(RCSO)] and that [Pt^0(PPh$_3$)$_2$[(*Z*)-(MeS)RCSO]] likewise gave rise to *cis*-(*E*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(RCSO)] illustrate that during the oxidative-addition reaction isomerization of the sulfine skeleton occurs. Three types of isomerization pathway are possible:

First, there could be an equilibrium between the pseudoallylic intermediates, analogous to the syn–anti interchange found in the complexes [PdCl(PR$_3$)(η^3-H$_2$CC(H)CH$_2$)].[39]

Second, a direct equilibrium between the two oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(RCSO)] can be envisaged, perhaps catalyzed by trace impurities. Isomerization under influence of base has been observed for free sulfines.[40]

A third possibility could be a process involving an impurity-catalyzed isomerization of free sulfine (generated by a dissociative process of the coordination compounds) followed by recoordination of the sulfine.

In order to gain more insight into the isomerization of oxidative-addition stereoisomers, we have studied the isomerization of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}Cl(PPh$_3$)$_2$(RSCSO)] (R = *p*-MeC$_6$H$_4$, Ph), oxidative-addition products of the sulfine (*E*)-(RS)ClCSO. The lability of the C–Cl bond with respect toward oxidative addition to Pt^0 should prohibit both a reductive coupling reaction of Cl and RSC=S=O and the existence of pseudoallylic intermediates. The results will be described in a forthcoming paper.[34] In order to investigate the isomerization of coordination stereoisomers in absence of an oxidative-addition process, we are now studying the complexes [Pt^0(P(c-Hx)$_3$)$_2$[(*E*)-(MeS)PhCSO]] and [Pt^0(P(c-Hx)$_3$)$_2$[(*Z*)-(MeS)PhCSO]]. The bulkiness of the P(c-Hx)$_3$ groups should make oxidative addition less attractive because cis-positioned P(c-Hx)$_3$ ligands in a square-planar Pt^{II} complex would be unfavorable. In contrast we might anticipate that pseudoallylic intermediates can still be formed.

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Registry No. [Pt^0(PPh$_3$)$_2$(C$_{12}$H$_8$CSO)]·0.5C$_6$H$_6$, 75701-23-4; *cis*-(*E*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(*p*-MeC$_6$H$_4$CSO)], 73358-19-7; *cis*-(*Z*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(*p*-MeC$_6$H$_4$CSO)], 73367-11-0; Pt^0(PPh$_3$)$_2$-[(*E*)-(MeS)(*p*-MeC$_6$H$_4$)CSO], 72539-18-5; Pt^0(PPh$_3$)$_2$[(*Z*)-(MeS)(*p*-MeC$_6$H$_4$)CSO], 72581-76-1; Pt^0(PPh$_3$)$_4$, 14221-02-4; Pt^0(PPh$_3$)$_2$[(*E*)-(MeS)PhCSO], 75701-24-5; Pt^0(PPh$_3$)$_2$[(*Z*)-MeS)-PhCSO], 75764-72-6; *cis*-(*E*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(PhCSO)], 75701-09-6; *cis*-(*Z*)-[Pt^{II}(MeS)(PPh$_3$)$_2$(PhCSO)], 75764-66-8.

Supplementary Material Available: A table of observed and calculated structure factors for [Pt^0(PPh$_3$)$_2$(C$_{12}$H$_8$CSO)]·0.5C$_6$H$_6$ (41 pages). Ordering information is given on any current masthead page.

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Contribution for the Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113 Japan

Isomers of Cobalt(III) Complexes Containing Quadridentate Ligands with a Six-Membered Chelate Ring. Optically Active 2,3,2-tet Derivatives

M. AJIOKA,* S. YANO, M. SABURI, and S. YOSHIKAWA*

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The preparation and characterization are described for the isomers for the (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (5*R*,7*R*-Me$_2$-2,3,2-tet) and for the (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane (1,5*R*,7*R*,11-Me$_4$-2,3,2-tet) complexes of the type *trans*-[CoCl$_2$(tetraamine)]$^+$. The isomers are designated by the different configurations of asymmetric nitrogens. The following isomers were isolated: *S*,*S* and *R*,*S* for the former and *R*,*S*,*S*,*R*, *S*,*R*,*S*,*S*, and *R*,*S*,*S*,*S* for the latter ligand. The six-membered ring in the *R*,*S* and *S*,*R*,*S*,*S* isomers has the chair conformation with an axial and an equatorial *C*-methyl group. The six-membered part for the *S*,*S*, *R*,*S*,*S*,*R*, and *R*,*S*,*S*,*S* isomers adopts a λ skew-boat conformation with two equatorial *C*-methyl groups. The ratio of the *S*,*S* and *R*,*S* isomers for the *trans*-[CoCl$_2$(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ at equilibrium was evaluated to be 2:1 (ΔG = 1.92 kJ mol^{-1}). All the isomers of the *trans*-[CoCl$_2$(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ and *trans*-[CoCl$_2$(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^+$ produce Λ-β-(*S*,*S*)-[CoCO$_3$(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ and Λ-β-(*R*,*S*,*S*,*S*)-[CoCO$_3$-(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^+$, respectively, by the reaction with carbonate ion in an aqueous solution. The (*R*,*R*)-2,4-pentanediamine parts in these carbonato complexes were considered to adopt chair conformations with one methyl group axial and the other equatorial. These carbonato complexes were converted to the *trans*-dichloro complexes with the same configurations about the nitrogen centers.

