Table III. Important Interatomic Dimensions for $VZn_2Cl_6(PPh_3)_2(THF)_2 \cdot 2CH_2Cl_2$[a]

A. Bond Distances (Å)

V–Zn	3.289 (1)	Zn–Cl(1)	2.197 (1)
–Cl(2)	2.501 (1)	–Cl(2)	2.324 (1)
–Cl(3)	2.526 (1)	–Cl(3)	2.293 (1)
–O	2.120 (3)	–P	2.392 (1)

B. Bond Angles (deg)

Cl(2)–V–Cl(2)′	180.00	Cl(2)–Zn–Cl(3)	97.22 (5)
–Cl(3)	87.08 (4)	–P	106.81 (5)
–O	88.5 (1)	Cl(3)–Zn–P	114.64 (5)
Cl(3)–V–Cl(3)′	180.00	V–Cl(2)–Zn	85.87 (4)
–O	91.0 (1)	V–Cl(3)–Zn	85.94 (4)
Cl(1)–Zn–Cl(2)	114.88 (6)		
–Cl(3)	112.10 (6)		
–P	110.58 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

two metals as expected for a Zn d^{10} configuration.

The dimensions of the tetrahedral $ZnCl_3PPh_3$ unit are reasonable when compared with those of the structurally characterized $ZnBr_3PPh_3$ anion,[8] which, to the best of our knowledge, provides the only close analogue to the zinc(II) portion of our trimer. The distortions from an ideal tetrahedron for these two zinc atoms are comparable. All angles around the zinc atom for the $ZnCl_3PPh_3$ unit range from 97.22 (5) to 114.88 (6)° as compared to the range of 101.2 (4)–115.9 (3)° for $ZnBr_3PPh_3^-$. The Zn–P distance in our vanadium compound is 2.392 (1) Å, a slightly shorter value than that for Zn–P, 2.425 (9) Å, in $ZnBr_3PPh_3$. The difference may be attributed to the larger bromine atoms that tend to force the PPh_3 away from the metal atom.

The Zn–Cl distances in $V(THF)_2[(\mu\text{-}Cl)_2ZnClPPh_3]_2$ are as expected: longer for the bridging chlorine atoms, Zn–Cl(2) = 2.324 (1) Å and Zn–Cl(3) = 2.293 (1) Å, and shorter for the terminal chlorine, Zn–Cl(1) = 2.197 (1) Å.

The coordination sphere of vanadium is also distorted. Whereas the Cl(2)–V–Cl(2)′ and Cl(3)–V–Cl(3)′ angles are of course ideal, 180.00° each, by symmetry, the other angles show the expected effects of the long V···Zn distances, with Cl(2)–V–Cl(3) smaller and Cl(2)–V–Cl(3)′ larger than 90°. The two V–Cl distances are very close; V–Cl(2) = 2.501 (1) Å and V–Cl(3) = 2.526 (1) Å.

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Registry No. $[V_2(\mu\text{-}Cl)_3(THF)_5PPh_3]_2[Zn_2Cl_6]$, 94090-06-9; $V(THF)_2[(\mu\text{-}Cl)_2ZnClPPh_3]_2$, 94090-08-1; $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, 89172-48-5.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal vibration parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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Stereochemistry and Relative Stability of Isomers of *trans*-Dichlorocobalt(III) Complexes with Chirally Substituted 3,7-Diazanonane-1,9-diamine

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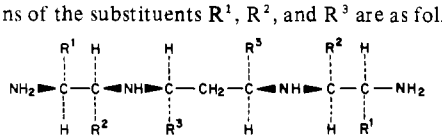
The stereochemistry of *trans*-dichlorocobalt(III) complexes with chiral derivatives of 3,7-diazanonane-1,9-diamine such as (2*S*,8*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (3,9-Me_2-2,3,2-tet), (3*S*,11*S*)-2,12-dimethyl-5,9-diazatridecane-3,11-diamine (2,10-Ip_2-2,3,2-tet), and (2*S*,10*S*)-1,11-diphenyl-4,8-diazaundecane-2,10-diamine (2,10-Bn_2-2,3,2-tet) was examined on the basis of ^{13}C NMR and circular dichroism (CD) measurements. The *trans*-dichloro complexes obtained by treating the corresponding carbonato complexes with hydrochloric acid adopt specifically the *RR* configuration with respect to the coordinated secondary nitrogen centers. The trans-*RR* isomers of 3,9-Me_2- and 2,10-Ip_2-2,3,2-tet isomerized in methanol (63 °C) to give rise to equilibrated mixtures of trans-*RR* and trans-*RS* isomers. The isomer ratio [*RS*]/[*RR*] was estimated as 1.65 ± 0.05 and 2.4 ± 0.4, respectively, for 3,9-Me_2- and 2,10-Ip_2-2,3,2-tet complexes. The observed influences of position or bulkiness of substituents on the isomer distribution were discussed, taking the steric interactions involved in the *RS* isomer into consideration. Λ-β-(Oxalato)cobalt(III) complexes with 2,3,2-tet derivatives including (3*S*,9*S*)-3,9-bis(aminomethyl)-2,10-dimethyl-4,8-diazaundecane (3,9-Ip_2-2,3,2-tet) were also prepared to interpret the fact that 3,9-Ip_2-2,3,2-tet gave no *trans*-dichloro complex.

A number of chirally substituted linear tetraamines have been synthesized in order to provide chiral circumstances to control the stereoselectivity of epimerization of amino acidates[1-3] and of decarboxylation of α-alkyl-α-aminomalonates[4-8] within cobalt(III) coordination sites. We have found that *trans*-dichlorocobalt(III) complexes with chirally substituted 3,7-diazanonane-1,9-diamine (2,3,2-tet) were most conveniently employed for preparing amino acidato[1-3] or α-alkyl-α-aminomalonato complexes.[6,7] Concurrently, fundamental stereochemistry of these tetraamine complexes has attracted attention, particularly with regard to the restricted occurrence of stereoisomers due to substituent effects.[9-14]

Table I. Structures and Abbreviations of Chiral 2,3,2-tet Derivatives[a]

R^1	R^2	R^3	abbrev
CH_3	H	H	2,10-Me_2-2,3,2-tet
H	CH_3	H	3,9-Me_2-2,3,2-tet
H	H	CH_3	5,7-Me_2-2,3,2-tet
$(CH_3)_2CH$	H	H	2,10-$Ip_2$2,3,2-tet
H	$(CH_3)_2CH$	H	3,9-Ip_2-2,3,2-tet
$C_6H_5CH_2$	H	H	2,10-Bn_2-2,3,2-tet

[a] Positions of the substituents R^1, R^2, and R^3 are as follows:



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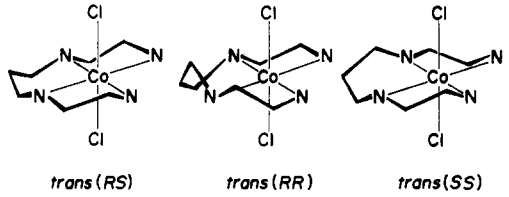

Figure 1. Structures of possible stereoisomers of *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$: trans-*RS*, trans-*RR*, and trans-*SS*.

