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Preparation and Stereochemistry of Cobalt(III) Complexes Containing (3*S*,8*S*)-3,8-Dimethyl-1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane or (4*S*,9*S*)-2,4,9,11-Tetramethyl-5,8-diaza-2,11-diphosphadodecane (*SS*-Me$_2$-mm-PNNP). Molecular Structure of $(+)_{589}$-*Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$(ClO_4)_2 \cdot H_2O$ (acac=$C_5H_7O_2^-$)

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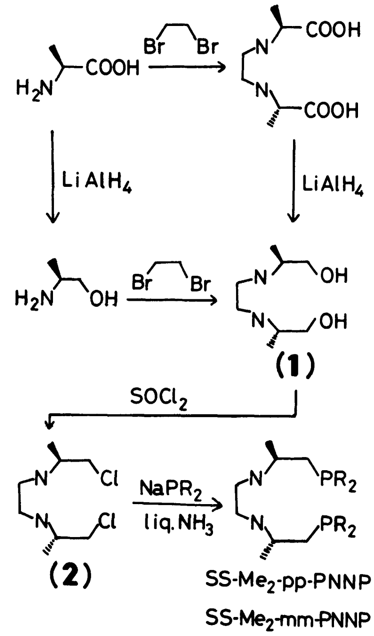
Two new optically active quadridentate phosphine ligands, (3*S*,8*S*)-3,8-dimethyl-1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane(*SS*-Me$_2$-pp-PNNP) and (4*S*,9*S*)-2,4,9,11-tetramethyl-5,8-diaza-2,11-diphosphadodecane-(*SS*-Me$_2$-mm-PNNP) and their cobalt(III) complexes, *trans*-[CoCl$_2$(*SS*-Me$_2$-pp- or *SS*-Me$_2$-mm-PNNP)]$^+$, *Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-pp-PNNP)]$^{2+}$ (acac=2,4-pentanedionate ion), *Λ*-*cisβ*-[Co(CO$_3$)(*SS*-Me$_2$-pp-PNNP)]$^+$, and *Δ*- and *Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$ were prepared and characterized. The molecular structure and the absolute configuration of $(+)_{589}$-*Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$(ClO_4)_2 \cdot H_2O$ were determined by X-ray analysis. Crystal data; monoclinic, C2, a=28.274(4)Å, b=9.266(1)Å, c=11.0901(9)Å, β=92.97(1)°, V=2901.6(5)Å^3, and Z=4. Three five-membered chelate rings in the complex form distorted gauche ($\delta\lambda\lambda$) conformations, and the methyl group on carbon of the apically linked chelate ring takes an axial disposition. Stereochemistry of all the complexes was discussed on the basis of the NMR, absorption and CD spectra.

In a previous paper,[1] cobalt(III) complexes containing 1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (pp-PNNP) or 2,11-dimethyl-5,8-diaza-2,11-diphosphadodecane (mm-PNNP) were prepared, and the absorption spectra and stereochemistry were compared with those of the corresponding (2-aminoethyl)-diphenylphosphine (edpp) complexes. All of these quadridentate phosphine complexes formed stereoselectively a particular geometrical isomer. Introduction of asymmetric carbon atoms into a chelate ligand often brings about remarkable stereoselectivity in the formation of a particular optical isomer.[2] In this paper, we have prepared two optically active quadridentate phosphine ligands, (3*S*,8*S*)-3,8-dimethyl-1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (*SS*-Me$_2$-pp-PNNP) and (4*S*,9*S*)-2,4,9,11-tetramethyl-5,8-diaza-2,11-diphosphadodecane (*SS*-Me$_2$-mm-PNNP), and their cobalt(III) complexes. The structure and absolute configuration of $(+)_{589}$-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$(ClO_4)_2 \cdot H_2O$ (acac=2,4-pentanedionate ion) have been determined by the X-ray diffraction method. Stereochemistry of other complexes was discussed by comparing the NMR, absorption, and circular dichroism spectra with those of the structurally known $(+)_{589}$-complex.

Experimental

Phosphine ligands, *SS*-Me$_2$-pp- and *SS*-*Me*$_2$-mm-PNNP, were prepared and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for preparing the ligands and complexes are deoxygenated by bubbling nitrogen for 20 min immediately before use. ^{1}H NMR, absorption and circular dichroism spectra were recorded on a Jeol JNM GX-400 spectrometer, a Hitachi 323 spectrophotometer and a Jasco J-40CS spectropolarimeter, respectively.

Preparation of Ligands. The optically active quadridentate phosphine ligands were prepared according to the synthetic route given in Scheme 1.



Scheme 1.

(2*S*,7*S*)-2,7-Dimethyl-3,6-diaza-1,8-octanediol (**1**) was prepared from (*S*)-alaninol (2-amino-1-propanol)[3] by a modified method of Holdiness *et al.*[4] (method **a**), or from (2*S*,7*S*)-2,7-dimethyl-3,6-diaza-octanedionic acid (EDDP)[5] (method **b**). Method **a**: To (*S*)-alaninol (63.8 g, 0.85 mol) in a 1 dm^3 three-necked round bottom flask was added dropwise 1,2-dibromoethane (25.3 g, 0.125 mol) over 1 h at 100 °C with stirring. Stirring was continued for 4 h at 100 °C, and then the solution was cooled to 0 °C and mixed with KOH (19.6 g, 0.35 mol) in ethanol (200 cm^3). After 1 h KBr precipitated was filtered, and the filtrate was evaporated under reduced pressure to remove ethanol, yielding an oily liquid. The liquid was distilled at *ca.* 130 Pa, giving unreacted (*S*)-alaninol at *ca.* 50 °C and the desired **1** at *ca.* 160 °C. Yield: 15.1 g, mp 99 °C, $[\alpha]_D$=+28 °(H$_2$O, 25 °C). Elemental analysis was performed on the hydrochloride salt of **1** (*vide infra*). Method **b**: To $LiAlH_4$ (15 g) in THF (400 cm^3) at 0 °C was added EDDP (14.8 g, 72.5 mmol) in small portions with stirring. The mixture foamed violently. The resulting solution was stirred at 0 °C for 30 min and then refluxed for 10 h. After cooling an aqueous solution (*ca.* 100 cm^3) saturated with KNa[*d*-tartrate]$\cdot 4H_2O$ was added dropwise to the solution. A white precipitate was filtered and washed twice with ethanol (50 cm^3×2). The filtrate and washings were combined, and the solvent was evaporated under reduced pressure. An oily liquid obtained was vacuum-distilled under the same conditions as in Method **a** to yield **1**. Yield: 6.05 g.