Introduction

The stereochemistry of cobalt(III) complexes of tetraamine ligands with a six-membered chelate ring has been of recent interest.[1-8] The methyl groups substituted in diamines or tetraamines affect significantly the configurations of metal complexes. Two conformations are possible for the (*R*,*R*)-2,4-pentanediamine (*R*,*R*-ptn) coordinated to a metal ion as a bidentate ligand. The chair conformation has one axial methyl group, the other being equatorial. In the λ skew-boat conformation, however, both methyl groups are disposed equatorially. Both conformations were actually observed in

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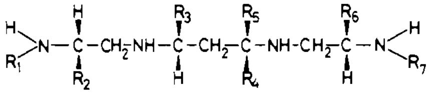

	R_1	R_2	R_3	R_4	R_5	R_6	R_7
a	-H	-H	-H	-H	-H	-H	-H
b	-H	$-CH_3$	-H	-H	-H	$-CH_3$	-H
c	$-CH_3$	$-CH_3$	-H	-H	-H	$-CH_3$	$-CH_3$
d	-H	-H	$-CH_3$	$-CH_3$	-H	-H	-H
e	$-CH_3$	-H	$-CH_3$	$-CH_3$	-H	-H	$-CH_3$
f	$-CH_3$	-H	$-CH_3$	-H	$-CH_3$	-H	$-CH_3$

Figure 1. Ligands used and referenced in this report: (a) 2,3,2-tet; (b) 2*S*,10*S*-Me_2-2,3,2-tet; (c) 1,2*S*,10*S*,11-Me_4-2,3,2-tet; (d) 5*R*,7*R*-Me_2-2,3,2-tet; (e) 1,5*R*,7*R*,11-Me_4-2,3,2-tet; (f) 1,5*R*,7*S*,11-Me_4-2,3,2-tet.

recent X-ray crystal analysis studies.[9-13] Thus, there are two possible conformations for the 2,4-pentanediamine part in metal complexes containing (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (5*R*,7*R*-Me_2-2,3,2-tet).

Recently, Mizukami prepared six kinds of *trans*-dichlorocobalt(III) complexes with tetraamine ligands derived from (*R*,*R*)- or (*R*,*S*)-2,4-pentanediamine by the usual air oxidation procedure[14] and characterized them on the basis of ^1H NMR, electronic absorption, and CD spectral measurements. For *trans*-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$, only one isomer (trans-*S*,*S*) was obtained, although two isomers are theoretically possible. In this isomer the central six-membered chelate ring takes the λ skew-boat conformation and the absolute configuration of the secondary nitrogen atoms are both *S*,[14] in spite of the fact that two isomers are theoretically possible.

We found that in methanolic solution *trans*-(*S*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ (Ia) isomerizes to the other *trans*-dichloro isomer, and we succeeded in the isolation of the new isomer.

In addition, we prepared a new tetraamine, (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane (1,5*R*,7*R*,11-Me_4-2,3,2-tet), which has a methyl group on both the terminal nitrogen atoms of 5*R*,7*R*-Me_2-2,3,2-tet.

The tetraamines used or cited in this report are shown in Figure 1.

Experimental Section

Measurements. Circular dichroism spectra were measured with a JASCO J-20 recording spectropolarimeter. Visible absorption spectra were recorded on a Shimadzu UV-210 spectrophotometer. The spectra were obtained in methanol for the *trans*-dichloro complexes and in water for the carbonato complexes. Proton magnetic resonance spectra were measured on a JEOL PS-100 spectrometer with sodium(trimethylsilyl)propanesulfonate as an internal standard, with use of D_2O–DCl solution for the *trans*-dichloro complexes and CD_3OD or D_2O solution for the carbonato complexes.

(*R*,*R*)-2,4-Pentanediamine, 5*R*,7*R*-Me_2-2,3,2-tet, and *trans*-(*S*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ (Ia) were prepared by the method of Mizukami.[14]

Preparation of (6*R*,8*R*)-6,8-Dimethyl-2,5,9,12-tetraazatridecane. Carbobenzoxyglycine[3] (20.9 g) and triethylamine (10.1 g) were dissolved in chloroform (300 mL), and the solution was stirred and cooled to −10 °C. Isobutyl chloroformate (13.1 g) was added dropwise. After a 1-min stirring, (*R*,*R*)-2,4-pentanediamine (4.08 g) was added over a period of 30 min. The mixture was allowed to stand overnight at room temperature. The reaction mixture was washed with water, and the chloroform layer was dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator, leaving the product, *N*,*N*′-bis(carbobenzoxyglycyl)-(*R*,*R*)-2,4-pentanediamine. The oily product was used in the next step without further purification.

The oil (22 g) was dissolved in dry tetrahydrofuran (50 mL), and the solution was added dropwise to a constantly stirred mixture of lithium aluminium hydride (10 g) in dry tetrahydrofuran (150 mL). After the addition had been completed, the mixture was heated under reflux for 20 h. The reaction mixture was cooled and then carefully quenched by the dropwise addition of water (20 mL). The mixture was refluxed for 40 min and cooled to room temperature, and the white precipitate was filtered off. The filtered solid was stirred and refluxed with two 200-mL portions of tetrahydrofuran. The combined filtrate and washings were acidified with hydrochloric acid. The solvent was removed, and the residue was washed twice with ether to remove benzyl alcohol. The aqueous solution was made strongly alkaline with NaOH and extracted with toluene (200 mL). The toluene layer was dried overnight over solid KOH. The solvent was removed by distillation, and the product, (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane, was then collected by vacuum distillation: bp 121 °C (3 mmHg), yield 7.7 g.

Preparation of *trans*-(*R*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ (Ib). The *trans*-(*S*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ (Ia) was dissolved in a minimum volume of methanol. The solution was refluxed for 30 min and then acidified with methanol saturated with hydrogen chloride gas. The solution containing trans-*S*,*S* and trans-*R*,*S* isomers was cooled to room temperature. The resulting green powder was filtered, washed with ethanol and ether, and air-dried. The trans-*R*,*S* isomer was separated from the trans-*S*,*S* isomer due to its low solubility in methanol. Anal. Calcd for $C_9H_{24}N_4Cl_3CoO_4$: C, 25.89; H, 5.79; N, 13.42. Found: C, 25.65; H, 5.62; N, 13.50.

Preparation of *trans*-(*R*,*S*,*S*,*R*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4$ (IIa). A solution of 1,5*R*,7*R*,11-Me_4-2,3,2-tet (5.0 g) in water (50 mL) was added to an aqueous solution containing cobalt(II) chloride hexahydrate (8.64 g), and the solution was aerated for 1 h. After the addition of concentrated hydrochloric acid (20 mL) and 60% perchloric acid (10 mL), the solution was concentrated on a water bath. Green crystals which separated were filtered, washed with ethanol and ether, and air-dried. Recrystallization was performed from 3 N hydrochloric acid; yield 5.03 g. Anal. Calcd for $C_{11}H_{28}N_4Cl_3CoO_4$: C, 29.65; H, 6.33; N, 12.57. Found: C, 29.37; H, 6.08; N, 12.24.