It was indicated that three stereoisomers exist for *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ ion:[15] trans-*RS*,[16] -*RR*, and -*SS*, the latter two being enantiomeric to each other as shown in Figure 1. For *trans*-dichloro complexes of (2*S*,10*S*)-4,8-diazaundecane-2,10-diamine (2,10-Me_2-2,3,2-tet[17]) and (4*R*,6*R*)-4,6-dimethyl-3,7-diazanonane-1,9-diamine (5,7-Me_2-2,3,2-tet[17]), two of three possible isomers, trans-*RR* and -*RS* for the former[11] and trans-*SS* and -*RS* for the latter,[14] were isolated separately to permit the estimation of their relative stabilities. Although the *trans*-dichlorocobalt(III) complex of (2*S*,8*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (3,9-Me_2-2,3,2-tet) has been prepared,[1,6] no detailed stereochemistry has been reported.

This paper describes the preparation and stereochemistry of *trans*-dichlorocobalt(III) complexes with novel chiral 2,3,2-tet derivatives. The structures and abbreviations of employed ligands are shown in Table I. Stereochemical influences of the position of bulkiness of substituents on the relative stability of the isomers (trans-*RS* and -*RR*) were also examined spectrometrically.

Experimental Section

Materials. The ligands 2,10-Me_2-2,3,2-tet[10,11] and 3,9-Me_2-2,3,2-tet[1] were prepared by the reported methods. The *trans*-dichlorocobalt(III) complexes *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ and *trans*-(*RR*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ were prepared by the method reported previously.[10,11]

(2*S*,10*S*)-1,11-Diphenyl-4,8-diazaundecane-2,10-diamine (2,10-Bn_2-2,3,2-tet). *N*-(*tert*-Butyloxy)carbonyl-L-phenylalanine[18] (74 g) and triethylamine (39 mL) were dissolved in chloroform (300 mL), and the resultant mixture was cooled to 0 °C. To the solution was added ethyl chloro carbonate (31.2 g) in one portion with stirring and cooling. After stirring had been continued for 15 min, 1,3-propanediamine (10.9 g) dissolved in chloroform (78 mL) was added drop by drop and, then, stirred for 1 h more at 50 °C. The precipitate thus formed was filtered off and washed with water. The filtrate was evaporated to remove chloroform under reduced pressure, and the residue was combined with the precipitate described above. It was recrystallized from ethanol. Colorless solid was collected, washed with diethyl ether, and air-dried; yield 61 g.

N,*N*-Bis(*N*-(*tert*-butyloxy)carbonyl-L-phenylalanyl)-1,3-propanediamine obtained as above was added to a 4 M HCl–methanol solution (20 equiv of HCl/*t*-Boc group; 1 M = 1 mol L^{-1}) and the resultant mixture kept on a water bath (40–50 °C) until the evolution of carbon dioxide ceased. Methanol was removed under reduced pressure. White solid thus obtained was added to a stirred suspension of lithium aluminum hydride (25 g) in dry tetrahydrofuran (THF; 500 mL) in small portions and the resultant mixture stirred under reflux for 24 h. After the solution was cooled to room temperature, a mixture of water (47 mL) and THF (30 mL) was added with vigorous stirring, and the mixture was refluxed for 1 h and cooled. Undissolved mass was filtered off and washed with THF (100 mL). The filtered cake was mixed with THF (200 mL) and the mixture heated under reflux for 1 h. After the filtration, the same procedure was repeated once. All filtrates and washings were united, and THF was removed under reduced pressure. Pale yellow viscous liquid thus obtained was used for preparing the dichlorocobalt(III) complex without further purification.

(3*S*,11*S*)-2,12-Dimethyl-5,9-diazatridecane-3,11-diamine (2,10-Ip_2-2,3,2-tet). This tetraamine was obtained in procedures similar to those for 2,10-Bn_2-2,3,2-tet, except for the use of (*tert*-butyloxy)carbonyl-L-valine in place of (*tert*-butyloxy)carbonyl-L-phenylalanine. The product was purified by distillation; bp 140–142 °C (2 mmHg).

(3*S*,9*S*)-3,9-Bis(aminomethyl)-2,10-dimethyl-4,8-diazaundecane (3,9-Ip_2-2,3,2-tet). (*S*)-2-Amino-3-methyl-1-butanol (L-valinol;[19] 80.7 g) was heated to 130 °C, and 1,3-dichloropropane (22.1 g) was added to it drop by drop with stirring. No external heating was necessary during the addition. After the addition of 1,3-dichloropropane had been completed, the mixture was stirred and heated at 130 °C for 5 h. Sodium methoxide, prepared from sodium metal (9.0 g) and methanol (150 mL), was added while warm, and the mixture was cooled. White precipitate was removed by filtration and washed with methanol. The filtrate and washings were united, and methanol was removed by distillation. Excess L-valinol was recovered by distillation under reduced pressure. The viscous liquid that remained was dissolved in water and the solution neutralized with hydrobromic acid (48%) with cooling. The solution was evaporated to dryness under vacuum, and the residue was mixed with phosphorous tribromide (105 mL). The mixture was heated at 80 °C on a steam bath with occasional shaking, until the evolution of hydrogen bromide gas had settled. Excess phosphorous tribromide was distilled off under reduced pressure, and the residue was dissolved in water and filtered. The filtrate was concentrated, and aqueous ammonia (28%; 740 mL) was added to it with cooling. The solution was heated under reflux for 8 h, cooled to room temperature, and concentrated under reduced pressure. To the resultant solution was added sodium hydroxide pellets in small portions to make it strongly alkaline. The mixture was extracted with toluene several times, and the extracts were dried over potassium hydroxide pellets. Toluene was removed, and the crude product was distilled under reduced pressure; bp 135–138 °C (2 mmHg).

***trans*-(*RR*)-$[CoCl_2(2,10\text{-}Ip_2\text{-}2,3,2\text{-tet})]ClO_4$.** To perchloric acid (60%; 7.4 g) diluted with water (10.5 mL) was added 2,10-Ip_2-2,3,2-tet (3.6 g) in small portions with stirring and cooling in an ice bath. This solution was added drop by drop to a suspension of $Na_3[Co(CO_3)_3]\cdot 3H_2O$[20] (4.7 g) in water (35 mL). The mixture was heated on a water bath at 60 °C for 10 min, cooled to room temperature, and filtered. To the deep red solution were added hydrochloric acid (35%; 7 mL) and perchloric acid (60%; 2 mL), successively, and the resultant solution was evaporated on a water bath. Bluish green crystals were collected, washed with ethanol and diethyl ether, and air-dried; yield 5.1 g. Anal. Calcd for $C_{13}H_{32}N_4O_4Cl_3Co$: C, 32.96; H, 6.81; N, 11.83. Found: C, 32.77; H, 7.01; N, 11.71.

Mixture of *trans*-(*RR*)- and *trans*-(*RS*)-$[CoCl_2(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]ClO_4$. 2,10-$Bn_2$-2,3,2-tet (6.0 g) dissolved in a mixture of hydrochloric acid (35%; 1.9 g) and water (10 mL) was added to a solution of $CoCl_2\cdot 6H_2O$ (4.7 g) in 50% aqueous ethanol (300 mL). Carbon dioxide free air was bubbled through the solution for 3.5 h. To the deep brown solution was added hydrochloric acid (35%; 70 mL). After the solution color turned to dark violet, perchloric acid (60%; 15 mL) was added, and the solution was warmed to 50 °C. Green precipitate was filtered off, washed with dilute perchloric acid and ethanol, and air-dried; yield 7.0 g. The product was found to be composed of two isomers (trans-*RR* and trans-*RS*) on the basis of ^{13}C NMR measurements (see text).