(2*S*,7*S*)-2,7-Dimethyl-1,8-dichloro-3,6-diazaoctane dihydrochloride (**2**) was prepared from **1**. HCl gas was bubbled under cooling into a chloroform solution (150 cm^3) of **1** (6.0 g, 34 mmol) in a 1 dm^3 three-necked round bottom flask, yielding white crystals (Found: C, 38.39; H, 8.93; N, 11.04%. Calcd for $C_8H_{22}N_2Cl_2O_2$=**1**·2HCl: C, 38.56; H, 8.93; N, 11.24%.). To the mixture was added $SOCl_2$ (12.5 g, 0.121 mol) dropwise over 15 min under cooling. The resulting solution was refluxed for 4 h in a water bath (60 °C), and then cooled in an ice bath. White crystals formed were filtered and recrystallized from hot isopropyl alcohol (200 cm^3). Yield: 4.5 g. Found: C, 33.72; H, 7.04; N, 9.84%. Calcd for $C_8H_{20}N_2Cl_4$(**2**): C, 33.59; H, 7.05; N, 9.79%.

(3S,8S)-3,8-Dimethyl-1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (SS-Me$_2$-pp-PNNP). To liquid ammonia (250 cm^3) containing metallic sodium (1.33 g, 57.8 mmol) in a 500 cm^3 three-necked round bottom flask was added dropwise diphenylphosphine[6] (11.0 g, 59.1 mmol) over 5 min with stirring at −78 °C. After stirring for 1 h, the color of the solution changed from deep blue to orange. To the orange solution was added compound **2** (4.15 g, 14.5 mmol) in small portions with stirring. Stirring was continued for 1 h, giving a colorless solution. After liquid ammonia had been evaporated, water (100 cm^3) and then diethyl ether (80 cm^3) were added to the residue with stirring. The ethereal layer was separated from the aqueous layer and dried over $MgSO_4$ (*ca.* 3 g) overnight. A viscous liquid was obtained by removing the solvent and unreacted diphenylphosphine under vacuum. The product (*ca.* 6.0 g) was used for preparing cobalt(III) complexes without further purification.

(4S,9S)-2,4,9,11-Tetramethyl-5,8-diaza-2,11-diphosphadodecane (SS-Me$_2$-mm-PNNP). To liquid ammonia (100 cm^3) containing metallic sodium (0.6 g, 26 mmol) in a 300 cm^3 three-necked round bottom flask was added dropwise tetramethyldiphosphine[7] (1.5 g, 12.3 mmol) with stirring at −78 °C. After stirring for 1 h, compound **2** (1.8 g, 6.3 mmol) was added to the resulting orange solution in small portions with stirring. After 1 h liquid ammonia was evaporated, and then water (50 cm^3) and diethyl ether (50 cm^3) were added successively to the residue with stirring. The ethereal layer was separated from the aqueous layer, dried over $MgSO_4$ (*ca.* 2 g) overnight, and then distilled under reduced pressure to remove the solvent and unreacted dimethylphosphine. The colorless oily product thus obtained (*ca.* 1.3 g) was used for preparing cobalt(III) complexes without further purification.

Preparation of Complexes. trans-*[CoCl$_2$(SS-Me$_2$-pp-PNNP)]ClO$_4$·0.5H$_2$O*: To a methanol solution (50 cm^3) of $Co(ClO_4)_2\cdot 6H_2O$ (1.30 g, 3.55 mmol) was added *SS*-Me$_2$-pp-PNNP (1.75 g, 3.99 mmol) with stirring. An orange solution was obtained. Methanol was removed under reduced pressure, and the residue was dissolved in dichloromethane (250 cm^3). Chlorine gas was bubbled into the dichloromethane solution for 10 min, and then nitrogen gas for 20 min to remove excess Cl_2. To the resulting green solution was added methanol (20 cm^3), and the solution was evaporated to a small volume under reduced pressure, yielding a green precipitate (the solution should not be evaporated to dryness since perchlorates of complexes are potentially explosive in a solid state). The precipitate was dissolved in hot methanol (150 cm^3). Solid $NaClO_4\cdot H_2O$ (22 g) was dissolved in the solution, which was stored in a refrigerator overnight. Green crystals yielded were filtered, washed with water and then diethyl ether, and air-dried. Yield: 627 mg. Additional crystals (234 mg) were obtained by concentrating the filtrate. Total yield: 34%. Found: C, 51.24; H, 5.00; N, 3.67%. Calcd for $C_{32}H_{39}N_2Cl_3CoO_{4.5}P_2$: C, 51.18; H, 5.23; N, 3.73%. The complex is soluble in methanol, dichloromethane, chloroform and acetone, but not in water, diethyl ether and benzene.

trans-*[CoCl$_2$(SS-Me$_2$-mm-PNNP)]ClO$_4$·0.5H$_2$O.* To *cis*-$[CoCl_2(en)_2]Cl$[8] (en=ethylenediamine) (2.5 g, 8.76 mmol) in a mixture of water (10 cm^3) and methanol (40 cm^3) was added *SS*-Me$_2$-mm-PNNP (0.871 g, 3.30 mmol) with stirring. After 1 h the solution was mixed with concd HCl(10 cm^3) and stirred for 4 h, the temperature of the solution being gradually raised from room temperature to 45 °C. The solution was cooled, filtered to remove $[Co(en)_3]Cl_3$ precipitated, and the filtrate was evaporated to dryness. Methanol (100 cm^3) was added to the residue, and the solution was filtered to remove insoluble $[Co(en)_3]Cl_3$. The filtrate was diluted with water (500 cm^3), and the solution was applied on a column (ϕ 8 cm×5 cm) of SP-Sephadex C-25 (Na^+ form). By elution with 0.05 mol dm^{-3} HCl, a blue eluate was collected, and evaporated to dryness under reduced pressure. The blue complex was extracted from the residue with ethanol, and the extract was evaporated again to dryness under reduced pressure. The residue was mixed with $LiClO_4\cdot 3H_2O$ (2 g) in water (15 cm^3), and the solution was stored in a refrigerator overnight, yielding blue crystals, which were filtered, washed with water and air-dried. Yield: 267 mg. Found: C, 28.73; H, 6.57; N, 5.06%. Calcd for $C_{12}H_{31}N_2Cl_3CoO_{4.5}P_2$: C, 28.68; H, 6.02; N, 5.57%. The complex is soluble in water, methanol and acetone, but not in dichloromethane, chloroform, diethyl ether and benzene.

Λ-cis*β-[Co(acac)(SS-Me$_2$-pp-PNNP)](ClO$_4$)$_2$·H$_2$O.* A methanol solution (75 cm^3) containing *trans*-[CoCl$_2$(*SS*-Me$_2$-pp-PNNP)]ClO$_4$·0.5H$_2$O (200 mg, 0.266 mmol) and Li(acac) (30 mg, 0.28 mmol) was stirred at room temperature for 7 h. The resulting orange-red solution was diluted with water (700 cm^3), and the solution was applied on a column (ϕ 3.5 cm×100 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaBr, a very small red band, a large red one, and a brown one were eluted successively. The eluate of the second red band was collected and concentrated to a small volume under reduced pressure. The red complex was extracted with chloroform, and the extract was evaporated to dryness. The residue was dissolved in water (10 cm^3), and the solution was mixed with $NaClO_4\cdot H_2O$ (0.2 g) in water (1 cm^3). Red crystals formed were filtered, washed with a very small amount of water and then diethyl ether, and air-dried. Yield: *ca.* 50 mg. Found: C, 50.29; H, 5.19; N, 3.28%. Calcd for $C_{37}H_{47}N_2Cl_2CoO_{11}P_2$: C, 50.07; H, 5.34; N, 3.16%. The complex is soluble in water, methanol, dichloromethane and acetone, but not in diethyl ether and benzene.