Preparation of *trans*-(*S*,*R*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4$ (IIb). The less soluble *trans*-(*S*,*R*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4$ was obtained from the *trans*-(*R*,*S*,*SR*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4$ by the method similar to that used for obtaining the *trans*-(*R*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ described above. A mixture of the isomers (*S*,*R*,*S*,*S* + *R*,*SSR*) recrystallized from 3 N hydrochloric acid until the CD gave no further change. Anal. Calcd for $C_{11}H_{28}N_4Cl_3CoO_4$: C, 29.65; H, 6.33; N, 12.57. Found: C, 29.66; H, 6.19; N, 12.33.

Preparation of *trans*-(*R*,*S*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4$ (IIc). Hydrochloric acid (6 N) was added to Λ-β-(*R*,*S*,*S*,*S*)-$[CoCO_3(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet})]ClO_4\cdot H_2O$ (0.27 g). The solution was warmed on a water bath for 30 min at 50 °C. The original violet color turned gradually to green. Then, this solution was cooled to room temperature and allowed to stand overnight. The resulting crystals were filtered, washed with ethanol and ether, and air-dried; yield 0.15 g. Anal. Calcd for $C_{11}H_{28}N_4Cl_3CoO_4$: C, 29.65; H, 6.33; N, 12.57. Found: C, 29.33; H, 6.46; N, 12.71.

Equilibrium Reaction of *trans*-(*S*,*S*)- and *trans*-(*R*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ in Methanol. A sample (15 mg) of either the trans-*S*,*S* or trans-*R*,*S* isomer was dissolved in methanol (10 mL). The solutions were stored at 35 °C, and the CD spectra were recorded every 24 h. After 1 week, the CD spectra of these two samples became identical with each other. The ratio of the isomers was calculated from the final CD curves. The same reaction in CD_3OD was followed by ^1H NMR measurements. The ratio of the isomers was estimated from the intensities of C-methyl peaks in the spectra. The results obtained by these two ways agreed with each other.

Preparation of Λ-β-$[CoCO_3(5R,7R\text{-}Me_2\text{-}2,3,2\text{-tet})]Cl\cdot 1.5H_2O$ (III). To an aqueous solution (10 mL) of *trans*-(*S*,*S*)-[$CoCl_2$(5*R*,7*R*-

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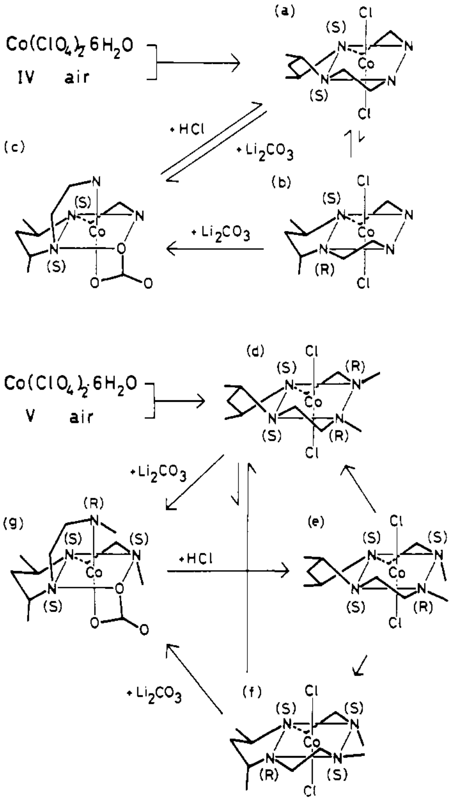

Figure 2. Relations of the complexes prepared in this study.

Me_2-2,3,2-tet)]ClO_4 (0.7 g) was added lithium carbonate (0.30 g). Instantly the solution turned from green to reddish violet. This mixture was warmed on a water bath at 70 °C for 30 min, undissolved lithium carbonate was removed by filtration, and the filtrate was cooled to room temperature. The resulting crystals were filtered, washed with ethanol followed by ether, and air-dried; yield 0.38 g. The perchlorate salt was changed to the chloride by anion-exchange resin. Anal. Calcd for $C_{10}H_{27}N_4ClCoO_{4.5}$: C, 32.48; H, 7.31; N, 15.16. Found: C, 32.71; H, 7.30; N, 15.58.

Preparation of Λ-β-(*R*,*S*,*S*,*S*)-[$CoCO_3$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$ClO_4 \cdot H_2O$ (IV). This was prepared from *trans*-(*R*,*S*,*S*,*R*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 (2.8 g) by the method similar to that described for the Λ-β-[$CoCO_3$(5*R*,7*R*-Me_2-2,3,2-tet)]$Cl \cdot 1.5H_2O$. This complex did not crystallize easily from the aqueous solution, so ethanol was added. The crystals which formed were filtered, washed with ethanol followed by ether, and air-dried: yield 90 mg. Anal. Calcd for $C_{12}H_{30}N_4ClCoO_8$: C, 31.83; H, 6.69; N, 12.37. Found: C, 31.90; H, 6.41; N, 12.25.

Results

Preparations. Three types of procedures were used for the preparation of *trans*-[$CoCl_2$(tetraamine)]$^+$ type complexes.

Method 1. Ia and IIa were prepared by the usual air oxidation.

Method 2. Ib and IIb were obtained from Ia or IIa by isomerizing the parent complexes in methanolic solution. When Ia was heated in methanolic solution, a new isomer having C_1 symmetry (Ib) was detected in the ^1H NMR spectrum. The isomer was separated from Ia due to its low solubility in methanol and purified by carefully repeated recrystallizations from dilute hydrochloric acid solution. IIa also isomerized in a similar manner as Ia to give a mixture of complexes. One of the complexes having C_1 symmetry (IIb) was isolated and purified by repeated recrystallizations.

Method 3. Ia and IIc were obtained by treatment of III and IV by reactions with concentrated HCl.