***trans*-(*RR*)-$[CoCl_2(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]ClO_4$.** *trans*-$[CoCl_2(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]ClO_4$ (isomeric mixture; 1.44 g) and sodium carbonate (1.5 g) were added to a mixture of water (30 mL) and methanol (10 mL), and the mixture was warmed on a water bath (60 °C). Upon complete dissolution of green starting material, reddish violet precipitate (Λ-β-$[CoCO_3(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]ClO_4$) began to appear. The suspension was kept heating for 30 min, sodium perchlorate (2.0 g) was added to it, and the resultant mixture was cooled to 0 °C. Crystals were collected, washed with ethanol and diethyl ether, and air-dried; yield 1.19 g.

The carbonato complex (crude; 1.14 g) was added to 6 M HCl (20 mL) and the resultant mixture heated on a steam bath. Methanol was added in small portions to make the complex dissolve completely. After the effervescence had ceased, perchloric acid (60%; 1 mL) was added. Green crystals were filtered off, washed with ethanol and diethyl ether,

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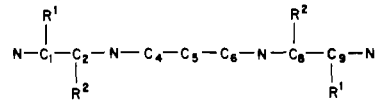
Table II. ^{13}C NMR Data[a] of the *trans*-(*RR*)-$[CoCl_2(tetraamine)]^+$ Ion

tetraamine		chem shift, ppm				
R^1	R^2	C_1, C_9	C_2, C_8	C_4, C_6	C_5	R^1 or R^2
H	H[b]	43.22	54.56	44.81	23.71	
CH_3	H[b]	60.29	51.76	44.38	23.96	$-CH_3$ 17.98
H	CH_3[b]	44.31	60.23	51.70	23.41	$-CH_3$ 17.98
$(CH_3)_2CH$	H[b]	61.39	57.00	44.44	23.41	$-CH_3$ 18.59, 19.26; >CH- 31.40
$C_6H_5CH_2$	H[c]	58.52	57.24	44.32	23.25	$-CH_2-$ 39.50; $-C_6H_5$ 127.41, 129.24, 129.48, 137.65
$C_6H_5CH_2$	H[c,d]	59.93, 59.44[e] 56.82, 56.02[e]		45.60	28.59	

[a] The order of carbon atoms is as follows:



[b] Obtained at 25 MHz. [c] Obtained at 100 MHz. [d] Data for *trans-RS* isomer. [e] These signals could not be distinguished into the two groups C_1, C_9 and C_2, C_8.

and air-dried; yield 1.12 g. It was recrystallized from methanol containing a small volume of HCl. Anal. Calcd for $C_{21}H_{32}N_4O_4Cl_3Co$: C, 44.27; H, 5.66; N, 9.83. Found: C, 44.39; H, 5.60; N, 10.35.

Λ-β-[Co(C_2O_4)(3,9-Ip_2-2,3,2-tet)]ClO_4·0.5H_2O.[21] To an aqueous solution (20 mL) of $K_3[Co(C_2O_4)_3]$[22] (1.83 g) was added 3,9-Ip_2-2,3,2-tet (1.0 g) with stirring. The solution temperature was raised to 50 °C until the reaction was completed (ca. 30 min). The resultant solution diluted with water (500 mL) was poured onto a column of SP-Sephadex C-25 (35-mm o.d. × 400-mm length; Na^+ form). The column was washed with water (1 L), and the adsorbed products were eluted with 0.05 M sodium perchlorate solution. Eluents for the band of unipositive-charged reddish violet complex were collected and concentrated on a rotary evaporator to afford reddish violet crystals that were filtered and washed with ethanol and diethyl ether; yield 1.36 g. Anal. Calcd for $C_{15}H_{33}N_4O_{8.5}ClCo$: C, 36.04; H, 6.65; N, 11.21. Found: C, 36.01; H, 7.17; N, 11.35.

Λ-β-[Co(C_2O_4)(2,10-Ip_2-2,3,2-tet)]Cl·NaCl·H_2O. To a solution of sodium oxalate (0.40 g) in water (30 mL) were added *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Ip_2\text{-}2,3,2\text{-tet})]ClO_4$ (0.94 g) and methanol (30 mL). The mixture was warmed on a water bath for 30 min. The resultant deep red solution was diluted with water (400 mL) and poured onto a column of SP-Sephadex C-25 (35-mm o.d. × 300-mm length; Na^+ form). The column was washed with water (1 L) and eluted with 0.05 M NaCl solution. The eluent for the band of red complex was collected and evaporated under reduced pressure almost to dryness. The residue was extracted with ethanol, and the extract was evaporated under reduced pressure to dryness. The residue was again extracted with ethanol to remove a small quantity of NaCl. The extract was evaporated almost to dryness under reduced pressure. The oily residue was mixed with ethanol (5 mL) and the resultant mixture warmed on a water bath to give red crystals. The whole was cooled in a refrigertor overnight, and the crystals were filtered off, washed with ethanol and diethyl ether, and air-dried. Anal. Calcd for $C_{15}H_{35}N_4O_5ClCoNa$: C, 35.79; H, 7.01; N, 11.13. Found: C, 36.18; H, 7.04; N, 10.68.

Λ-β-[Co(C_2O_4)(2,10-Bn_2-2,3,2-tet)]ClO_4. To a solution of oxalic acid dihydrate (0.15 g) in water (10 mL) was added Λ-β-$[CoCO_3(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]ClO_4$ (0.57 g), and the mixture was warmed on a water bath. Methanol was added in small portions to obtain complete dissolution of the complex. After the effervescence ceased, the solution was concentrated on a rotary evaporator, and the oily residue was dissolved in ethanol. To the solution was added sodium perchlorate (2.0 g) dissolved in water, and the suspension was warmed at 30 °C for 2 h and, then, cooled to room temperature. Crystals formed were collected, washed with ethanol and diethyl ether, and air-dried; yield 0.35 g. Anal. Calcd for $C_{23}H_{36}N_4O_8ClCo$: C, 44.34; H, 5.38; N, 9.00. Found: C, 44.78; H, 5.89; N, 8.70.

Λ-β-[Co(C_2O_4)(3,9-Me_2-2,3,2-tet)]ClO_4. To a solution of sodium oxalate (0.20 g) in water (30 mL) was added *trans*-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ (0.42 g) and the resultant mixture heated on a boiling water bath for 30 min. Small amounts of impurities were removed by filteration, and to the filtrate was added sodium perchlorate (2.0 g). After cooling, crystals were collected, washed with ethanol and diethyl ether, and air-dried; yield 0.38 g. Anal. Calcd for $C_{11}H_{24}N_4O_8ClCo$: C, 30.39; H, 5.56; N, 12.89. Found: C, 30.29; H, 5.74; N, 12.67.

Λ-β-[Co(C_2O_4)(2,10-Me_2-2,3,2-tet)]ClO_4·2H_2O. This complex was prepared by the same procedure as for the above complex, except for the use of *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ in place of *trans*-(*RR*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$; yield 0.28 g. Anal. Calcd for $C_{11}H_{28}N_4O_{10}ClCo$: C, 28.06; H, 5.99; N, 11.90. Found: C, 28.46; H, 5.78; N, 11.43.