$(-)_{589}$-Δ-cisβ-[Co(acac)(SS-Me_2-mm-PNNP)]$(ClO_4)_2\cdot0.5NaClO_4\cdot H_2O$ and $(+)_{589}$-Λ-cisβ-[Co(acac)(SS-Me_2-mm-PNNP)]$(ClO_4)_2\cdot H_2O$. A mixture of $[Co(acac)_3]$[9)] (380 mg, 1.08 mmol), *SS*-Me_2-mm-PNNP (200 mg, 0.320 mmol) and active charcoal (*ca.* 50 mg) in methanol (100 cm^3) was stirred at room temperature for 10 h, and filtered. The filtrate was diluted with water (1 dm^3) and applied on a column (ϕ3.5 cm×10 cm) of SP-Sephadex C-25. After complexes with the +1 charge contained in the adsorbed product had been eluted with 0.05 mol dm^{-3} NaCl, those with the +2 charge were eluted with 0.2 mol dm^{-3} NaCl. The orange eluate obtained was diluted with water (3 dm^3) and applied on a column (ϕ 3 cm×30 cm) of SE-Toyopearl.[10)] Yellow-orange and orange bands (F-1 and F-2) were eluted successively with 0.3 mol dm^{-3} NaCl. Each eluate of F-1 and F-2 was mixed with excess $NaClO_4\cdot H_2O$ (*ca.* 2 g), and concentrated to a small volume under reduced pressure, yielding orange crystals which were filtered, washed with cold water, and air-dried. Yield (F-1): 10 mg. Found: C, 29.43; H, 5.72; N, 3.99%. Calcd for $C_{17}H_{39}N_2Cl_{2.5}CoNa_{0.5}O_{13}P_2$: C, 29.15; H, 5.61; N, 4.00%. Yield (F-2): 80 mg. Found: C, 32.04; H, 5.96; N, 4.52%. Calcd for $C_{17}H_{39}N_2CoCl_2O_{11}P_2$: C, 31.94; H, 6.15; N, 4.38%. Both complexes are soluble in water, methanol and acetone, but not in chloroform, dichloromethane, diethyl ether and benzene. Complexes F-1 and F-2 were assigned as the *Δ-cisβ* and *Λ-cisβ* isomers, respectively (*vide post*).

Λ-cisβ-[Co(CO_3)(SS-Me_2-pp-PNNP)]$ClO_4\cdot1.5(NaClO_4)\cdot H_2O$. To a methanol solution (100 cm^3) of *trans*-[$CoCl_2$(*SS*-Me_2-pp-PNNP)]$ClO_4\cdot0.5H_2O$ (300 mg, 0.40 mmol) were added $(NH_4)_2CO_3$ (100 mg, 1.04 mmol) and active charcoal (50 mg). The mixture was stirred for 2 h at room temperature and filtered. The filtrate was diluted with water (2 dm^3), and the solution applied on a column (ϕ 3.5 cm×90 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.05 mol dm^{-3} NaCl, and the eluate of the first main red band was concentrated to a small volume under reduced pressure. The concentrate was mixed with chloroform to extract the red complex into the chloroform layer. The chloroform was evaporated under reduced pressure, and the residue was dissolved in water (25 cm^3). The solution was mixed with $NaClO_4\cdot H_2O$ (3.0 g) in water (5 cm^3), and stored in a refrigerator overnight, yielding a pink precipitate, which was filtered, washed with a small amount of water, and air-dried. Yield: 205 mg. Found: C, 42.74; H, 4.12; N, 2.85%. Calcd for $C_{33}H_{40}N_2CoCl_{2.5}Na_{1.5}O_{14}P_2$: C, 42.50; H, 4.32; N, 3.00%. The complex is soluble in water, methanol, acetone, dichloromethane and chloroform, but not in diethyl ether and benzene.

Optical Resolution of cisβ-[Co(acac)(pp-PNNP)]$(ClO_4)_2\cdot H_2O$. The complex was prepared by the method reported[1)] and resolved by the follwing method. An aqueous solution of *cisβ*-[Co(acac)(pp-PNNP)]$(ClO_4)_2\cdot H_2O$ (*ca.* 100 mg) was applied on a column (ϕ 3.5 cm×100 cm) of SP-Sephadex C-25. On elution with 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$, two bands appeared. The eluate of the fast-moving band was collected, diluted ten times with water, and the solution was applied on a column (ϕ 3.5 cm×5 cm) of SP-Sephadex C-25. The adsorbed complex was eluted with 0.2 mol dm^{-3} NaCl. On addition of excess $NaClO_4\cdot H_2O$ the eluate gave crystalline $(+)_{589}$-*cisβ*-[Co(acac)(pp-PNNP)]$(ClO_4)_2\cdot NaCl$. From the slow-moving band the antipode was obtained. Found: C, 46.93; H, 4.74; N, 2.99%. Calcd for $C_{35}H_{41}N_2Cl_3CoNaO_{10}P_2$: C, 46.71; H, 4.51; N, 3.11%.

X-Ray Analysis. Single crystals of $(+)_{589}$-[Co(acac)(*SS*-Me_2-mm-PNNP)]$(ClO_4)_2\cdot H_2O$ were obtained by recrystallizing the complex from methanol-water (3:2). Crystal data are as follows; Formula: $C_{17}H_{39}N_2Cl_2CoO_{11}P_2$, FW=639.3, Crystal system: monoclinic, Space group: C2, a=28.274(4) Å, b=9.266(1) Å, c=11.0901(9) Å, β=92.97(1)°, V=2901.6(5) $Å^3$, D_m=1.45 g cm^{-3}, D_x=1.46 g cm^{-3}, Z=4, $\mu(Mo\,K\alpha)$=0.962 mm^{-1}. A specimen with dimensions 0.30×0.40×0.76 mm^3 was used for the X-ray work. Diffraction data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation at 298 K. Within the range $2\theta<60°$, 3229 independent reflections ($|F_o|\geqq3\sigma(|F_o|)$) were obtained. In order to determine the absolute configuration, intensity data for Bijvoet pair reflections were also collected up to $2\theta=40°$. The intensity data were corrected for Lorentz-polarization effects, and for absorption. The calculations of the structure analysis were performed on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III[11)]. The coordinate of the cobalt atom was deduced from a three dimensional Patterson function, and those of other atoms except hydrogens were determined by successive Fourier syntheses. The positions of all the hydrogen atoms were identified in subsequent difference-Fourier maps. The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. The weighting scheme $\sigma_w=[\sigma_{count}^2+(0.015|F_o|)^2]^{-1}$ was employed. At the final stage, refinements were carried out on two enantiomeric models, *Δ* and *Λ*, using 4503 intensities including the Bijvoet pair reflections. The R and R_w values were reduced to 0.053 and 0.078, respectively for the *Λ*-configuration, whereas the values were 0.062 and 0.086 for the *Δ*-configuration, respectively. Thus application of the R-factor ratio test[12)] showed that the *Δ*-model can be rejected at the 99.5% confidence level. This result confirms that two asymmetric carbon atoms in the *SS*-Me_2-mm-PNNP ligand have the *S*-configuration. Table 1 lists the atomic parameters for non-hydrogen atoms. Complete lists of observed and calculated structure factors, hydrogen atomic parameters, and thermal parameters for non-hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8552).