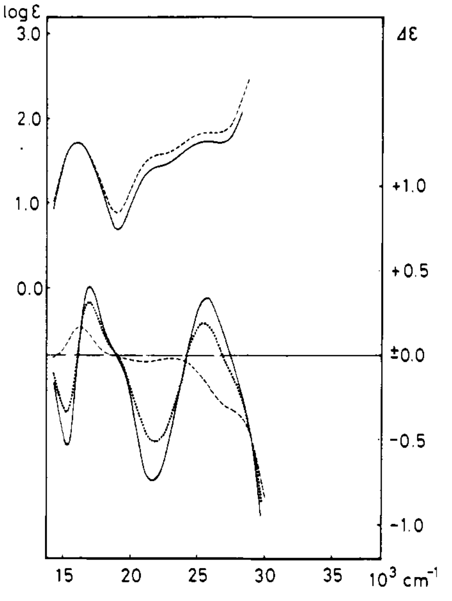

Figure 3. Absorption and CD spectra: (i) —, *trans*-(*S*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4; (ii) ---, *trans*-(*R*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4; (iii) ···, equilibrium mixture in MeOH.

Table I. Numerical Data of Absorption (AB) and Circular Dichroism (CD)

complexes	AB ν, 10^3 cm^{-1} (log ε)	CD ν, 10^3 cm^{-1} ($\epsilon_l - \epsilon_r$)
trans-(*S*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 (Ia)	16.00 (1.71)	15.24 (−0.54)
		16.95 (+0.41)
	22.1 (1.4)	21.69 (−0.75)
	25.77 (1.7)	25.64 (+0.34)
trans-(*R*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 (Ib)	16.00 (1.72)	16.26 (+0.17)
	22.3 (1.6)	21.10 (−0.04)
	26.0 (1.8)	
trans-(*R*,*S*,*S*,*R*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 (IIa)	15.75 (1.58)	15.20 (+0.98)
	20.62 (1.56)	20.49 (−1.59)
	24.57 (1.82)	25.64 (+0.25)
trans-(*S*,*R*,*S*,*S*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 (IIb)	15.58 (1.73)	15.70 (−0.33)
	20.83 (1.69)	20.41 (+0.80)
	24.75 (1.99)	25.97 (−0.19)
trans-(*R*,*S*,*S*,*S*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 (IIc)	15.50 (1.60)	14.49 (−0.42)
		16.26 (+0.69)
	21.60 (1.48)	20.49 (−0.61)
	24.45 (1.87)	24.39 (+0.19)
Λ-β-[$CoCO_3$(5*R*,7*R*-Me_2-2,3,2-tet)]$Cl \cdot 1.5H_2O$ (III)	19.42 (2.20)	18.35 (+2.47)
		20.49 (−1.51)
	27.78 (2.12)	25.51 (+2.47)
		28.57 (+0.41)
Λ-β-[$CoCO_3$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$ClO_4 \cdot H_2O$ (IV)	18.87 (2.24)	18.05 (+2.19)
		20.37 (−0.46)
	26.88 (2.17)	25.13 (+0.55)
		28.01 (+0.42)

Carbonato complexes (III, IV) were prepared by the reaction of *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$ and *trans*-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ with Li_2CO_3, respectively. For each tetraamine complex, only one isomer was obtained whatever isomers of dichloro complexes used as the starting material.

Spectra. The assignment of the geometry of the present complexes is based on (a) the ^1H NMR signals of the *C*-methyl groups, (b) the electronic absorption and CD spectra, and (c) the reactions of the complexes shown in Figure 2. The electronic absorption spectra and circular dichroism curves for the dichloro and carbonato complexes are given in Figures 3–5. Their band locations and intensities are tabulated in Table I. The ^1H NMR spectra for the dichloro and carbonato com-

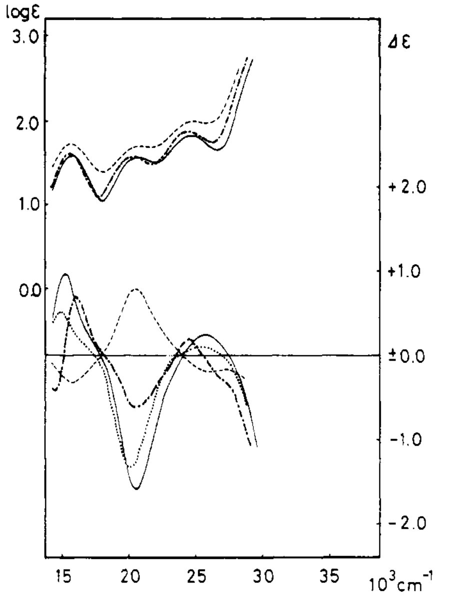

Figure 4. Absorption and CD spectra: (i) —, *trans*-(*R*,*S*,*S*,*R*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]ClO_4$; (ii) ---, *trans*-(*S*,*R*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]ClO_4$; (iii) -·-, *trans*-(*R*,*S*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]ClO_4$; (iv) ···, *trans*-(*R*,*S*,*R*,*R*)-$[CoCl_2(1,2S,10S,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]ClO_4$.

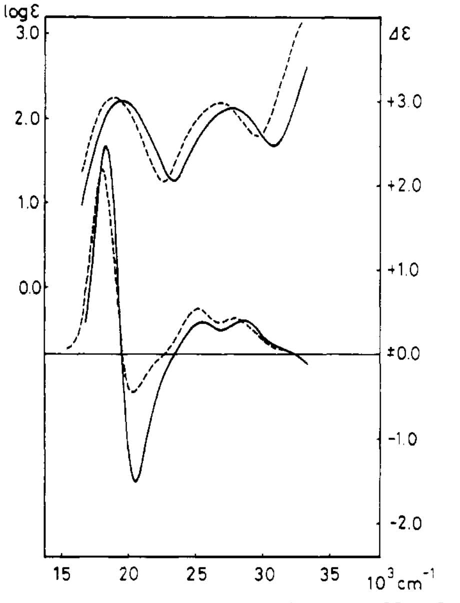

Figure 5. Absorption and CD spectra: (i) —, Λ-β-$[CoCO_3(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]Cl\cdot 1.5H_2O$; (ii) ---, Λ-β-$[CoCO_3(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]ClO_4\cdot H_2O$.

plexes are given in Figures 6 and 7.