Measurements. Visible absorption spectra were measured with a Shimadzu UV-210 recording spectrophotometer. Circular dichroism (CD) spectra were recorded on a Jasco J-500 recording spectropolarimeter. ^{13}C NMR spectra were obtained at 25.03 MHz with broad-band proton decoupling on a JEOL PFT-100 spectrometer, employing the solvent deuterium signal as an internal lock. Samples of *trans*-dichloro- and (oxalato)cobalt(III) complexes were dissolved in methano-d_1 and deuterium oxide, respectively, as the chloride form, after treating the perchlorate salt with tetraphenylarsonium chloride. Me_4Si sealed in a glass capillary was used as an external reference.

Estimation of Isomer Ratio of *trans*-(*RR*)- and *trans*-(*RS*)-Dichlorocobalt(III) Complexes at Equilibrium. A sample (ca. 0.2 g) of *trans*-(*RR*)-$[CoCl_2(tetraamine)]ClO_4$ (tetraamine = 3,9-Me_2- or 2,10-Ip_2-2,3,2-tet) dissolved in methanol was heated under reflux for 5 h. A slight insufficient molar amount of tetraphenylarsonium chloride hydrochloride was added, and the white precipitate was removed. The filtrate was concentrated under reduced pressure almost to dryness, and the residue was extracted with methanol (5 mL). The extract was evaporated to dryness, and the residue was dissolved in methanol-d_4. The ^1H NMR spectrum of the solution thus obtained was recorded on a JEOL GX-400 spectrometer. The isomer ratio was determined on the basis of intensities of several methyl resonances.

Results and Discussion

A. Stereochemistry of *trans*-Dichlorocobalt(III) Complexes with Chiral 2,3,2-tet Derivatives. Hamilton and Alexander[15] showed that *trans*-(*RS*)-$[CoCl_2(2,3,2\text{-tet})]^+$ is produced in the standard air-oxidation procedure,[23] while the treatment of β-$[CoCO_3(2,3,2\text{-tet})]^+$[21] with HCl produces the racemic (trans-*RR* + *SS*) dichloro complex. It was found,[11] however, that *trans*-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ prepared by the air-oxidation method is a mixture of two diastereomers, *RR* and *RS* (Figure 2a,b; $R^1 = CH_3$, $R^2 = H$), and that the trans-*RR* isomer is readily obtained in the pure form by treating Λ-β-$[CoCO_3(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ with HCl. This carbonato complex is produced in the reaction of $Na_3[Co(CO_3)_3]$ with 2,10-Me_2-2,3,2-tet partly neutralized with $HClO_4$. Hence, in recent papers[1,6] we directly prepared *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]ClO_4$ by adding HCl and $HClO_4$ to a reaction mixture of the above two components without the isolation of the carbonato complex.

(21) Topological isomers having cis geometry are designated as α or β, rather than sym-cis or uns-cis. For the complexes with a bidentate ligand such as CO_3^{2-} or $C_2O_4^{2-}$, which should assume the adjacent cis coordination sites upon coordination, the term "cis" is omitted.

(22) Bailar, J. C.; Jones, E. M. *Inorg. Synth.* **1939**, *1*, 37.

(23) (a) Bosnich, B.; Gillard, R. D.; McKenzie, E. D.; Webb, G. A. *J. Chem. Soc. A* **1966**, 1331. (b) Hamilton, H. G.; Alexander, M. D. *Inorg. Chem.* **1966**, *5*, 2060.

Table III. Visible Absorption and CD Spectral Data of Cobalt(III) Complexes with Chiral 2,3,2-tet Derivatives

complex	absorption $\nu_{max}/10^3$ cm^{-1} (ϵ)	CD $\nu_{ext}/10^3$ cm^{-1} ($\Delta\epsilon$)
trans-(*RR*)-[$CoCl_2$(2,10-Me_2-2,3,2-tet)]ClO_4[a]	16.26 (47)	15.20 (−0.74), 16.95 (+0.28)
	21.98 (30), 26.53 (53)	21.74 (−0.62), 25.64 (+0.35)
trans-(*RR*)-[$CoCl_2$(3,9-Me_2-2,3,2-tet)]ClO_4[a]	16.13 (54)	15.15 (−0.99), 17.01 (+0.25)
	22.22* (31),[c] 25.97 (57)	21.41 (−0.51), 25.25 (+0.40)
trans-(*RR*)-[$CoCl_2$(2,10-Ip_2-2,3,2-tet)]ClO_4[a]	16.26 (47)	15.27 (−0.84), 17.12 (+0.20)
	22.22* (34), 26.53* (59)	21.79 (−0.62), 25.64 (+0.36)
trans-(*RR*)-[$CoCl_2$(2,10-Bn_2-2,3,2-tet)]ClO_4[a]	16.26 (47)	15.27 (−0.96), 17.12 (+0.22)
	22.20* (33), 25.97 (59)	21.74 (−0.74), 25.51 (+0.34)
Λ-β(*RR*)-[$Co(C_2O_4)$(2,10-Me_2-2,3,2-tet)]ClO_4[b]	20.00 (137)	18.52 (+1.91), 20.88 (−0.58)
	27.93 (170)	26.60 (−0.06), 29.24 (+0.15)
Λ-β(*RR*)-[$Co(C_2O_4)$(3,9-Me_2-2,3,2-tet)]ClO_4[b]	19.92 (137)	18.42 (+2.17), 20.75 (−0.82)
	27.78 (177)	26.67 (−0.06), 29.07 (+0.23)
Λ-β(*RR*)-[$Co(C_2O_4)$(2,10-Ip_2-2,3,2-tet)]Cl[b]	20.00 (144)	18.62 (+2.69), 21.14 (−0.37)
	27.93 (189)	26.74 (−0.09), 29.24 (+0.23)
Λ-β(*RR*)-[$Co(C_2O_4)$(3,9-Ip_2-2,3,2-tet)]ClO_4[b]	19.84 (134)	18.45 (+2.39), 20.92 (−0.55)
	27.70 (174)	26.53 (−0.04), 28.99 (+0.27)
Λ-β(*RR*)-[$Co(C_2O_4)$(2,10-Bn_2-2,3,2-tet)]ClO_4[a]	19.76 (153)	18.52 (+2.64), 21.01 (−0.33)
	27.47 (185)	26.74 (−0.04), 28.74 (+0.11)

[a] Obtained in methanol. [b] Obtained in water. [c] Asterisks indicate shoulders.

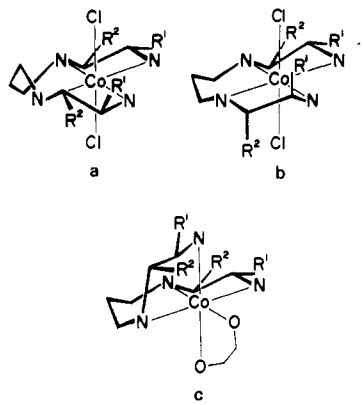


Figure 2. Possible structures of cobalt(III) complexes with chiral 2,3,2-tet derivatives: (a, b) *trans*-(*RR*)- and *trans*-(*RS*)-dichlorocobalt(III) complexes; (c) (oxalato)cobalt(III) complex. R^1 and R^2 correspond to those in Table I.