Results and Discussion

The optically active quadridentate phosphine ligands, *SS*-Me_2-pp- and *SS*-Me_2-mm-PNNP were prepared from (*S*)-alanine according to the same route as that for achiral pp- and mm-PNNP ligands.[1)] The cobalt(III) complexes with these chiral ligands were also prepared by methods similar to those for the corresponding achiral PNNP complexes.[1)] Chemical properties such as stability or solubility in various solvents of the new complexes are similar to those of the corresponding PNNP complexes.

The absorption spectra of [$CoCl_2$(*SS*-Me_2-pp- or *SS*-Me_2-mm-PNNP)]$^+$ shown in Fig. 1 are very similar to those of *trans*-[$CoCl_2$(pp- or mm-PNNP)]$^+$,[1)] respectively, indicating the trans (Cl,Cl) isomer. The spectral data are listed in Table 2. On the other hand,

TABLE 1. POSITIONAL PARAMETERS FOR NON-HYDROGEN ATOMS

Atom	x	y	z	B_{eqv}/Å^2
Co	1332(1)	0	2582(1)	2.9
P(1)	1104(1)	−1920(2)	1512(1)	3.8
P(2)	1435(1)	1407(2)	1031(1)	4.1
N(1)	1315(2)	−1368(6)	4026(4)	3.7
N(2)	2013(1)	−383(5)	2623(4)	3.4
C(1)	520(2)	−1822(11)	734(6)	6.0
C(2)	1478(2)	−2647(8)	398(6)	5.2
C(3)	1336(3)	3318(8)	1351(6)	6.4
C(4)	1134(3)	1146(11)	−457(6)	7.1
C(5)	1065(2)	−3312(8)	2639(6)	5.1
C(6)	996(2)	−2671(8)	3893(6)	4.7
C(7)	494(2)	−2301(10)	4108(6)	5.7
C(8)	1812(2)	−1818(8)	4352(5)	4.4
C(9)	2163(2)	−755(8)	3908(5)	4.3
C(10)	2297(2)	836(8)	2126(5)	4.5
C(11)	2824(3)	512(11)	2050(7)	6.9
C(12)	2075(2)	1180(8)	896(6)	5.2
C(13)	1436(3)	3368(9)	5141(7)	6.0
C(14)	1197(2)	2343(7)	4220(5)	4.0
C(15)	713(2)	2338(8)	4024(6)	5.0
C(16)	474(2)	1461(8)	3195(5)	4.6
C(17)	−59(2)	1565(11)	2965(7)	6.6
O(1)	1489(1)	1548(5)	3698(3)	3.9
O(2)	669(1)	457(5)	2546(3)	4.0
Cl(1)	2617(1)	5348(2)	2641(1)	4.9
Cl(2)	4377(1)	660(3)	2311(2)	6.8
O(3)	2325(3)	4829(11)	3329(6)	11.1
O(4)	2482(4)	6668(9)	1936(7)	13.1
O(5)	2779(5)	4384(9)	1723(9)	18.2
O(6)	3022(3)	5662(18)	3153(10)	19.6
O(7)	4350(4)	2146(11)	2165(8)	13.4
O(8)	4482(3)	199(11)	3488(6)	12.1
O(9)	4081(4)	−221(14)	1657(10)	17.2
O(10)	4817(5)	416(15)	1877(11)	18.3
O(w)	1078(2)	9458(9)	6528(6)	8.9

The x, y, and z values are multiplied by 10^4. The thermal parameters are given by the equivalent temperature foctors.

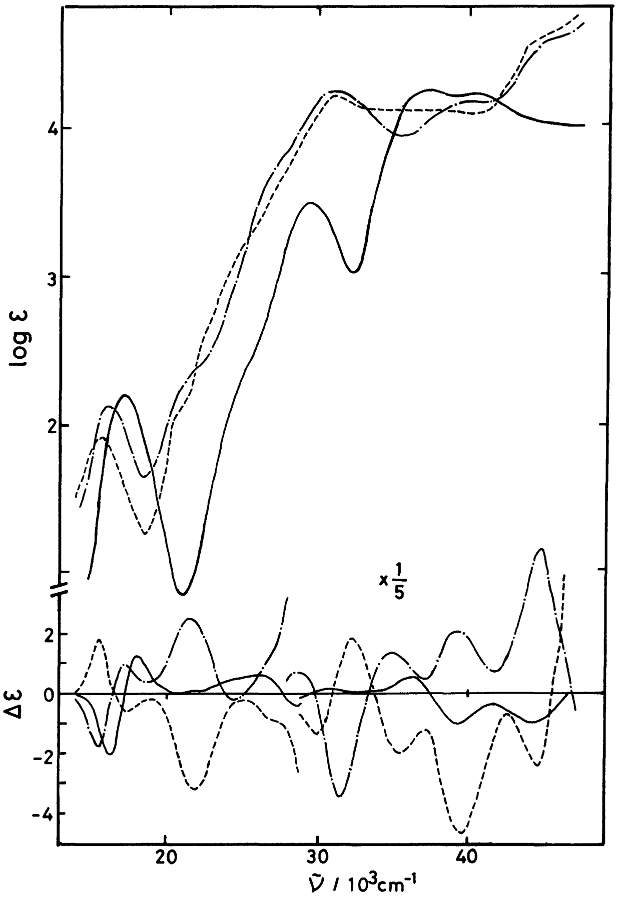
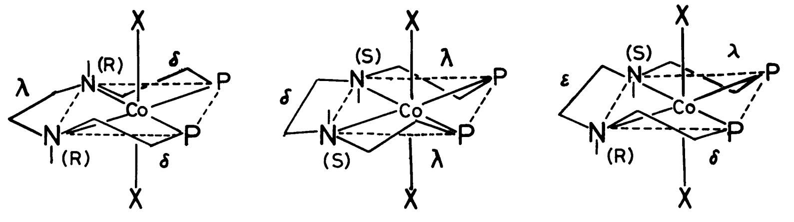


Fig. 1. Absorption and CD spectra of *trans*-[CoCl$_2$(*SS*-Me$_2$-mm-PNNP)]$^+$ (——), *trans*-[CoCl$_2$(*SS*-Me$_2$-pp-PNNP)]$^+$ (–·–·–), and *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(*S*-pdpp)$_2$]$^+$ (------).

