Complexes and Configurations of Ligands. Three topological isomers are possible for the dichlorotetramine complexes of cobalt(III). However, it is rare that all three isomers are prepared by the usual air-oxidation procedure. In fact, the *trans* isomer is preferentially produced in the 2,3,2-tet and 3,2,3-tet complexes of cobalt(III).[2,3] While, on the contrary, the main products are *cis*-dichloro isomers (*cisα*, *cisβ*) in the triethylenetetramine complexes of cobalt(III).[18–20] This difference may be roughly attributed to the reaction rate, the solubility, and the steric factor of the complexes.

In the present study, dichlorotetramine cobalt(III) complexes were prepared by using the usual air-oxidation procedure. The green dichloro isomers only could be isolated from the reaction solution when any of the five tetramines (*RR*-2,3″,2-tet, *RS*-2,3″,2-tet, *N,N′*-Me_2-*RS*-2,3″,2-tet, *RRRR*-3″,2,3″-tet, and a racemic pair of *RSSR*- and *SRRS*-3″,2,3″-tet) was employed as a ligand. In the case of the [$CoCl_2$-(*RSRS*-3″,2,3″-tet)]$^+$ complexes, however, the blue-violet salt of [$CoCl_2$(*RSRS*-3″,2,3″-tet)]Cl and the green salt of [$CoCl_2$(*RSRS*-3″,2,3″-tet)]ClO_4 could be

Table 1. Numerical data of absorption (AB) and circular dichroism (CD) $\tilde{\nu}$ in 10^3 cm^{-1}, (log ε) and (ε_l-ε_r)

Complex	AB		CD	
trans-[CoCl$_2$(*RS*-2,3″,2-tet)]ClO$_4$	16.16	(1.64)		
	21.83	(1.57)		
	25.45	(1.76)		
	32.26	(3.17)		
	39.53	(4.40)		
trans-[CoCl$_2$(*RR*-2,3″,2-tet)]ClO$_4$	16.16	(1.70)	15.27	(−0.42)
			16.95	(+0.36)
	ca. 21.80	(*ca.* 1.45)	21.51	(−0.60)
	26.11	(1.75)	25.32	(+0.26)
	32.57	(3.15)	30.58	(−1.21)
	39.52	(4.35)	40.32	(+7.66)
trans-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$	15.77	(1.57)		
	20.83	(1.48)		
	24.88	(1.84)		
	ca. 31.80	(*ca.* 3.23)		
	39.06	(4.39)		
trans-[CoCl$_2$(*RRRR*-3″,2,3″-tet)]ClO$_4$·H$_2$O	15.90	(1.64)	15.87	(+0.59)
	21.74	(1.56)	21.05	(−1.04)
	25.45	(1.81)	26.32	(+0.57)
	32.26	(3.33)	33.33	(−1.65)
	39.06	(4.37)	39.37	(+16.49)
trans-[CoCl$_2$(*RSSR*-3″,2,3″-tet)]Cl·H$_2$O	15.87	(1.60)	15.15	(−0.23)
			16.81	(+0.07)
	21.41	(1.53)	21.28	(+0.07)
	25.19	(1.81)	26.04	(−0.29)
	31.95	(3.25)	30.30	(−0.39)
			34.01	(+2.68)
	39.06	(4.41)	37.04	(−5.39)
trans-[CoCl$_2$(*RSRS*-3″,2,3″-tet)]ClO$_4$	15.77	(1.66)		
	21.28	(1.53)		
	25.19	(1.86)		
	31.95	(3.23)		
	38.91	(4.34)		

isolated from the reaction solution as described in detail in Experimental. The six green complexes and the blue-violet complex prepared here were assigned to the *trans*(Cl–Cl) and *cis*(Cl–Cl) structures respectively from their characteristic color and absorption spectra, as shown in Figs. 5—7 and Table 1.

The configurational assignments of the asymmetric carbon atoms in the ligands of *RR*-2,3″,2-tet, *RS*-2,3″,2-tet, *N*,*N*′-Me$_2$-*RS*-2,3″,2-tet, and *RRRR*-3″,2,3″-tet were confirmed unequivocally from the preparative processes of these tetramines described in Experimental.