Table II summarizes ^{13}C NMR data for *trans*-dichlorocobalt(III) complexes with chiral tetraamines. The ^{13}C NMR spectrum of *trans*-(*RR*)-[$CoCl_2$(2,10-Me_2-2,3,2-tet)]$^+$ shows five resonances. This spectral feature is in accord with the C_2 symmetry of the complex, where pairs of the methyl, methine, and two kinds of methylene carbons adjacent to the secondary nitrogen should be, respectively, in the identical circumstances. The carbon resonances are assigned tentatively to the respective carbons on the basis of assumptions proposed by Brubaker and Johnson.[24]

The *trans*-[$CoCl_2$(3,9-Me_2-2,3,2-tet)]$^+$ ion produced via the carbonato complex[1] also showed five resonances in the ^{13}C NMR spectrum (Table II). Further, the CD curve of the 3,9-Me_2-2,3,2-tet complex resembles that of *trans*-(*RR*)-[$CoCl_2$(2,10-Me_2-2,3,2-tet)]$^+$ as shown in Figure 3. Numerical absorption and CD spectral data are summarized in Table III. It is determined, therefore, that *trans*-[$CoCl_2$(3,9-Me_2-2,3,2-tet)]$^+$ ion adopts the *RR* configuration with respect to the secondary nitrogen centers (Figure 2a; R^1 = H, R^2 = CH_3). The ^1H NMR spectrum at 400 MHz coincides with this structure, as will be shown later.

In the same manner as for 2,10- and 3,9-Me_2-2,3,2-tet, 2,10-Ip_2-2,3,2-tet afforded the *trans*-dichloro complex assignable to the *RR* configuration on the basis of its ^{13}C NMR features (seven resonance peaks; Table II) and CD spectral pattern (Figure 3). However, 3,9-Ip_2-2,3,2-tet gave rise to no *trans*-dichlorocobalt(III) complex by the same procedure, though the formation of carbonato complex [CoCO(3,9-Ip_2-2,3,2-tet)]$^+$ could be acknowledged

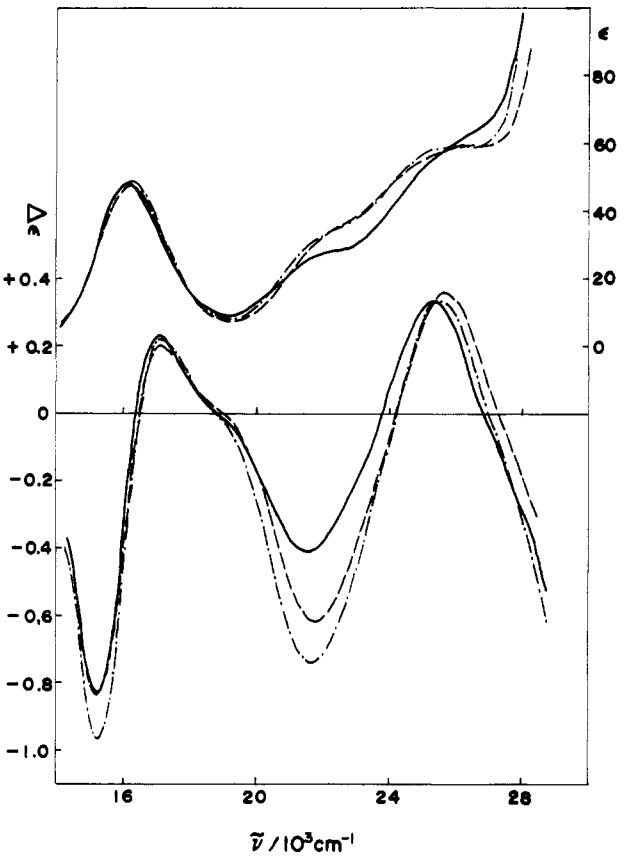


Figure 3. Visible absorption and CD specctra for Λ-β-(oxalato)cobalt(III) *trans*-(*RR*)-dichlorocobalt(III) complex of 3,9-Me_2-2,3,2-tet (—), 2,10-Ip_2-2,3,2-tet (- - -), and 2,10-Bn_2-2,3,2-tet (-·-).

distinctly. An attempt to obtain *trans*-dichloro complex of this tetraamine by the air-oxidation process also failed.

The reaction of $Na_3[Co(CO_3)_3]$ with 2,10-Bn_2-2,3,2-tet did not proceed smoothly due to the low solubility of the ligand in water so that the *trans*-dichloro complex was prepared by the air-oxidation process, using aqueous ethanol as solvent. The ^{13}C NMR spectrum of the product showed 12 resonances in the methylene and methine carbon regions (24–60 ppm). Evidently, the product should be regarded as a mixture of *trans*-(*RR*)- and *trans*-(*RS*)-[$CoCl_2$(2,10-Bn_2-2,3,2-tet)]$^+$, since the spectrum can be rationalized as the superimposition of five resonances to the trans-*RR* and nine resonances due to the trans-*RS* with incidental overlaps of two pairs of resonances for the latter (39.20 and 45.60 ppm; vide infra). If the product consists only of trans-*RR* isomer,

(24) Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1982**, *21*, 2223.

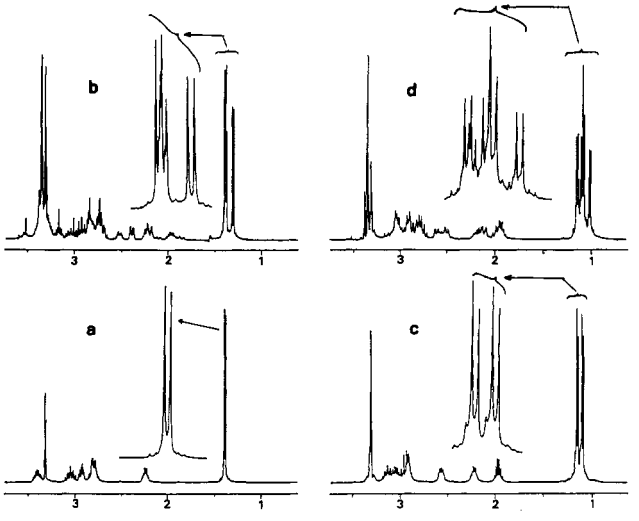


Figure 4. 400-MHz ^{1}H NMR spectra: (a) *trans*-(*RR*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (b) *trans*-(*RR*)- and *trans*-(*RS*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ at equilibrium; (c) *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Ip_2\text{-}2,3,2\text{-tet})]^+$; (d) *trans*-(*RR*)- and *trans*-(*RS*)-$[CoCl_2(2,10\text{-}Ip_2\text{-}2,3,2\text{-tet})]^+$ at equilibrium.

the spectrum should show five resonances in this region.

The isomeric mixture was converted to β-$[CoCO_3(2,10\text{-}Bn_2\text{-}2,3,2\text{-tet})]^+$, followed by the treatment with HCl and $HClO_4$. The *trans*-dichloro complex thus obtained was found to *RR* the *RR* configuration as expected (Figure 2a; $R^1 = CH_2C_6H_5$, $R^2 = H$), on the basis of its ^{13}C NMR (Table II) and CD (Figure 3; Table III) features. The ^{13}C NMR data for the *RS* isomer listed in Table II were picked out from the spectrum of the isomeric mixture by comparing it with that of the *RR* isomer.

It is established, therefore, that the *trans*-dichlorocobalt(III) complexes with most chiral tetraamines of the type in Table I adopt specifically trans-*RR* configuration, when they are prepared via the carbonato complexes. On the other hand, mixtures of *RS* and *RR* isomers tend to be produced by the air-oxidation procedure. An exception is the case of 3,9-Ip_2-2,3,2-tet, which does not form any *trans*-dichloro complex.