Discussion

A. Dichloro Complexes. The dichloro complexes obtained are green, which is characteristic of the *trans*-$[CoCl_2N_4]^+$ type. The visible absorption spectra of Ia, Ib, IIa, IIb, and IIc are very similar to each other and give the typical *trans*-$[CoCl_2N_4]^+$ absorptions (Figures 3 and 4).

Three isomers are known for the *trans*-dichloro complex of 2,3,2-tet (Figure 1a): trans-*R*,*R* trans-*S*,*S* and trans-*R*,*S*.[3] The trans-*R*,*S* isomer was prepared by an air oxidation and the chiral isomers (*R*,*R* and *S*,*S*) were obtained from the carbonato complex. In the case of 2*S*,10*S*-Me_2-2,3,2-tet (Figure 1b) complex, two isomers, *R*,*R* and *R*,*S*, were obtained.[17] In a similar manner two isomers are possible for the *trans*-dichloro complex of 5*R*,7*R*-Me_2-2,3,2-tet, shown in Figure 2a,b. The structure in Figure 2a has the trans-*S*,*S* configuration, in which the central six-membered chelate ring takes a λ skew-boat conformation with two equivalent equatorial methyl groups. Mizukami prepared *trans*-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]ClO_4$ by an air oxidation and obtained the *S*,*S* isomer (Ia). The ^1H NMR spectrum of Ia shows a C-methyl doublet at 1.4 ppm (Figure 6a), indicating that the two methyl groups are in the same chemical environment. This ^1H NMR spectrum is consistent with the structural features for the structure in Figure 2a.

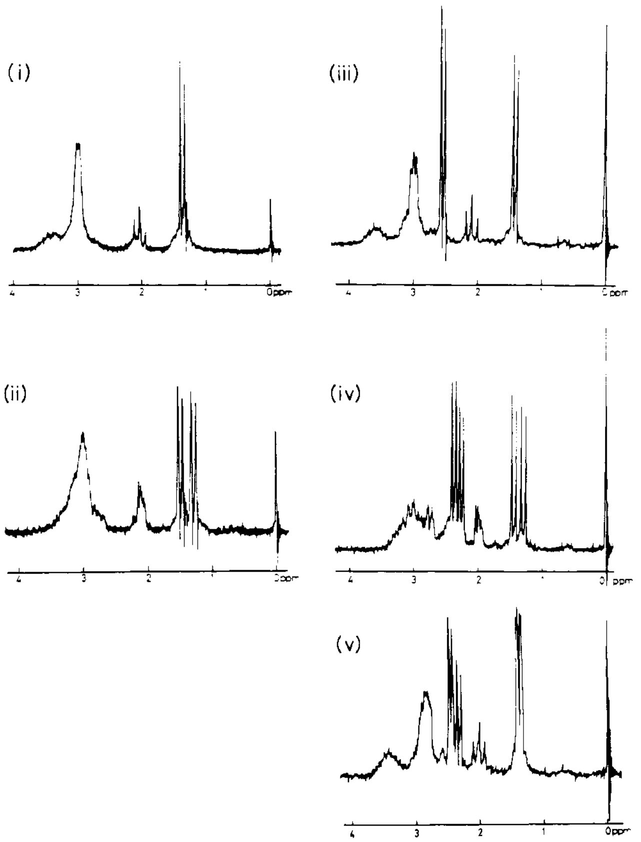

Figure 6. ^1H NMR spectra of *trans*-dichloro complexes: (i) *trans*-(*S*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$; (ii) *trans*-(*R*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$; (iii) *trans*-(*R*,*S*,*S*,*R*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$; (iv) *trans*-(*S*,*R*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$; (v) *trans*-(*R*,*S*,*S*,*S*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$.

The other structure, trans-*R*,*S* isomer, has the central six-membered rings in the chair conformation with one methyl group axial and the other equatorial and two five-membered rings in the conformation of opposite chirality (Figure 2b). The ^1H NMR spectrum for the trans-*R*,*S* isomer should give rise to two methyl doublets of the equal intensities, since the axial methyl group should exhibit, in principle, a different chemical shift from that of the equatorial methyl group. The ^1H NMR spectrum of Ib, which was obtained from methanolic solution of the trans-*S*,*S* isomer, has two C-methyl doublets of the equal intensities centered at 1.3 and 1.5 ppm (Figure 6b). For the trans-*R*,*S* isomer, the conformational effects will not contribute to the CD, because the five-membered rings has the opposite conformation. The vicinal effects from C-methyl groups would be relatively small on the CD of *trans*-$[CoCl_2N_4]^+$ type complexes as discussed previously.[16] The CD curve of Ib is fairly different from and apparently less intense than that of Ia (trans-*S*,*S* isomer (Figure 3)). Consequently, these CD and ^1H NMR data support that the

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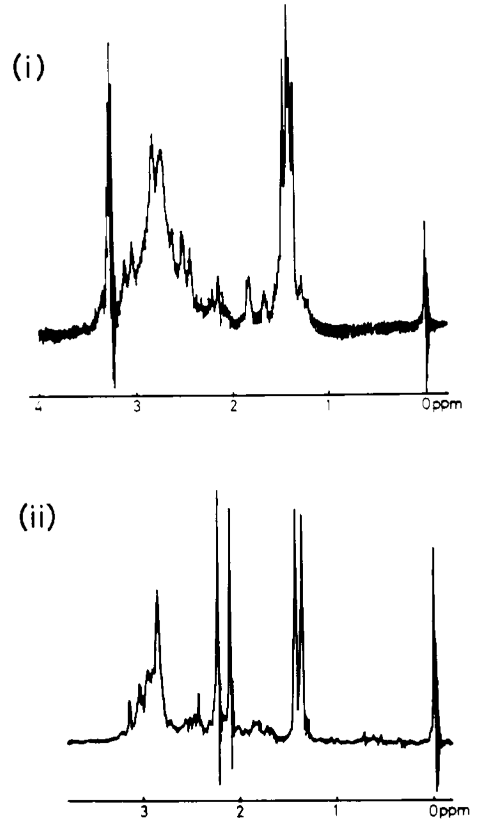

Figure 7. ^{1}H NMR spectra of carbonato complexes: (i) Λ-β-$[CoCO_3(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$ (in CD_3OD); (ii) Λ-β-$[CoCO_3(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$ (in D_2O).

new isomer Ib should be assigned to the trans-*R*,*S* configuration.