However, when *RS*-2,4-pentanediamine was employed as the starting material in Method III, the products of the reaction contained three isomers of 3″,2,3″-tet, *meso* (*RSRS*), and a pair of racemic (*RSSR* and *SRRS*) tetramines. These three isomers were separated, resolved, and characterized on the basis of the following considerations. The molecular models indicate that *RSRS*-3″,2,3″-tet and racemic (*RSSR* and *SRRS*) 3″,2,3″-tet tend to form *cis*-[CoCl$_2$(*RSRS*-3″,2,3″-tet)]$^+$ and *trans*-[CoCl$_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]$^+$ complexes respectively by the steric regulation of the ligands. In the first stage, a mixture of *meso* and racemic tetramine was separated by complexing with the cobalt(III) ion as follows (see Experimental). The green chloride salt was obtained in the step of air-oxidation, and then from its filtrate blue-violet chloride and green perchlorate salts were obtained. The first green chloride could be resolved into the optically active form ((+)$_{600}$-*trans*-isomer). This complex may be assigned to *trans*-[CoCl$_2$(*RSSR*- and *SRRS*-3″,2,3″-tet)]Cl·H$_2$O. The blue-violet chloride salt may be assigned to *cis*-[CoCl$_2$(*RSRS*-3″,2,3″-tet)]Cl on the basis of a molecular-model study. This *cis*-dichloro complex was converted to *trans*-dichloro complex in the methanolic solution. The absorption spectrum of this *trans*-dichloro complex is in accord with that of the secondarily obtained green perchlorate salt, which was converted to the *cis*-dichloro form in concentrated hydrochloric acid. The green perchlorate salt may be *trans*-[CoCl$_2$(*RSRS*-3″,2,3″-tet)]ClO$_4$.

In the second stage, the configuration of the tetramine ligand in (+)$_{600}$-*trans*-dichloro complex was determined. The molecular models indicate that the most stable forms among the possible isomers in [Co(ox) (*RSSR*-3″,2,3″-tet)]$^+$ and [Co(ox) (*SRRS*-3″,2,3″-tet)]$^+$ are the *Δ*-*cisβ* and *Λ*-*cisβ* isomer respectively. The oxalatotetramine complex prepared from the

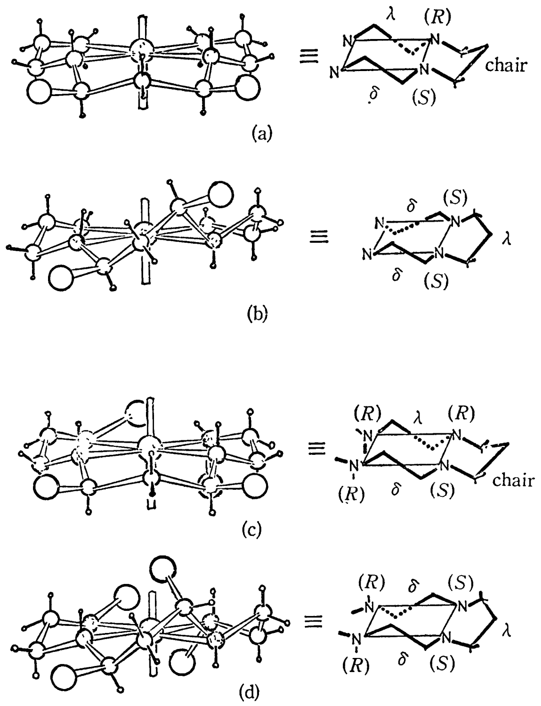

Fig. 1. Schematic structures of *trans*-[CoCl$_2$(2,3″,2-tet)]$^+$.
(a) *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]$^+$
(b) *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]$^+$
(c) *trans*-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$
(d) *trans*-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$.

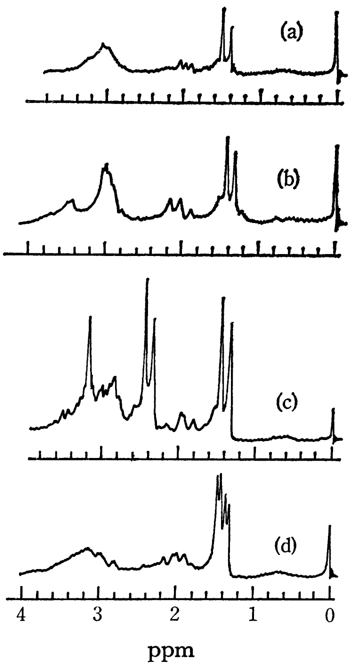

Fig. 2. PMR spectra (60 MHz) of
(a) *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]Cl,
(b) *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]Cl,
(c) *trans*-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]Cl,
(d) *trans*-[CoCl$_2$(*RRRR*-3″,2,3″-tet)]Cl, in diluted DCl.