B. Relative Stabilities of trans-*RR* and trans-*RS* Isomers. a. 3,9-Me_2-2,3,2-tet and Other Dimethyl-Substituted 2,3,2-tet Complexes. It was observed that the CD curve of *trans*-(*RR*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ ion in methanol varies considerably before and after the heating under reflux for 5 h. Further heating of the sample solution caused no additional CD change. The possibility of isomerization from trans to any cis isomer was unlikely, because the solution exhibited no substantial change in the visible spectra during the heating. The CD change could be most reasonably attributed to the transformation from trans-*RR* to -*RS* to attain the equilibrium between these two species, as found for 2,10- and 5,7-Me_2-2,3,2-tet complexes.[11,14]

The 400-MHz ^{1}H NMR spectrum of the equilibrated mixture (Figure 4b) differs markedly from that of the pure trans-*RR* isomer (Figure 4a). While the latter shows a single methyl doublet centered at 1.38 ppm (J = 6.4 Hz), the former exhibits three doublets due to the methyl groups, one of which coincides with that of the *RR* isomer. The remaining two, which appeared at 1.31 (J = 6.4 Hz) and 1.39 ppm (J = 7.3 Hz) with almost equal intensities, can be ascribed to two methyl groups of the *RS* isomer, in which the methyl groups are intrinsically different from each other owing to the difference of their own orientations. When the peak area of the highest field doublet is compared with that of the others in Figure 4b, the isomer ratio at equilibrium is estimated as $[RS]/[RR] = 1.65 \pm 0.05$, which corresponds to $-\Delta G = 1.25 \pm 0.09$ kJ·mol^{-1} (25 °C). It was impossible to confirm this value by comparing it with that for the result employing the *RS* isomer since the isolation of the *RS* isomer was unsuccessful.

For the 2,10-Me_2-2,3,2-tet system the isomer ratio at equilibrium was found to be $[RS]/[RR] = 7.6 \pm 0.3$, ($-\Delta G = 5.02 \pm 0.12$ kJ·mol^{-1}).[11] We supposed that the trans-*RR* isomers of 2,10- and 3,9-Me_2-2,3,2-tet would be of approximately equal conformation energy, because for both complexes the tetraamine framework is identical and the methyl substituents preferentially take the equatorial orientation (Figures 5a,c). The trans-*RS* isomers of these tetraamines are thermodynamically more stable than the *RR* isomers, reflecting the pronounced stability difference between the *RS* and *RR* + *SS* isomers of the parent 2,3,2-tet complex.[15] But, the *RS* isomer of 3,9-Me_2-2,3,2-tet is apparently destabilized by 3.77 kJ·mol^{-1} in comparison with the corresponding 2,10-Me_2-2,3,2-tet complex, taking the *RR* isomers as a reference of conformation energy.

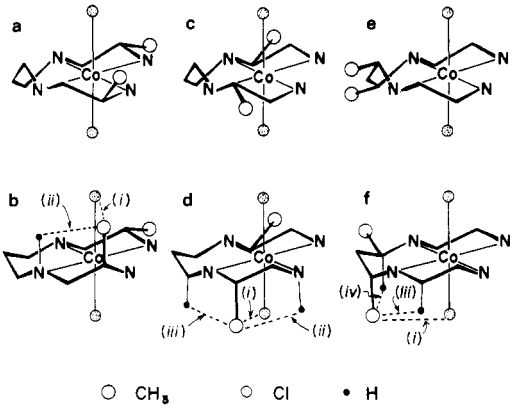


Figure 5. Structures of isomers of *trans*-dichloro complexes and dominant steric interactions of the axial methyl group, indicated as (i)–(iv) (see text): (a) *trans*-(*RR*)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (b) *trans*-(*RS*)-$[CoCl_2(2,10\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (c) *trans*-(*RR*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (d) *trans*-(*RS*)-$[CoCl_2(3,9\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (e) *trans*-(*SS*)-$[CoCl_2(5,7\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$; (f) *trans*-(*RS*)-$[CoCl_2(5,7\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$.

The most significant intramolecular steric interactions that destabilize the trans-*RS* isomers must be those between the axial methyl group and the coordinated chloride. These interactions are indicated as (i) on Figure 5b,d. The other common interaction expected for these structures is that between the axial methyl and the axially directed N-bonded proton, indicated as (ii). In addition, the interaction between the axial methyl and the axial C-bonded proton, indicated as (iii), should be involved in the *RS* isomer of Figure 5d. The difference between the *RS* isomers is probably ascribed to the fact that the interaction (iii) arises only for the 3,9-Me_2-2,3,2-tet complex. It is interesting to note that the observed energy difference (3.77 kJ·mol^{-1} or 0.90 kcal·mol^{-1}) corresponds well to the diaxial 1,3-interaction between an axial methyl and an axial proton, evaluated as 3.55 kJ·mol^{-1} (or 0.85 kcal·mol^{-1}) for methylcyclohexane.[25]

The dominant steric interactions involved in *trans*-(*RS*)-$[CoCl_2(5,7\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ ion are regarded as (i), (iii), and (iv) depicted in Figure 5f. The interaction (iv), which occurs between the axial methyl and the axial C-bonded proton within the six-membered ring, seems to resemble closely the CH_3 H diaxial 1,3-interaction for methylcyclohexane. The trans-*SS* isomer of 5,7-Me_2-2,3,2-tet, with two equatorial methyl groups (Figure 5e), is considered to be in a conformation energy level comparable to that of trans-*RR* isomers of 2,10- and 3,9-Me_2-2,3,2-tet. Considering that the interactions (i) and (iii) are found in common for the structures in Figures 5d and f, we supposed that, if the interactions (ii) and (iv) would sufficiently compensate each other, the trans-*RS* isomers of 3,9- and 5,7-Me_2-2,3,2-tet would be of similar conformation energy as well.

In fact, however, the trans-*RS* isomer of $[CoCl_2(5,7\text{-}Me_2\text{-}2,3,2\text{-tet})]^+$ is less stable by 1.92 kJ·mol^{-1} than the trans-*SS* isomer.[14] Thus, an energy difference as much as 3.17 kJ·mol^{-1} is postulated between the *RS* isomers of 5,7- and 3,9-Me_2-2,3,2-tet, the former being less stable than the latter. Most of such a conformation energy difference is probably attributable to the difference between (ii) and (iv). The N-bonded proton partici-

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Table IV. ^{13}C NMR Data of (Oxalato)cobalt(III) Complexes with Chiral 2,3,2-tet Derivatives[a]

tetraamine		chem shift, ppm			
R^1	R^2	$C_1, C_9, C_2, C_8, C_3, C_6$	C_5	oxalate	R^1 or R^2
H	H	43.53, 44.38, 46.76 49.50, 51.33, 56.76	23.90	169.53 (2)[b]	
CH_3	H	46.21, 49.07, 52.00 52.67, 56.69, 62.12	23.47	169.65 (2)	$-CH_3$ 17.80 (2)
$(CH_3)_2CH$	H	46.51, 49.20, 54.68 59.99, 61.88, 62.85	23.53	169.72 (2)	$-CH_3$ 19.81, 20.12, 21.03, 21.28; >CH- 32.07 (2)
$C_6H_5CH_2$	H	46.03, 49.01, 55.41 57.85, 58.65, 60.53	23.24	169.65 (2)	$-CH_2-$ 38.83 (2); C_6H_5- 128.44, 128.93, 130.21, 137.77, 138.14
H	CH_3	43.16, 46.76, 50.35 (2) 57.06, 63.95	23.84	169.72 (2)	$-CH_3$ 14.33, 14.69
H	$(CH_3)_2CH$	44.14 (3), 46.88 65.84, 72.76	24.02	169.78 (2)	$-CH_3$ 15.42 (2), 21.95 (2); >CH- 25.97, 26.58

[a] The order of carbon atoms of tetraamine is the same as in Table II. [b] The value in parentheses refers to the overlapped resonances.

pating in (ii) has been revealed not to point completly axially,[26] so that this interaction is considered not as effective in destabilization of the *RS* isomer as the interaction (iv).