TABLE 2. ABSORPTION (AB) AND CD SPECTRAL DATA IN THE VISIBLE TO NEAR ULTRAVIOLET REGION (Solvent: CH$_3$OH, at 298K)

Complex	AB ($\tilde{\nu}$/10^{3}cm^{-1} (logε))	CD ($\tilde{\nu}$/10^{3}cm^{-1} (Δε))
(+)$_{589}$-*trans*-[CoCl$_2$(*SS*-Me$_2$-pp-PNNP]$^+$	16.15(2.12), 21.5(2.3)$^{a)}$, 26.5(3.6)$^{a)}$, 31.05(4.15)$^{a)}$, 39.5(4.15)$^{a)}$, 45.0(4.58)$^{a)}$	15.75(+1.00), 17.25(+1.00), 21.75(+2.56) 24.50(−0.25), 28.90(+3.63), 31.50(−17.3) 35.00(+6.81), 39.50(+10.5), 45.00(+20.4)
(+)$_{589}$-*trans*-[CoCl$_2$(*SS*-Me$_2$-mm-PNNP)]$^+$	16.95(2.20), 24.5(2.2)$^{a)}$, 29.40(3.48), 37.10(4.24), 40.2(4.21)$^{a)}$	16.50(+2.08), 18.25(+1.24), 26.50(+0.55), 28.8(−0.41), 30.75(+0.64), 36.50(+2.61) 39.50(−5.19), 44.50(−5.30)
(+)$_{589}$-*Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-pp-PNNP)]$^{2+}$	19.20(2.90), 28.0(3.9)$^{a)}$, 32.0(4.36)	18.7(+7.25), 21.0(−1.52), 25.0(−7.0)$^{a)}$, 28.0(−29.6), 31.3(+38.2), 35.5(−5.03), 39.5(−10.3), 44.0(+14.7)
(+)$_{589}$-*Λ*-*cisβ*-[Co(CO$_3$)(*SS*-Me$_2$-pp-PNNP)]$^+$	19.50(2.41), 24.5(2.49)$^{a)}$, 31.75(4.10), 38.00(3.88), 44.5(4.5)$^{a)}$	18.40(+2.02), 20.75(−1.78), 24.75(+0.40), 31.25(−6.02), 34.0(+1.45), 37.5(+2.15)$^{a)}$, 40.10(−2.80)
(+)$_{589}$-*Λ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$	20.0(2.67)$^{a)}$, 22.7(2.73), 29.7(3.45)$^{a)}$, 39.5(4.39)	20.00(+6.11), 23.25(−1.19), 25.75(2.2)$^{a)}$, 29.70(−11.9), 34.0(+0.9), 36.9(−14.2), 40.7(−8.24), 45.3(−0.70)
(−)$_{589}$-*Δ*-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$	21.8(2.72), 29.8(3.44)$^{a)}$, 39.0(4.39)	20.0(−4.92), 23.0(+0.90), 29.8(+10.8), 34.3(−0.98), 36.5(+8.79), 40.5(−15.1), 44.5(+3.26)

a) Shoulder.



(1) **(2)** **(3)**

Fig. 2. Three possible diastereomers of *trans*-[CoCl$_2$(*SS*-Me$_2$-pp-PNNP)]$^+$.

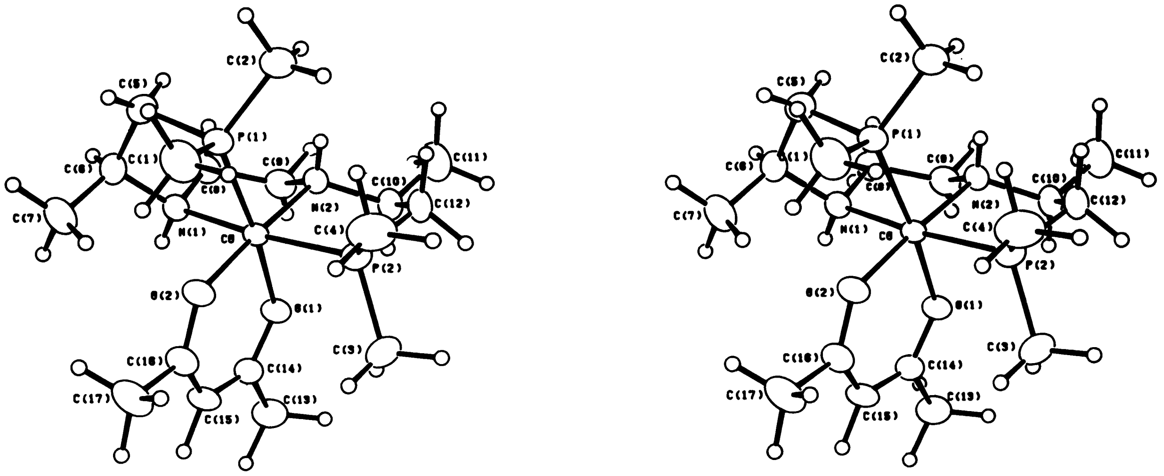


Fig. 3. ORTEP stereoview of (+)$_{589}$-Λ-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$.

the CD spectrum of [CoCl$_2$(*SS*-Me$_2$-pp-PNNP)]$^+$ is nearly enantiomeric to that of *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(*S*-pdpp)$_2$]$^+$ (*S*-pdpp=(*S*)-NH$_2$CH(CH$_3$)CH$_2$-P(C$_6$H$_5$)$_2$)[13] over the whole region as shown in Fig. 1, although the structures of the two complexes are similar, and all the chiral carbon atoms are the same *S* configuration. For the *SS*-Me$_2$-pp-PNNP complex, there are two more chiral sources, the chiral nitrogen atoms and the chiral conformation of the N–N chelate ring. In a previous paper,[13] we reported that the vicinal effect of the chiral nitrogen atom in the *trans* (Cl,Cl),*cis*(P,P)-[CoCl$_2$(N-P)$_2$]$^+$-type complex is very small, since the CD spectra of *S*-pdpp and *S*-prdpp (*S*(C),*S*(N)-CH$_2$CH$_2$CH$_2$NHCHCH$_2$P(C$_6$H$_5$)$_2$) complexes of this type are very similar. The latter complex has a chiral nitrogen donor atom of the *S*-configuration. Thus the effect of chiral conformation of the N–N chelate ring may be responsible for the big difference in CD spectra between the *SS*-Me$_2$-pp-PNNP and the *S*-pdpp complexes. The *trans*-[CoCl$_2$(*SS*-Me$_2$-pp-PNNP)]$^+$ complex has three possible diastereomers as shown in Fig. 2. The methyl groups of the δ and λ N–P chelate conformations have equatorial and axial dispositions, respectively, to the chelate ring. Since the complex shows only one kind of methyl signal in the ^{1}H NMR spectrum (-CH$_3$: 1.83 ppm), isomer **3** in Fig. 2 which has an equatorial and an axial methyl group can be excluded. Isomer **2** will be the least stable among the three isomers because of two axially disposed methyl groups. Thus the complex can be assigned as isomer **1**, where both methyl groups take an equatorial disposition, and the N–P and N–N chelate rings have the δ and λ conformations, respectively. In this isomer both nitrogen donor atoms become necessarily the *R* configuration. A structurally related tetraammine complex, (−)$_{589}$-*trans*-[Co(NO$_2$)$_2$(*SS*-3,8-Me$_2$-trien)]-ClO$_4$ (*S*,*S*-3,8-Me$_2$-trien=(*SS*)-NH$_2$CH$_2$CH(CH$_3$)NH-CH$_2$CH$_2$NHCH(CH$_3$)CH$_2$NH$_2$) forms three chelate rings of δ, λ, and δ conformations, and has two equatorial methyl groups and two *R*-nitrogen donor atoms.[14] The *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(*S*-pdpp)$_2$]$^+$ complex has no N–N chelate ring, and the N–P chelate rings will be stabilized in the δ conformation with an equatorial methyl group.[13] Thus the enantiomeric CD pattern of the *SS*-Me$_2$-pp-PNNP complex to that of the *S*-pdpp complex may be attributable to the extremely strong vicinal effect of the λ-(N–N) chelate ring compared with that of δ-(N–P) chelate one. Five-membered N–P chelate rings in cobalt(III) complexes often form a distorted gauche (nearly envelope) conformation,[15] and the vicinal effect of such a chelate ring would be smaller than that of a chelate ring with the typical gauche conformation.