For investigation of the relative stability of the trans-(*S*,*S*) and trans-*R*,*S* isomers, the ratio of these isomers in methanolic solution at equilibrium was determined. The results obtained by two methods (^{1}H NMR and CD) were quite similar, i.e., trans-*S*,*S*:trans-*R*,*S* = 2:1 (ΔG = 1.92 kJ mol^{-1}). Analogous isomerization has been found in the case of the *trans*-dichlorocobalt(III) complex of 2*S*,10*S*-Me$_2$-2,3,2-tet,[17] which has the C-methyl groups on both five-membered chelate rings. The trans-*R*,*R* isomer of $[CoCl_2(2S,10S\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$ has a six-membered ring with a λ skew-boat conformation and two equatorial methyl groups on the five-membered rings. On the other hand, the trans-*R*,*S* isomer has a six-membered ring in a chair conformation and an axial and an equatorial methyl groups at the outer chelate rings. The result of the equillibrium reaction in methanol is trans-*R*,*R*:trans-*R*,*S* = 1:9, showing that the isomer having an axial methyl group on a five-membered ring was preferentially formed (90%). In the 5*R*,7*R*-Me$_2$-2,3,2-tet case, however, the proportion of the isomer having an axial methyl group on the six-membered ring was only 33%. These facts suggest that an axial methyl group on a six-membered ring is less favorable than that on a five-membered ring. This would be ascribed to the steric replusions between the methyl groups and apical chloride, according to the examination of molecular models. The quantitative study of the 5,7-Me$_2$-2,3,2-tet system by strain energy minimization calculations will be reported elsewhere.

The ^{1}H NMR spectrum of complex IIa has C-methyl and N-methyl doublets at 1.4 and 2.5 ppm, respectively, indicating C_2 symmetry for the complex (Figure 6c). Seven possible structures, which differ in the configuration of the asymmetric secondary nitrogen atoms, were shown in Figure 8. Three of these adopt skew-boat conformations, and the other four adopt chair conformations. The structure in Figure 8a, in which all methyl groups are situated in equatorial positions, is considered to be more stable than the structure in Figure 8b, where the N-methyl groups are situated in axial positions. Accordingly, complex IIa is assigned to the structure in Figure 8a and designated as *trans*-(*R*,*S*,*S*,*R*)-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$. The absorption and CD spectra of this complex (Figure 4a) are somewhat different from those of *trans*-(*S*,*S*)-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$ in spite of the similarity in the chelate conformations. The difference is attributed to the vicinal effect from the two additional N-methyl groups.

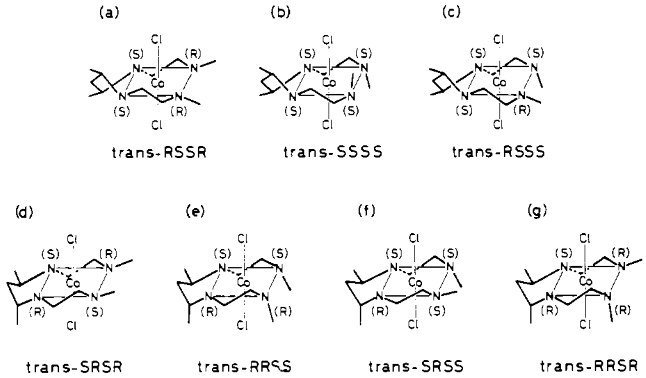

Figure 8. Seven possible isomers of *trans*-$[CoCl_2(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-}tet)]^+$.

The complex IIa could be isomerized in a similar way as for the *trans*-$[CoCl_2(5R,7R\text{-}Me_2\text{-}2,3,2\text{-}tet)]^+$ ion. One of the complexes having C_1 symmetry was isolated from an equilibrated mixture by repeated recrystallizations from 3 N hydrochloric acid. The ^{1}H NMR spectrum of this complex (Figure 6d) has four methyl doublets centered at 1.3, 1.4, 2.3, and 2.4 ppm, indicating that all the methyl groups are in the different environments. Two of these at lower field are attributed to the two N-methyl groups. The doublets at 1.3 and 1.4 ppm are assigned to the C-methyl groups. In the ^{1}H NMR spectra of Ib and IIb, the differences between the chemical shifts of the two C-methyl doublets are almost the same. Consequently, the conformation of 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet in IIb will be similar to that of 5*R*,7*R*-Me$_2$-2,3,2-tet in Ib. Four possible structures for the chair isomer, which differ in the orientations of two methyl groups, are shown on Figure 8d–g. In these structures the trans-*R*,*R*,*S*,*R* (Figure 8f) and trans-*S*,*R*,*S*,*S* (Figure 8g) are thought to be more stable than the other two on the basis of examination of molecular models. The repulsion between the two N-methyl groups is pronounced when they are oriented in the same direction, as in Figure 8d,e.

The CD spectrum of the C_1 isomer shown in Figure 4b has a positive peak at 21 000 cm^{-1} ($\Delta\epsilon$ = +0.8). According to previous studies the vicinal effect of the asymmetric nirogen atoms appears in this region.[18-20] Since the configurations of "inner" nitrogen atoms of both trans-*R*,*R*,*S*,*R* and trans-*S*,*R*,*S*,*S* isomers are *R* and *S* (meso), there appears only the contributions of the "outer" nitrogen atoms, simply designated as *R*,*R* or *S*,*S*. The contributions of the *R*,*R* and *S*,*S* con-

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(17) Goto, M.; Makino, M.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1879–1882.

(18) Saburi, M.; Tsujito, Y.; Yoshikawa, S. *Inorg. Chem.* **1970**, *9*, 1476–1487.

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figurations will be shown as a negative and a positive peak, respectively, in this region. Therefore, the structure of the isolated complex (IIb) is assigned to the *trans*-(*S*,*R*,*S*,*S*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ ion.