Thus, it is clarified that position change of axial methyl groups attached to the 2,3,2-tet skeleton causes a stability change of the trans-*RS* isomer relative to that of the corresponding *RR* or *SS* isomer, influenced by the altering of intramolecular steric repulsions involving such methyl groups.

b. 2,10-Ip_2-2,3,2-tet Complex. In the monosubstituted cyclohexane series, isopropyl groups give rise to a slightly greater diaxial 1,3-interaction than methyl groups, i.e., 4.50 kJ·mol^{-1} (1.08 kcal·mol^{-1}) for the former and 3.55 kJ·mol^{-1} (0.85 kcal·mol^{-1}) for the latter per interaction.[25] It is assumed, therefore, that the interactions (i) and (ii) for the structure in Figure 5b will be affected by replacing the axial methyl with an isopropyl group, which results in the change of the [*RS*]/[*RR*] ratio at equilibrium.

In a similar manner as found for the 3,9-Me_2-2,3,2-tet complex, the CD curve of *trans*-(*RR*)-[$CoCl_2$(2,10-Ip_2-2,3,2-tet)]$^+$ in methanol varies by heating for 5 h. The ^1H NMR spectra (at 400 MHz) before and after the heating were given in Figure 4c,d. The spectrum of pure *RR* isomer (Figure 4c) shows two doublets centered at 1.08 (J = 7.0 Hz) and 1.14 ppm (J = 6.7 Hz), which are assignable to either of the diastereotopic methyl groups of isopropyl substituents. On the other hand, the isomeric mixture (Figure 4d) exhibits five doublets (1.01, 1.08, 1.10, 1.14, 1.15 ppm). It was noticed that the doublet at 1.08 ppm is slightly more intense and the one at 1.14 ppm is slightly less intense than the others. The doublet at 1.08 ppm looks like an overlap of two resonances, one of which comes from the *RR* and the other from the *RS* isomer. Thus, it is determined that the *RS* isomer of *trans*-[$CoCl_2$(2,10-Ip_2-2,3,2-tet)]$^+$ has four methyl doublets at 1.01 (J = 6.7 Hz), 1.08 (7.0 Hz), 1.10 (6.7 Hz), and 1.15 (6.7 Hz) ppm, reflecting the inequality of four methyl groups within the complex ion.

The isomer ratio for the 2,10-Ip_2-2,3,2-tet complex, estimated from the relative intensities of the doublets in Figure 4d, is [*RS*]/[*RR*] = 2.4 ± 0.4, i.e. $-\Delta G$ = 2.5 ± 0.4 kJ·mol^{-1}. The tendency that the *RS* isomer is more favorable than the *RR* is held even in the case of this tetraamine. If it is possible to presume that the *RR* isomers of 2,10-Ip_2- and 2,10-Me_2-2,3,2-tet adopt a comparable conformation energy, the observed difference of as much as 2.5 kJ·mol^{-1} between the *RS* isomers with these tetraamines can be attributed to the change in the interactions (i) and (ii) of Figure 5b. The change of (ii) due to the replacement of a methyl by an isopropyl may be similar to that found for a cyclohexane ring, evaluated as ca. 1 kJ·mol^{-1}.[25] Then, the change of (i) caused by the substituent change is estimated as ca. 1.5 kJ·mol^{-1}, a value acceptable for the substituent effect for the interaction (i).

C. (Oxalato)cobalt(III) Complexes with Chiral 2,3,2-tet. In order to elucidate the previously mentioned exceptional feature of 3,9-Ip_2-2,3,2-tet, (oxalato)cobalt(III) compelxes with chiral 2,3,2-tet were prepared, since β-[$Co(C_2O_4)$(3,9-Ip_2-2,3,2-tet)]ClO_4 could be isolated as a pure crystalline product. The ^{13}C NMR spectra of oxalato complexes with tetraamines exhibited the resonances in accord with the total constituent number for each ligand, though occasional overlaps of two or more signals were often encountered. Thus, it was determined that the oxalato complexes of all the examined 2,3,2-tet derivatives including 3,9-Ip_2-2,3,2-tet take the β geometry. The ^{13}C NMR data for oxalato complexes are summarized in Table IV, but the assignment of every resonance to the individual carbon was difficult.

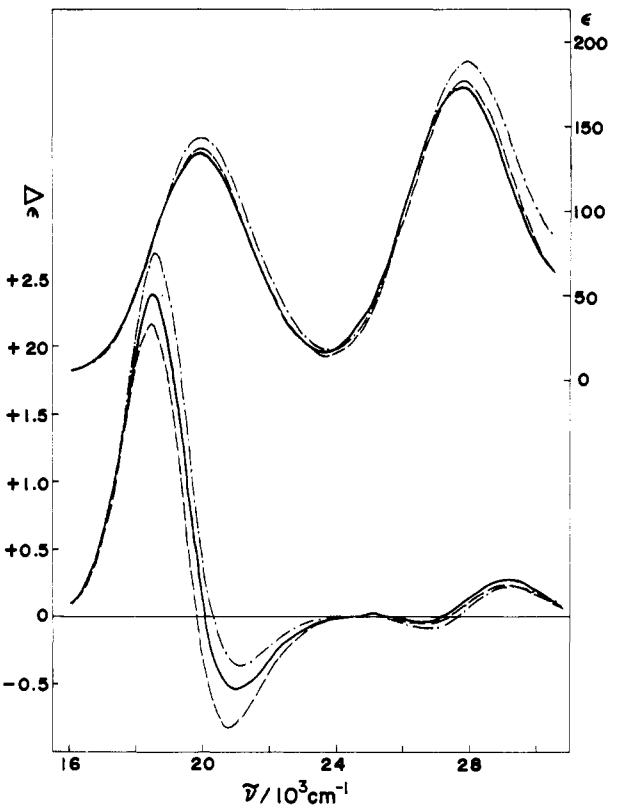

Figure 6. Visible absorption and CD spectra of Λ-β-(oxalato)cobalt(III) complexes with 3,9-Ip_2-2,3,2-tet (—), 3,9-Me_2-2,3,2-tet (- - -), and 2,10-Ip_2-2,3,2-tet (-·-).

The oxalato complex of 3,9-Ip_2-2,3,2-tet and other tetraamines showed a dominant positive CD extremum in the first d–d transition ($^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h)) region, as indicated in Figure 6. The spectral data are listed in Table III. The observed resemblance in CD pattern between these oxalato complexes and Λ-β-[$Co(C_2O_4)$(5,7-Me_2-2,3,2-tet)]$^+$ ion[27] indicates that the oxalato complexes examined here adopt exclusively the Λ-β configuration.

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Furthermore, it was noted that the visible absorption maxima of oxalato complexes were very close to each other (Table III). The isopropyl groups of 3,9-Ip_2-2,3,2-tet brought about no remarkable decrease of the ligand field strength of the tetraamine in comparison with others. It was presumed, therefore, that the steric effects caused by the isopropyl group attached to the carbon adjacent to the secondary nitrogen are not so significant as to exclude the formation of *trans*-dichloro complex with 3,9-Ip_2-2,3,2-tet. Molecular model examines also suggests no obvious stereochemical reason for the fact that *trans*-(*RR*)-$[CoCl_2$(3,9-Ip_2-2,3,2-tet)$]^+$ is not produced even from the carbonato complex.