The CD spectrum of the *SS*-Me$_2$-mm-PNNP complex resembles that of the *SS*-Me$_2$-pp-PNNP complex in the Ia absorption band region (14000—19000 cm^{-1}), indicating similar chiral skeletal structures for both complexes. In the higher energy region, however, the CD spectra are quite different from each other. These differences may be attributable to the difference in substitutent on the phosphorus atom, methyl and phenyl groups.

For the [Co(O-O)(*SS*-Me$_2$-pp- or *SS*-Me$_2$-mm-PNNP)]$^{n+}$-type complexes (O-O=acac, CO$_3^{2-}$), two geometrical isomers cisα and cisβ are possible, and each geometrical isomer can form diastereomers arising from the chiral carbon and nitrogen atoms. The structure of (+)$_{589}$-[Co(acac)(*SS*-Me$_2$-mm-PNNP)](ClO$_4$)$_2$·H$_2$O, which was formed in much larger amounts than the other (−)$_{589}$-isomer, was determined by X-ray analysis. Figure 3 shows a stereoview of the complex cation with the numbering scheme of the atoms. The selected bond distances and angles are listed in Table 3. The complex ion has the Λ-cisβ configuration. The three chelate rings form distorted gauche ($\delta\lambda\lambda$) or envelope conformations as shown in Fig. 4. One methyl group (C(7)) at C(6) lies in an axial disposition to the chelate ring, while the other methyl group (C(11)) is in an equatorial disposition to the chelate ring. Such an axial methyl group has been found in Λ-*cisβ*-[Co(CO$_3$)(*SS*-3,8-Me$_2$-trien)]ClO$_4$.[16,17]

The Co-P distances (2.208(2), 2.196(2) Å) are slightly shorter than those found in [Co(edmp)$_2$(dmpe)]Br$_3$·2H$_2$O (Co-edmp=2.294(3), 2.245(4); Co-dmpe=2.273(4), 2.295 (3) Å),[18] (+)$_{589}$-Λ-[Co(en)$_2$(dmpe)]Br$_3$·1.5H$_2$O (2.264(3), 2.248(3) Å),[19] and (+)$_{589}$-Λ-*fac*-[Co(edmp)$_3$]Br$_3$·3H$_2$O (2.231(5), 2.239(4), 2.242(5) Å,[20] where edmp and dmpe denote NH$_2$CH$_2$CH$_2$P(CH$_3$)$_2$ and (CH$_3$)$_2$PCH$_2$CH$_2$P-(CH$_3$)$_2$, respectively. The bond distances of Co-N(1) and Co-O(1) (trans to the P atom) are longer by 0.057 and 0.043 Å, respectively, than those of Co-N(2) and Co-O(2) (cis to the P atom), indicating trans influence of the P donor atom.[15] The average Co-N distance (2.015 Å) is fairly longer than that of the corresponding central two Co-N bonds in (+)$_{589}$-Λ-*cisβ*-[Co(CO$_3$)(*SS*-3,8-Me$_2$-trien)]ClO$_4$ (1.949 Å),[17] whereas the N-Co-N angles of these phosphine and trien complexes are similar (85.2(2) and 86.7(2)°, respectively). The chelate angles of P(1)-Co-N(1) (84.7(1)°) and P(2)-Co-N(2) (86.6(1)°) are nearly the same as those (84—86°) found in the edpp (NH$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$)[13,15] and edmp[18,20] complexes of cobalt(III).

TABLE 3. SELECTED BOND LENGTHS(l/Å) AND BOND ANGLES (ϕ/°) FOR (+)$_{589}$-Λ-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)] (ClO$_4$)$_2$·H$_2$O.

Co	-P(1)		2.208(2)	N(2)	-C(9)		1.505(7)
Co	-P(2)		2.196(2)	N(2)	-C(10)		1.506(8)
Co	-N(1)		2.043(5)	C(5)	-C(6)		1.535(10)
Co	-N(2)		1.986(4)	C(6)	-C(7)		1.491(9)
Co	-O(1)		1.936(4)	C(8)	-C(9)		1.500(9)
Co	-O(2)		1.893(4)	C(10)	-C(11)		1.529(9)
P(1)	-C(1)		1.825(6)	C(10)	-C(12)		1.505(9)
P(1)	-C(2)		1.798(7)	C(13)	-C(14)		1.527(10)
P(1)	-C(5)		1.803(7)	C(14)	-C(15)		1.375(9)
P(2)	-C(3)		1.830(8)	C(15)	-C(16)		1.378(9)
P(2)	-C(4)		1.833(8)	C(16)	-C(17)		1.518(9)
P(2)	-C(12)		1.837(7)	C(14)	-O(1)		1.269(7)
N(1)	-C(6)		1.509(8)	C(16)	-O(2)		1.314(8)
N(1)	-C(8)		1.493(8)				
P(1)	-Co	-P(2)	96.0(1)	C(4)	-P(2)	-C(12)	109.0(4)
P(1)	-Co	-N(1)	84.7(1)	Co	-N(1)	-C(6)	116.7(3)
P(1)	-Co	-N(2)	96.6(1)	Co	-N(1)	-C(8)	108.4(4)
P(2)	-Co	-N(1)	172.1(1)	C(6)	-N(1)	-C(8)	110.5(5)
P(2)	-Co	-N(2)	86.6(1)	Co	-N(2)	-C(9)	106.9(3)
P(1)	-Co	-O(1)	172.7(1)	Co	-N(2)	-C(10)	113.5(3)
P(1)	-Co	-O(2)	85.7(1)	C(9)	-N(2)	-C(10)	112.9(4)
P(2)	-Co	-O(1)	91.2(1)	P(1)	-C(5)	-C(6)	111.5(5)
P(2)	-Co	-O(2)	91.8(1)	N(1)	-C(6)	-C(5)	107.1(5)
N(1)	-Co	-O(1)	88.3(2)	N(1)	-C(6)	-C(7)	111.6(6)
N(1)	-Co	-O(2)	96.1(2)	C(5)	-C(6)	-C(7)	113.7(5)
N(2)	-Co	-O(1)	84.9(2)	N(1)	-C(8)	-C(9)	111.6(5)
N(2)	-Co	-O(2)	177.4(2)	N(2)	-C(9)	-C(8)	107.6(4)
N(1)	-Co	-N(2)	85.5(2)	N(2)	-C(10)	-C(11)	114.3(6)
O(1)	-Co	-O(2)	93.0(2)	N(2)	-C(10)	-C(12)	106.7(5)
Co	-P(1)	-C(1)	115.8(3)	C(11)	-C(10)	-C(12)	110.6(6)
Co	-P(1)	-C(2)	120.9(2)	P(2)	-C(12)	-C(10)	108.4(4)
Co	-P(1)	-C(5)	103.3(2)	C(13)	-C(14)	-C(15)	120.7(6)
C(1)	-P(1)	-C(2)	104.0(3)	C(13)	-C(14)	-O(1)	113.0(5)
C(1)	-P(1)	-C(5)	106.1(4)	C(15)	-C(14)	-O(1)	126.3(6)
C(2)	-P(1)	-C(5)	105.5(3)	C(14)	-C(15)	-C(16)	123.8(6)
Co	-P(2)	-C(3)	113.1(2)	C(15)	-C(16)	-C(17)	121.5(6)
Co	-P(2)	-C(4)	123.2(3)	C(15)	-C(16)	-O(2)	125.3(6)
Co	-P(2)	-C(12)	100.3(2)	C(17)	-C(16)	-O(2)	113.2(6)
C(3)	-P(2)	-C(4)	103.5(4)	Co	-O(1)	-C(14)	125.4(4)
C(3)	-P(2)	-C(12)	106.7(4)	Co	-O(2)	-C(16)	125.7(4)