$(+)_{600}$-*trans*-dichloro complex was optically active ($\Delta\varepsilon=+0.53$ at 17730 cm^{-1} and $\Delta\varepsilon=-2.09$ at 19920 cm^{-1}) and gave more than three kinds of methyl signals in the PMR spectrum in D$_2$O. These facts seem to indicate that the oxalatotetramine complex takes Δ-*cisβ* configuration.[16] The details of this compound will be reported later.[17] This oxalatotetramine complex of cobalt(III) was almost quantitatively coverted to the *trans*-dichlorotetramine complex of cobalt(III) by warming in a concd HCl solution. The absorption and CD spectra of the resulting *trans*-dichloro complex was cosistent with those of the $(+)_{600}$-*trans*-isomer used as the starting material. Therefore, it seems that the $(+)_{600}$-[CoCl$_2$(3″,2,3″-tet)]$^+$ complex can be assigned to *trans*-[CoCl$_2$(*RSSR*-3″,2,3″-tet)]$^+$.

Conformation and Structure. As stated previously,[1,10,11] *RR*-, *SS*-, and *RS*-2,4-pentanediamine are expected to give λ- and δ-skew-boat and chair conformations respectively in six-membered chelate rings. Also, it is generally understood that substituting groups on carbon atoms in puckered chelate rings always tend to take equatorial positions. When the tetramines prepared here coordinate to the cobalt(III) ion, each of the three chelate rings in the tetramine complexes of cobalt(III) can be expected to have a specific conformation because of the steric regulation coming from the methyl groups on the α-carbon atoms as *C*-substituted triethylenetetramine cobalt(III) complexes.[12,20–22]

For the above reasons, the pentanediamine part of *RR*-2,3″,2-tet is expected to give a λ-skew-boat conformation in the complex of *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]$^+$. Then, both of the five-membered chelate rings seem to take the *δ-gauche* conformation, and both cf secondary nitrogen atoms seem to take the *S*-configuration as shown in Fig. 1-b. Accordingly, the two methyl groups are equivalent to each other, because this presumed structure has the C$_2$ symmetry. The molecular models indicate that the structure shown in Fig. 1-b (C$_2$) is formed without any great steric hindrance and involves a smaller steric interaction among the chelate rings than the other possible structure. This most probable structure was confirmed by the fact that the PMR spectrum of *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]$^+$ gave only one sharp doublet of the methyl signal at 1.4 ppm as shown in Fig. 2-b.

From a similar consideration, *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]$^+$ seems to take the *trans-N*(*S*),*N*(*R*)-[(*δ-gauche*) (chair) (*λ-gauche*)] structure as shown in Fig. 1-a. As shown in Fig. 2-a, the PMR spectrum of *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]$^+$ gave a doublet of the methyl signal at 1.5 ppm, in accord with the above assignment.

The structural consideration of *trans*-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ gives three probable structure. In the first structure, all the methyl groups take equatorial positions and the six-membered chelate ring gives a chair conformation. In the second (an enantiomeric pair of Fig. 1-c), one *N*-methyl and two *C*-methyl groups exist in equatorial positions, while the other *N*-methyl group exists in an axial position. In this structure, the six-membered chelate ring gives a chair conformation. In the third structure (an enantiomeric pair of Fig. 1-b), the six-membered chelate ring forms a skew-boat conformation in which one *C*-methyl group takes an equatorial position and