As described previously,[10,11] the isomerization from Λ-*cis*-β-(*RR*)- to *trans*-(*RR*)-$[CoCl_2$(2,10-Me_2-2,3,2-tet)$]^+$ proceeds without difficulty in hydrochloric acid solution and is usually facilitated by the addition of perchlorate ion, which enhances particularly the crystallization of *trans*-dichlorocobalt(III) complex. Similar enhanced crystallization of *trans*-(*RR*)-dichloro complexes could be observed for 3,9-Me_2-, 2,10-Ip_2-, and 2,10-Bn_2-2,3,2-tet in this study. A plausible explanation for the exceptional case of 3,9-Ip_2-2,3,2-tet may be that Λ-*cis*-β(*RR*)-$[CoCl_2$(3,9-Ip_2-2,3,2-tet)$]^+$, which can be developed from Λ-β-(*RR*)-$[CoCO_3$(3,9-Ip_2-2,3,2-tet)$]^+$, isomerizes to the corresponding *trans*-(*RR*)-dichloro complex only very slowly and/or the trans complex is highly soluble even as the perchlorate salt.

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Registry No. *trans*-(*RR*)-$[CoCl_2$(2,10-Ip_2-2,3,2-tet)$]ClO_4$, 94404-88-3; *trans*-(*RR*)-$[CoCl_2$(2,10-Bn_2-2,3,2-tet)$]ClO_4$, 94404-90-7; *trans*-(*RS*)-$[CoCl_2$(2,10-Bn_2-2,3,2-tet)$]ClO_4$, 94481-28-4; *trans*-(*RR*)-$[CoCl_2$(2,10-Me_2-2,3,2-tet)$]ClO_4$, 60801-69-6; *trans*-(*RR*)-$[CoCl_2$(2,3,2-tet)$]^+$, 27957-84-2; *trans*-(*RS*)-$[CoCl_2$(3,9-Me_2-2,3,2-tet)$]^+$, 73396-01-7; *trans*-(*RS*)-$[CoCl_2$(2,10-Ip_2-2,3,2-tet)$]^+$, 94481-29-5; Λ-β-$[CoCO_3$(2,10-Bn_2-2,3,2-tet)$]ClO_4$, 94404-92-9; Λ-β-$[Co(C_2O_4)$(3,9-Ip_2-2,3,2-tet)$]ClO_4$, 94404-94-1; Λ-β-$[Co(C_2O_4)$(2,10-Ip_2-2,3,2-tet)]Cl, 94426-36-5; Λ-β-$[Co(C_2O_4)$(2,10-Bn_2-2,3,2-tet)$]ClO_4$, 94404-96-3; Λ-β-$[Co(C_2O_4)$(3,9-Me_2-2,3,2-tet)$]ClO_4$, 94404-98-5; *trans*-$[CoCl_2$(3,9-Me_2-2,3,2-tet)$]ClO_4$, 73396-02-8; Λ-β-$[Co(C_2O_4)$(2,10-Me_2-2,3,2-tet)]-ClO_4, 94405-00-2; $Na_3[Co(CO_3)_3]$, 75632-02-9; $K_3[Co(C_2O_4)_3]$, 14239-07-7; 2,10-Bn_2-2,3,2-tet, 94405-01-3; 2,10-Ip_2-2,3,2-tet, 94405-03-5; 3,9-Ip_2-2,3,2-tet, 94405-04-6; *N*-(*tert*-butyloxy)carbonyl-L-phenylalanine, 13734-34-4; 1,3-propanediamine, 109-76-2; *N,N'*-bis(*N*-*tert*-butyloxy)carbonyl-L-phenylalanyl)-1,3-propanediamine, 94405-02-4; (*tert*-butyloxy)carbonyl-L-valine, 13734-41-3; L-valinol, 2026-48-4; 1,3-dichloropropane, 142-28-9.

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Chiral Octahedral Iron and Ruthenium Complexes. Use of Diastereotopic Phosphorus Atoms for the Direct Observation of Hidden Coupling Constants

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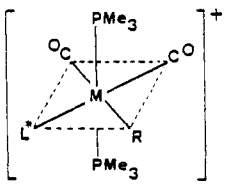
A series of asymmetric phosphorus ligands was synthesized and used to prepare chiral octahedral iron and ruthenium complexes $(MR(CO)_2L^*(PMe_3)_2)^+A^-$. Their geometrical configuration was deduced from IR and NMR (^1H, ^{31}P) spectroscopic studies. Due to the presence of an asymmetric center directly bonded to the metal atom, the two axial PMe_3 ligands are shown to be diastereotopic and this allows, for the first time, a direct determination of the phosphorus–phosphorus coupling constants between chemically identical ligands by ^{31}P NMR. The conformation of the asymmetric ligands relative to the other ligands, CO, R, and the two axial PMe_3 groups, is shown to be an important factor in determining the magnitude of the proton inequivalence between the two PMe_3 ligands.

Introduction

Octahedral complexes having two identical ligands L in mutually trans positions possess a symmetry plane. This equatorial plane is the sole element of symmetry if the four equatorial ligands are different, a ≠ b ≠ c ≠ d, or if two of these ligands are identical but have a cis orientation, a = b ≠ c ≠ d (C_s symmetry).

Removal of the symmetry plane can be achieved by introducing an asymmetric ligand in the equatorial plane. Although the metal itself is not an asymmetric center, such complexes having no symmetry element are chiral and belong to the C_1 symmetry group. Therefore the axial ligands L are diastereotopic.

This report describes the synthesis of iron and ruthenium chiral octahedral complexes **1**, where the equatorial ligand L* is asymmetric. A number of two-electron ligands were used, but special attention was focused on asymmetric phosphines where an atom of phosphorus is the asymmetric center. Various chiral phosphines PhP(R')R'' were synthesized for this purpose and stereoselectively introduced in the equatorial plane of octahedral complexes of the type $(MR(CO)_2L'(PMe_3)_2)^n$ (n = 0, L' = I, Br, Cl; n = 1+, L' = CO, NCMe, PR_3 (R = Me, CH_2Ph)) some of which were previously described.[1] An NMR study of these complexes was performed in order to establish whether the anisochrony expected for the diastereotopic PMe_3 axial ligands can be detected in their ^1H and ^{31}P spectra. Should the ^{31}P of these PMe_3 ligands be observed to be anisochronous, another point of interest would be the possibility of obtaining the values of trans and cis phosphorus–phosphorus coupling constants from ^{31}P spectra, since these complexes have three phosphorus ligands.



M = Fe, Ru.

1

Results

Synthesis of Asymmetric Phosphine Ligands. Asymmetric phosphorus ligands of various types have been synthesized in high yield by consecutive substitution of the two chlorine atoms of dichlorophenylphosphine in a one-pot reaction.[2]

$$PhPCl_2 \xrightarrow{I} PhP(R')Cl \xrightarrow{II} PhP(R')R''$$

In the first step, an organocadmium derivative R'_2Cd (R' = alkyl or aryl) was reacted at low temperature with $PhPCl_2$ to afford the corresponding chlorophosphine. Similarly, bulky alcohols or secondary amines led selectively to chloro esters (R' = OR) or chloro amides ($R' = NR_2$). In the second step, the remaining

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