The geometrical structure of the other isomer (−)$_{589}$-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$ can be assigned as the cisβ form, since it shows two kinds of –CH$_3$(acac) signals at 2.50 and 2.68 ppm in the ^{1}H NMR spectrum. Figure 5 compares the absorption and CD spectra with those of (+)$_{589}$-Λ-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$. The CD spectrum of the (−)$_{589}$-isomer is nearly enantiomeric to that of the (+)$_{589}$-Λ-*cisβ*-isomer over the whole region. Thus the (−)$_{589}$-isomer is assigned as the Δ-*cisβ*-isomer. This isomer has further two possible

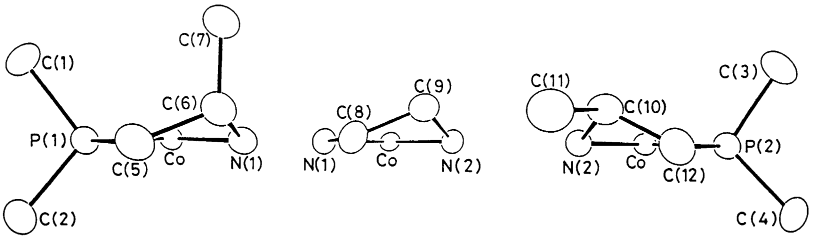


Fig. 4. Three chelate rings of (+)$_{589}$-Λ-*cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$.

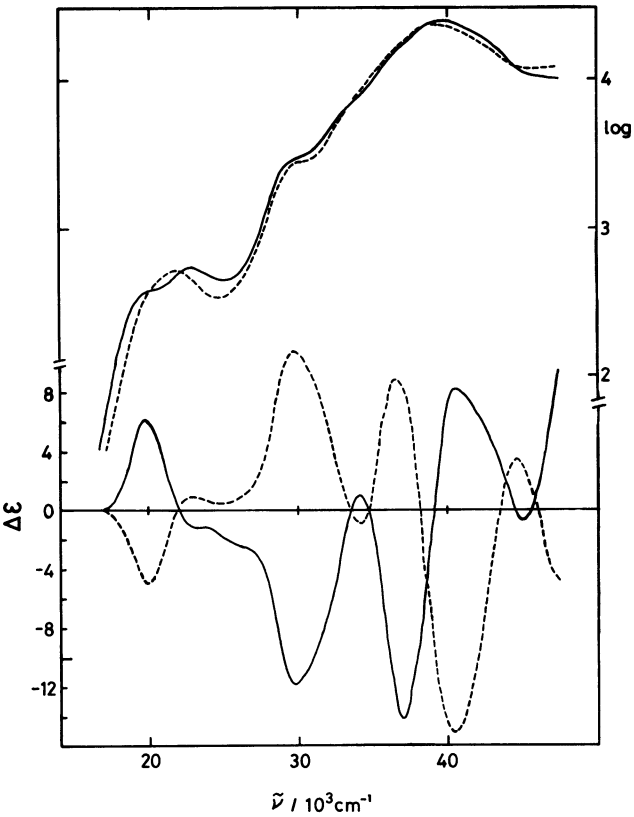


Fig. 5. Absorption and CD spectra of $(+)_{589}$-Λ-*cis*β-$[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}mm\text{-}PNNP})]^{2+}$ (——) and $(-)_{589}$-Δ-*cis*β-$[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}mm\text{-}PNNP})]^{2+}$ (------).

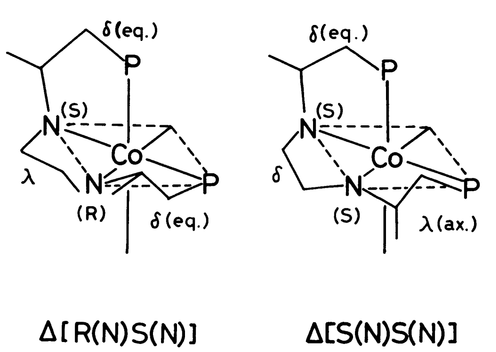


Fig. 6. Two possible diastereomers of Δ-*cis*β-$[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}mm\text{-}PNNP})]^{2+}$.

diastereomers arising from the absolute configuration of the nitrogen donor atom as shown in Fig. 6. In the $\Delta[R(\mathrm{N})S(\mathrm{N})]$-isomer, both methyl groups on carbon take an equatorial disposition, while in the $\Delta[S(\mathrm{N})S(\mathrm{N})]$-isomer, the methyl group on carbon of the meridional-(PNN) coordination moiety (in-plane) becomes axial. No cisβ complex having such an axial "in-plane" methyl group has been reported probably because of large intra- and interligand steric interactions with this methyl group. Thus the $(-)_{589}$-isomer can be assigned as the $\Delta[R(\mathrm{N})S(\mathrm{N})]$-cis$\beta$-isomer shown in Fig. 6. This isomer was obtained by reaction of $[\mathrm{Co(acac)_3}]$ with the ligand in methanol in poor yield, the formation ratio of it to the other $(+)_{589}$-Λ-*cis*β-isomer being *ca.* 1/8. The reaction of *trans*-$[\mathrm{CoCl_2}(SS\text{-}\mathrm{Me_2\text{-}mm\text{-}PNNP})]^+$ with Li(acac) in methanol afforded only the Λ-*cis*β-isomer, no other isomer being formed. In either experiment no *cis*α-isomer was yielded. These experimental results indicate that $[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}mm\text{-}PNNP})]^{2+}$ is the most stable in the $\Lambda[R(\mathrm{N})R(\mathrm{N})]$-cis$\beta$ structure, although this structure has an axially disposed methyl group on carbon of the apically linked N–P chelate ring. The reason for such selectivity is not clear at present. Saburi *et al.*[16] reported that structurally related $[\mathrm{Co(CO_3)}(SS\text{-}3,8\text{-}\mathrm{Me_2\text{-}trien})]^+$ is more stable in the Λ-cisβ form than in other forms. Complexes of such a (3*S*,8*S*)-dimethyl-substituted quadridentate ligand seem to be stabilized in the Λ-cisβ form, irrespective of the kind of terminal donor atoms.