Although other isomers were detected by ^1H NMR spectroscopy, the amounts were too small to be isolated. The isomer shown in Figure 2e, which seemed to be unstable, was obtained via the carbonato complex (vide infra).

B. Carbonato Complexes and Related *trans*-Dichloro Derivatives. It is interesting to examine the complex ions [$CoCO_3$(tetraamine)]$^+$ (tetraamine = 5*R*,7*R*-Me_2-2,3,2-tet and 1,5*R*,7*R*,11-Me_4-2,3,2-tet), which occur only as the cis modification. Since these carnonato complexes are easily converted to the dichloro complexes, it is of interest to examine the stereochemistry of these systems.

The formation of [$CoCO_3$(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$, through the reaction of Ia or Ib with CO_3^{2-}, was followed by means of ^1H NMR measurements in D_2O. Only one isomer was obtained whether Ia or Ib was used as the starting material. The ^1H NMR spectrum of the carbonato complex (III) shows a methyl doublet at 1.3 ppm in D_2O but two methyl doublets at 1.4 and 1.5 ppm in CD_3OD, indicating the unsymmetrical-cis (cis-*β*) geometry (Figure 7a). Previously we have determined the molecular structure of $(-)_{546}$-Λ-*β*-[Co(ox)-(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 by X-ray crystallographic study,[11] in which the six-membered chelate ring takes a chair conformation with one methyl group axial and the other equatorial and the *S* configuration about the two secondary nitrogen atoms. The observed similarity in the CD between the carbonato (Figure 5a) and oxalato[15] complexes strongly suggests that these complexes have similar geometries. Thus the carbonato complex prepared here is assigned to the Λ-*β*-*S*,*S* configuration (Figure 2c).

The *trans*-dichloro complex prepared from the carbonato complex under strongly acidic condition proved to be identical with Ia. The retention at the chiral secondary nitrogen centers is generally observed in the conversion under strong acidic conditions,[6,18] so that the configurations of both asymmetric nitrogen atoms of this carbonato complex are assigned to *S*,*S*. This supports the assignment described above.

The reaction of *trans*-(*R*,*S*,*S*,*R*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 with Li_2CO_3 gave a carbonato complex (IV). The ^1H NMR spectrum of this complex in D_2O (Figure 7b) has two singlets with equal intensities at 2.1 and 2.2 ppm assigned to the two methyl groups on the outer nitrogen atoms. A doublet centered at 1.4 ppm is ascribed to the two C-methyl groups, overlapping by chance. The spectrum did not change with repeated recrystallization. Accordingly, complex IV is not a mixture of two cis-*α* isomer but a pure cis-*β* isomer. The CD spectrum of this complex (Figure 5b) has a positive peak at 18 000 cm^{-1}, indicating the Λ-*β* configuration. On the basis of these data, the complex is assigned to Λ-*β*-[$CoCO_3$-(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$.

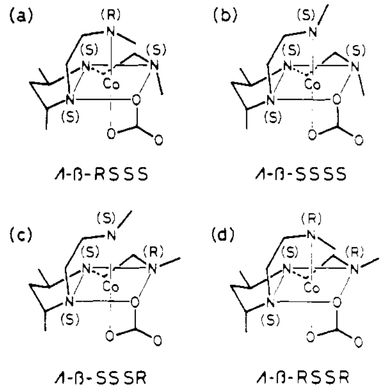

Figure 9. Four possible isomers of Λ-*β*-[$CoCO_3$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$.

Table II. Conformations of the (*R*,*R*)- or (*S*,*S*)-2,4-Pentanediamine Part in Complexes

complexes	conformns of six-membered rings	ref
ob-[Co(*R*,*R*-2,4-ptn)$_3$]Cl_3·H_2O	(λ-skew-boat)$_3$	9
lel-[Co(*R*,*R*-2,4-ptn)$_3$]Cl_3·2H_2O	(λ-skew-boat)$_3$	10
trans-(*S*,*S*)-[Co(NO_2)$_2$(2*R*,4*R*,9*R*,11*R*-Me_4-3,2,3-tet)]NO_2	(λ-skew-boat)$_2$	12
Λ-*β*-[Co(ox)(2*S*,4*S*,9*S*,11*S*-Me_4-3,2,3-tet)]Br·3H_2O	(chair)$_2$	13
trans-(*S*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4	λ-skew-boat	14
trans-(*R*,*S*)-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4	chair	*a*
Λ-*β*-[Co(ox)(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4	chair	11, 15
Λ-*β*-[$CoCO_3$(5*R*,7*R*-Me_2-2,3,2-tet)]Cl·1.5H_2O	chair	*a*
trans-(*R*,*S*,*S*,*R*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4	λ-skew-boat	*a*
trans-(*S*,*R*,*S*,*S*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4	chair	*a*
trans-(*R*,*S*,*S*,*S*)-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4	λ-skew-boat	*a*
Λ-*β*-[$CoCO_3$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4·H_2O	chair	*a*

[a] Newly synthesized and characterized in this study.

The *trans*-dichloro complex (IIc) obtained by the reaction of this carbonato complex with hydrochloric acid was different from the already obtained IIa or IIb. The ^1H NMR spectrum of the present complex (Figure 6e) has two closely spaced C-methyl doublets at about 1.4 ppm, which are ascribed to two nonequivalent equatorial methyl groups on the basis of their chemical shifts. This observation indicates that the C_2 symmetry of the skew-boat structure is perturbed by the unsymmetrical arrangement of the two N-methyl groups. Only the trans-*R*,*S*,*S*,*S* structure (Figure 8c) is consistent with these observations. It is reasonable to assume that the configurations of asymmetric secondary nitrogen atoms are retained in this reaction, because the isomer obtained here is not the most stable IIa. Therefore, the structure of the parent carbonato complex was thought to be Λ-*β*-*R*,*S*,*S*,*S* or Λ-*β*-*S*,*S*,*S*,*R* (Figure 9a,b). The structure in Figure 9a can be regarded as the most stable among the structures in Figure 9, since the same arrangement of N-methyl groups as in Figure 9a has been found in the (oxalato)cobalt(III) complexes of (6*R*,8*S*)-6,8-dimethyl-2,5,9,12-tetraazatridecane (Figure 1f) and Λ-*β*-[Co(ox)(1,5*R*,7*S*,11-Me_4-2,3,2-tet)]ClO_4·H_2O.[19] Thus, we concluded that the complex ion [$CoCO_3$-(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ obtained here has the Λ-*β*-*R*,*S*,*S*,*S* configuration.