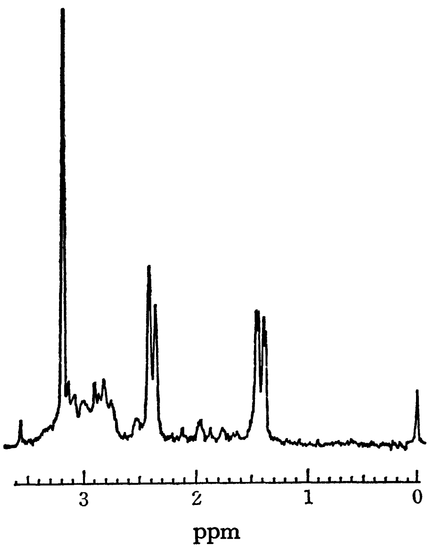

Fig. 3. PMR spectrum (100 MHz) of *trans*-[$CoCl_2$(N,N'-Me_2-*RS*-2,3″,2-tet)]Cl in 3—4 M DCl.

the other *C*-methyl group is orientated in an axial position. In addition, two *N*-methyl groups take equatorial positions in this third structure. The first structure does not seem to be formed because of the great steric hindrance among the two *N*-methyl groups in equatorial positions. The structure of *trans*-[$CoCl_2$(N,N'-Me_2-*RS*-2,3″,2-tet)]$^+$ is probably the second or the third.

The PMR spectra of the *trans*-[$CoCl_2$(N,N'-Me_2-*RS*-2,3″,2-tet)]$^+$ complex are shown in Fig. 2-c (60 MHz) and Fig. 3 (100 MHz). The two kinds of doublets at 1.4 ppm can probably be assigned to the two *C*-methyl groups. The broad doublet at 2.4 ppm, in which two kinds of doublets seem to overlap, is probably to be assigned to the *N*-methyl groups. The sharp singlet at 3.2 ppm may be assigned to the signal of amino protons, because the intensity of the signal depends upon the concentration of DCl. However, it is difficult to assign the detailed structure of *trans*-[$CoCl_2$(N,N'-Me_2-*RS*-2,3″,2-tet)]$^+$, because all four methyl groups are nonequivalent to each other in such a structure as shown in Fig. 1-c or Fig. 1-d. All attempts at the optical resolution of *trans*-[$CoCl_2$ (N,N'-Me_2-*RS*-2,3″,2-tet)]$^+$ have been unsuccessful so far.

Both six-membered chelate rings in *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$ seem to take a λ-skew-boat conformation in which each of the two α-carbon atoms has an equatorial methyl group. In this case, the central five-membered chelate ring and both secondary nitrogen atoms unequivocally take the δ-*gauche* and *S*-configurations respectively. In this presumed structure (C_2 symmetry), the two methyl groups near the five-membered chelate ring are equivalent to one another, and the two methyl groups far away are also equivalent to one another as shown in Fig. 4-a. Actually, the PMR spectrum of *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$ gave two doublets of a methyl signal at 1.40 ppm and 1.45 ppm respectively as shown in Fig. 2-d. Accordingly, it seems that the structure of *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$ can be assigned to *trans*-*N*(*S*), *N*(*S*)-[(λ-skew-boat) (δ-*gauche*) (λ-skew-boat)] as shown in Fig. 4-a.

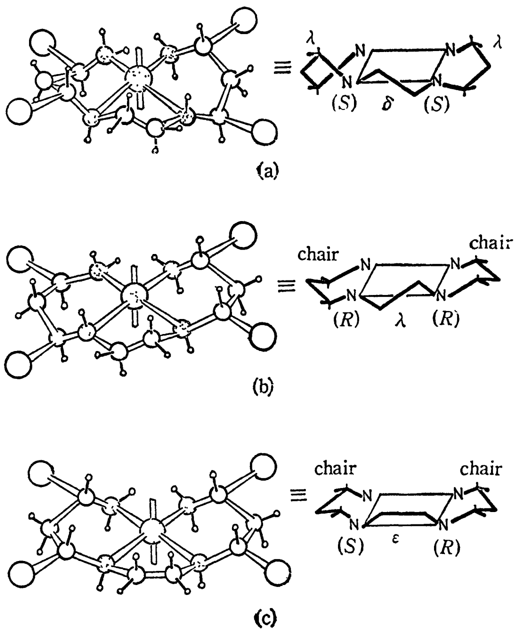

Fig. 4. Schematic structures of *trans*-[$CoCl_2$(3″,2,3″-tet)]$^+$.
(a) *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$
(b) *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]$^+$
(c) *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$

The most probable structrue for *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]$^+$ seems to be the *trans*-*N*(*R*), *N*(*R*)-[(chair) (λ-*gauche*) (chair)] structure as shown in Fig. 4-b. Studies with molecular models disclose that this assumed structure has a more strain-free and complete puckered conformation than the other possible structure. Also, it has been considered that the skeletal structure shown in Fig. 4-b is the most stable form in *trans*-[CoX_2(3,2,3-tet)]$^+$ (X=Cl, Br, NO_2)$^{5-9)}$ and its analogs.$^{23,24)}$ The PMR spectrum of *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]Cl·H_2O could not be obtained, because this complex was not sufficiently soluble in D_2O.