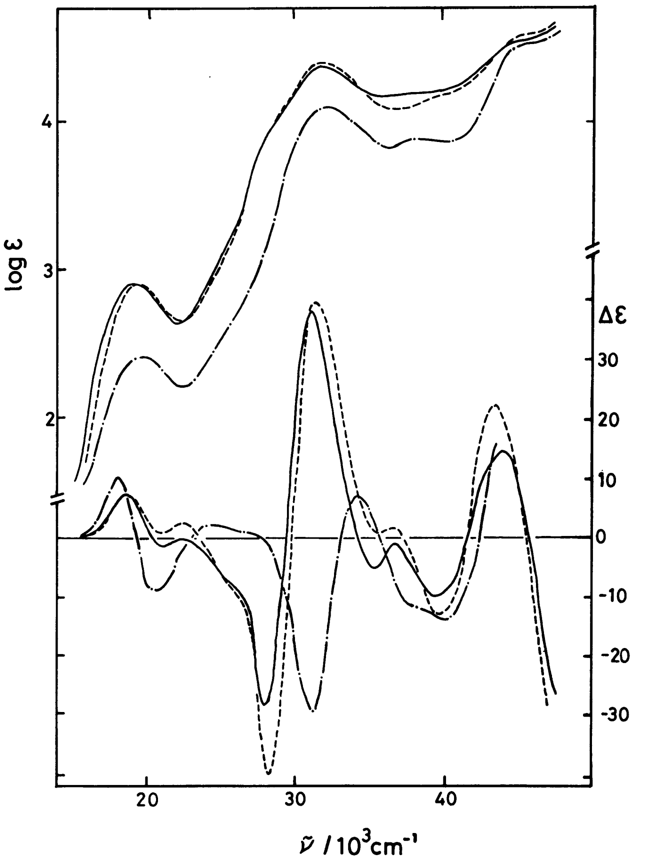


Fig. 7. Absorption and CD spectra of $(+)_{589}$-Λ-*cis*β-$[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}pp\text{-}PNNP})]^{2+}$ (——), $(+)_{589}$-Λ-*cis*β-$[\mathrm{Co(acac)(pp\text{-}PNNP)}]^{2+}$ (------) and $(+)_{589}$-Λ-*cis*β-$[\mathrm{Co(CO_3)}(SS\text{-}\mathrm{Me_2\text{-}pp\text{-}PNNP})]^+$ (-·-·-).

Both $[\mathrm{Co(acac)}(SS\text{-}\mathrm{Me_2\text{-}pp\text{-}PNNP})]^{2+}$ and $[\mathrm{Co(CO_3)}(SS\text{-}\mathrm{Me_2\text{-}pp\text{-}PNNP})]^+$ yielded only the $(+)_{589}$-isomer by reactions of *trans*-$[\mathrm{CoCl_2}(SS\text{-}\mathrm{Me_2\text{-}pp\text{-}PNNP})]^+$ with Li(acac) and $\mathrm{(NH_4)_2CO_3}$, respectively. For the acac complex, the reaction of $[\mathrm{Co(acac)_3}]$ with the ligand also formed only the same isomer. The ^{1}H NMR spectra of these acac and carbonato complexes clearly indicate that both of them are the cisβ isomer. Figure 7 shows absorption and CD spectra of these complexes together with those of $(+)_{589}$-*cis*β-$[\mathrm{Co(acac)(pp\text{-}PNNP)}]^{2+}$.

The CD spectral patterns of both *SS*-Me$_2$-pp-PNNP complexes resemble that of (+)$_{589}$-*Λ-cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$ in the first absorption band region, a positive and a negative CD band from the low energy side. Thus the complexes can be assigned as the *Λ-cisβ*-isomer. All the nitrogen donor atoms in these isomers will have the same *R* configuration as those in *Λ-cisβ*-[Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$, since the *R*(N)*S*(N) isomer has two methyl groups in an axial disposition, and the *S*(N)*S*(N) isomer can not form the *Λ* configuration. As stated above, the *SS*-Me$_2$-pp-PNNP complexes formed only the *Λ-cisβ*-isomer. Neither the *cisα*- nor the *Δ-cisβ*-isomer which corresponds to the minor product ((−)$_{589}$-isomer) of [Co(acac)(*SS*-Me$_2$-mm-PNNP)]$^{2+}$ was detected.

The *cisβ*-[Co(acac)(pp-PNNP)]$^{2+}$ complex, which was only isomer obtained from *trans*-[CoCl$_2$(pp-PNNP)]$^+$ and Li(acac) in methanol,[1] shows an absorption spectrum nearly the same as that of the corresponding *SS*-Me$_2$-pp-PNNP complex. The CD spectrum of the resolved (+)$_{589}$-isomer is also very similar to that of the *SS*-Me$_2$-pp-PNNP complex which was assigned to the *Λ* configuration. Thus (+)$_{589}$-*cisβ*-[Co(acac)(pp-PNNP)]$^{2+}$ is assigned as the *Λ*-isomer,[21] and the two nitrogen donor atoms will have the same *R* configuration as those in the *SS*-Me$_2$-pp-PNNP complex. The presence of two chiral carbon atoms in the *SS*-Me$_2$-pp-PNNP complex seems to little affect both absorption and CD spectra.

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21) In a previous paper (Ref. 22)), we incorrectly assigned the absolute configuration of (+)$_{589}$-*cisβ*-[Co(acac)(*SS*-Me$_2$-pp-PNNP)]$^{2+}$, (+)$_{589}$-*trans*(P,N)- and (+)$_{589}$-*trans*(P,P)-[Co(acac)(edpp)$_2$]$^{2+}$, and (+)$_{589}$-*trans*(P,N)-[Co(O–O)(edpp)$_2$]$^+$ (O–O=CO$_3^{2-}$, C$_2$O$_4^{2-}$ and CH$_2$(CO$_2$)$^{2-}$) to *Δ*. All of these isomers should be assigned to *Λ*.

22) M. Atoh, I. Kinoshita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **55**, 3179 (1982).