Conclusion

The central 2,4-pentanediamine part of 5*R*,7*R*-Me_2-2,3,2-tet and 1,5*R*,7*R*,11-Me_4-2,3,2-tet in the *trans*-dichloro complexes is not fixed in the skew-boat conformation by two C-methyl groups. The conformations adopted by the (*R*,*R*)-2,4-pentanediamine part in several complexes are summarized in Table II.

Further, the ligand 5*R*,7*R*-Me_2-2,3,2-tet gives the Λ-*β* configuration in the carbonato complex stereospecifically. The behavior of the 1,5*R*,7*R*,11-Me_4-2,3,2-tet complex is quite similar to that of the 5*R*,7*R*-Me_2-2,3,2-tet complex for the isomerism generated by the orientations of N-methyl groups. We expect that the complexes with these libands will be able to be used as good templates in asymmetric ligand reactions.

Acknowledgment. Expenses for the work were defrayed by a grant-in-aid from the Ministry of Education (Grant 475657).

Registry No. Ia, 55683-80-2; Ib, 76108-95-7; IIa, 76108-97-9; IIb, 76108-99-1; IIc, 76109-01-8; III, 76081-91-9; IV, 76081-93-1; Λ-β-*S*,*S*-[CoCO$_3$(5*R*,7*R*-Me$_2$-2,3,2-tet)]ClO$_4$, 76109-03-0; *trans*-*R*,*S*,-*R*,*R*-[CoCl$_2$(1,2*S*,10*S*,11-Me$_4$-2,3,2-tet)]ClO$_4$, 76095-36-8; 1,5*R*,7*R*,11-2,3,2-tet, 76108-93-5; *N*,*N'*-bis(carbobenzoxyglycyl)-(*R*,*R*)-2,4-pentanediamine, 76081-85-1; carbobenzoxyglycine, 1138-80-3; (*R*,*R*)-2,4-pentanediamine, 34998-98-6.

Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas 66045

Unique Octaiodide Configuration in Congested Macrocyclic Ligand Complexes

ALAN J. JIRCITANO, MITCHELL C. COLTON, and KRISTIN BOWMAN MERTES*

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The crystal and molecular structures of the iodine reaction products of complexes of palladium(II) and platinum(II) with the tetraaza macrocyclic ligand tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine have been determined. The complexes analyze for 8 I/macrocycle, exhibit thermal stability up to 180 °C, and are isomorphous, crystallizing in the space group $P2_1/n$. Unit cell dimensions for the palladium complex are $a = 7.756$ (7) Å, $b = 29.86$ (3) Å, $c = 17.64$ (3) Å, and $\beta = 112.9$ (1)°, and those for the platinum analogue are $a = 7.771$ (7) Å, $b = 29.95$ (7) Å, $c = 17.67$ (5) Å, and $\beta = 113.2$ (2)° with $Z = 4$. Within the macrocyclic cation the immediate coordination sphere of the metal is nearly planar; however, the overall geometry of the macrocyclic complex conforms to a hyperbolic paraboloid with cavities of 2.68 Å about the axial metal sites. The anion consists of discrete Z-shaped nonplanar chains of I_8^{2-}, each I_8^{2-} composed of two I_3^- units weakly associated with an elongated I_2.

Introduction

Novel and exciting chemistry has developed from the search for anisotropically behaving systems, particularly in the area of electrical conductivity. One approach to the design of highly conducting systems involves the synthesis of mixed-valent compounds.[1-5] Here electron transport is facilitated via partially occupied valence shells. With application of this rationale, considerable attention has been directed toward the utilization of the electron-acceptor properties of I_2 to remove electron density from a selected donor molecule.[6-20] The choice of iodine is judicious considering its propensity for forming stable catenated species capable of packing favorably in the crystal lattice by occupying channels in the one-dimensional network. The stoichiometry of the polyiodide acceptor product, the result of the interaction of the proposed electron-donor molecules with I_2, varies. A case in point involves the partially oxidized metal bis(dioximates). Bis(benzoquinone dioximato), (bqd)$_2$, complexes of nickel(II) and palladium(II) can be oxidized by I_2 to form [M(bdq)$_2$][I]$_{0.5}$.[16] Chains of I_3^- reside in channels in the crystal lattice in these complexes as determined by resonance Raman and ^{129}I Mössbauer techniques.[9] The analogous reaction of the bis(diphenylglyoximato), (dpg)$_2$,[13,17-20] systems with I_2 results in [M(dpg)$_2$][I] in which I_5^- chains reside in channels formed by the ligand phenyl groups.[6,7] Higher polyiodides, I_7^-, I_8^{2-}, I_9^-, and I_{16}^{4-}, can also occur although structural characterizations by X-ray crystallographic techniques have been minimal.[21-26] In general, however, even the higher polyiodides

Table I. Crystallographic Data

compd	[Pd(TAAB)][I$_8$]	[Pt(TAAB)][I$_8$]
fw	1534.13	1662.82
a, Å	7.756 (7)	7.771 (7)
b, Å	29.86 (3)	29.95 (7)
c, Å	17.64 (3)	17.67 (5)
β, deg	112.9 (1)	113.2 (2)
V, Å^3	3764 (8)	3786 (16)
d(calcd), g cm^{-3}	2.708	2.847
d(obsd) (flotation), g cm^{-3}	2.71 (1)	2.84 (1)
Z	4	4
space group	$P2_1/n$	$P2_1/n$
abs coeff, cm^{-1}	71.46	105.2
transmission coeff limits	0.2434–0.4591	0.3512–0.4586
no. of independent reflections	6657	6703
no. with $I > 3\sigma(I)$	4883	4581
final R_1	0.036	0.056
final R_2	0.042	0.059

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