As the *RS*-2,4-pentanediamine parts of *RSRS*-3″,2,3″-tet tend to take chair conformations in a six-membered chelate ring, the most probable structure for the complex of *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$ may be the form shown in Fig. 4-c. This structure, in which the central five-membered chelate ring takes an envelope conformation, has great strain in the bond angles of the two secondary nitrogen atoms, and it seems to be quite unstable compared with the structures of the other *trans*-dichlorotetramine complexes prepared here. Also, it was clear from the change in the absorption spectra that *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]ClO_4 rapidly aquated with a steric change in water and dilute hydrochloric acid, whereas the other *trans*-dichlorotetramine complexes prepared here aquated very slowly, retaining their configurations, and did not aquate in dilute hydrochloric acid. This may be related to the structural considerations presented above.

It is difficult to assign the structure of *cis*-[$CoCl_2$-

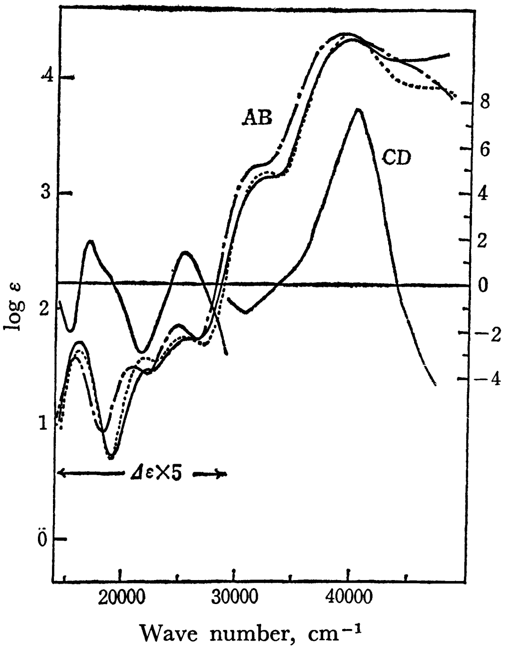

Fig. 5. Absorption (AB) and CD spectra of
(——) *trans*-[$CoCl_2$(*RR*-2,3″,2-tet)]ClO_4,
(⋯⋯) *trans*-[$CoCl_2$(*RS*-2,3″,2-tet)]ClO_4,
(—·—) *trans*-[$CoCl_2$(*N,N′*-Me_2-*RS*-2,3″,2-tet)]ClO_4 in CH_3OH.

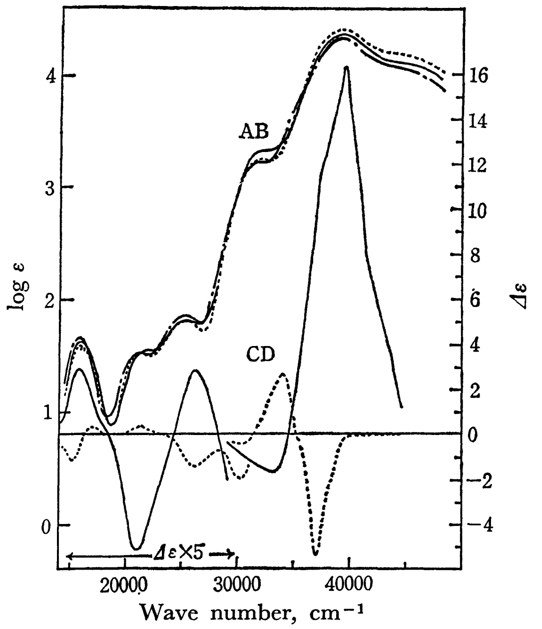

Fig. 6. Absorption (AB) and CD spectra of
(——) *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$ClO_4 \cdot H_2O$,
(⋯⋯) *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]$Cl \cdot H_2O$,
(—·—) *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]ClO_4 in CH_3-OH.

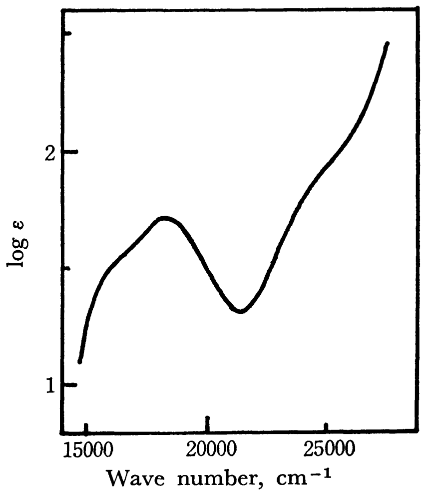

Fig. 7. Absorption spectrum of *cis*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]Cl in 12 M HCl.

(*RSRS*-3″,2,3″-tet)]$^+$ in detail at present. This complex readily aquated in water and smoothly isomerized to the *trans*-dichloro form in methanol. In addition, the complex of *cis*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]Cl was not sufficiently soluble in water and hydrochloric acid. Because of the above facts, the PMR spectrum of this complex could not be obtained.

Absorption Spectra. The absorption spectra of the complexes prepared here are shown in Figs. 5—7 and Table 1. The absorption spectra of *trans*-[$CoCl_2$(*RR*-2,3″,2-tet)]$^+$ and *trans*-[$CoCl_2$(*RS*-2,3″,2-tet)]$^+$ are almost identical with each other. However, the first, the second, and the charge-transfer bands of *trans*-[$CoCl_2$(*N,N′*-Me_2-RS-2,3″,2-tet)]$^+$ are shifted to longer wavelength than those of *trans*-[$CoCl_2$(*RR*-2,3″,2-tet)]$^+$ and *trans*-[$CoCl_2$(*RS*-2,3″,2-tet)]$^+$ (Fig. 5 and Table 1). Such a relationship is in accord with the phenomenon that the absorption bands of *trans*-[$CoCl_2$(*N,N′*-Me_2-en)$_2$]$^+$,[25] *trans*-[$CoCl_2$(*N*-Me-pn)$_2$]$^+$,[26] and *trans*-[$CoCl_2$(*N,N′*-Me_2-pn)$_2$]$^+$,[27] are shifted to longer wavelength than those of *trans*-[$CoCl_2en_2$]$^+$ and *trans*-[$CoCl_2pn_2$]$^+$ respectively.

As shown in Fig. 6, the absorption bands of *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$ are shifted to longer wavelength than those of *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$ and *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]$^+$, which are almost identical with each other. It is difficult to discuss this result in detail at present. However, it seems to be related to the steric interaction among chelate rings and to strain in the bond angles of the secondary nitrogen atoms.

Figure 7 shows the absorption spectrum of *cis*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$ in a 12 M HCl solution. It is apparent from this spectrum that the blue-violet complex of [$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$ takes the *cis*-dichloro configuration.

As shown in Figs. 5, and 6 and Table 1, the absorption bands of six *trans*-dichloro complexes are shifted from lower to higher wave numbers with a decrease in the number of the six-membered chelate ring or the secondary nitrogen atom, *i.e.*, in this order: *trans*-[$CoCl_2$(*N,N′*-Me_2-*RS*-2,3″,2-tet)]$^+$ $\simeq$ *trans*-[$CoCl_2$(*RSRS*-3″,2,3″-tet)]$^+$ $<$ *trans*-[$CoCl_2$(*RSSR*-3″,2,3″-tet)]$^+$ $\simeq$ *trans*-[$CoCl_2$(*RRRR*-3″,2,3″-tet)]$^+$ $<$ *trans*-[$CoCl_2$(*RR*-2,3″,2-tet)]$^+$ $\simeq$ *trans*-[$CoCl_2$(*RS*-2,3″,2-tet)]$^+$. Also, a similar relationship holds between the *trans*-dichloro bisdiamine complexes of cobalt(III). The absorption bands of *trans*-[$CoCl_2$(diamine)$_2$]$^+$ are shifted to higher wave numbers in this sequence: *trans*-[$CoCl_2$(*N,N′*-Me_2-en)$_2$]$^+$ [25] $\simeq$ *trans*-[$CoCl_2$(*N,N′*-Me_2-pn)$_2$]$^+$ [27] $<$ *trans*-

$[CoCl_2tn_2]^+$[28] $\simeq$ *trans*-$[CoCl_2(2,4\text{-ptn})_2]^+$[11] $<$ *trans*-$[CoCl_2en_2]^+ \simeq$ *trans*-$[CoCl_2pn_2]^+$.

The above results show that the absorption bands are shifted to lower wave numbers in the order of *N*-nonsubstituted α-diamine, *N*-nonsubstituted β-diamine, and *N*-substituted α-diamine chelate in such *trans*-dichloro complexes of cobalt(III).

CD Spectra. The CD spectrum of *trans*-$[CoCl_2(RR\text{-}2,3'',2\text{-tet})]^+$ is shown in Fig. 5 and Table 1. The CD spectrum of *trans*-$[CoCl_2(RR\text{-}2,3'',2\text{-tet})]^+$ is very similar to the spectra of *trans*-*N*(*R*),*N*(*R*)-$[CoCl_2(2,3,2\text{-tet})]^+$[5–7] and *trans*-$[CoCl_2(SS\text{-diMe-}2,3,2\text{-tet})]^+$[29], which are assigned to the trans-[(*δ*-*gauche*)(*λ*-skew-boat)(*δ*-*gauche*)] structure. Such a similarity between the CD spectra of the three complexes strongly suggests that *trans*-$[CoCl_2(RR\text{-}2,3'',2\text{-tet})]^+$ should be assigned to the *trans*-*N*(*S*),*N*(*S*)-[(*δ*-*gauche*)(*λ*-skew-boat)(*δ*-*gauche*)] structure shown in Fig. 1-b.

As shown in Fig. 6 and Table 1, *trans*-$[CoCl_2(RRRR\text{-}3'',2,3''\text{-tet})]^+$ gives a CD curve very similar to that of *trans*-$[CoCl_2(RR\text{-}2,4\text{-ptn})_2]^+$.[11] Also, the spectrum of *trans*-$[CoCl_2(RR\text{-}2,3'',2\text{-tet})]^+$ in the region of about 16000 to 45000 cm^{-1} resembles that of *trans*-$[CoCl_2(RRRR\text{-}3'',2,3''\text{-tet})]^+$.

Figure 6 shows the CD spectrum of *trans*-$[CoCl_2(RSSR\text{-}3'',2,3''\text{-tet})]^+$, which is assigned to the *trans*-*N*(*R*), *N*(*R*)-[(chair)(*λ*-*gauche*)(chair)] structure (Fig. 4-b). This spectrum is appreciably different from the CD spectra of $(-)_{589}$-*trans*-$[CoCl_2(3,2,3\text{-tet})]^+$,[5–8] and *trans*-$[CoCl_2(R\text{-appn})]^+$,[23,24] which are very similar to each other. However, the backbones of 3,2,3-tet and *R*-appn[30] in these two complexes are identified as taking the same configuration as the backbone of *RSSR*-3″,2,3″-tet in *trans*-$[CoCl_2(RSSR\text{-}3'',2,3''\text{-tet})]^+$. Such a difference in CD spectra may be elucidated as follows: the two terminal, six-membered chelate rings in $(-)_{589}$-*trans*-$[CoCl_2(3,2,3\text{-tet})]^+$ and *trans*-$[CoCl_2(R\text{-appn})]^+$ are flexible, and it is conceivable that a conformational equilibrium exists where the terminal rings flip from the nonchiral to the chiral, skew-boat conformations. On the other hand, such a flipping in *trans*-$[CoCl_2(RSSR\text{-}3'',2,3''\text{-tet})]^+$ is not likely because of the preference of the methyl groups for an equatorial orientation.

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SS-diMe-2,3,2-tet: $NH_2CH(CH_3)CH_2NHCH_2CH_2CH_2NHCH_2CH(CH_3)NH_2$.

30) *R*-appn: $NH_2CH_2CH_2CH_2NHCH_2CH(CH_3)NHCH_2CH_2CH_2NH_2$.