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Preparation and Stereochemistry of Cobalt(III) Complexes Containing 2,11-Diphenyl-5,8-diaza-2,11-diphosphadodecane or (4*S*,9*S*)-4,9-Dimethyl-2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane, $(C_6H_5)(CH_3)PCH_2CHRNHCH_2CH_2NHCHRCH_2P(CH_3)(C_6H_5)$ (R=H or CH_3)

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New quadridentate ligands having two chiral phosphorus donor atoms, 2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane (mp-PNNP) and (4*S*,9*S*)-4,9-dimethyl-2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane (*SS*(C)-mp-PNNP), and their cobalt(III) complexes, *trans*-$[CoCl_2$(mp- or *SS*(C)-mp-PNNP)$]^+$ and *cis*β-[Co(acac)(mp- or *SS*(C)-mp-PNNP)$]^{2+}$ (acac=2,4-pentanedionate ion) were prepared and characterized. For both mp- and *SS*(C)-mp-PNNP, the dichloro and acac complexes formed three and four isomers, respectively, which were separated by column chromatography or fractional crystallization. No *cis*α-acac complex was yielded. The acac complexes of *SS*(C)-mp-PNNP formed a *Λ*-isomer stereoselectively. The absolute configurations of the phosphorus donor atoms in the *SS*(C)-mp-PNNP complexes were assigned on the basis of the ^1H NMR and CD spectra. It was shown that the phosphorus donor atoms at chemically unequivalent coordination positions in *cis*β-[Co(acac)(*SS*(C)-mp-PNNP)$]^{2+}$ give remarkably different vicinal effects on the CD spectra.

In previous papers, we have reported preparation and stereochemistry of octahedral cobalt(III) complexes containing new quadridentate phosphine ligands of the PNNP type, $(R_2PCH_2CH_2NHCH_2-)_2$ (R=CH_3: mm-PNNP, R=C_6H_5: pp-PNNP),[1] and the optically active methyl-substituted derivatives, $(R_2PCH_2CH(CH_3)NHCH_2-)_2$ (R=CH_3: *SS*(C)-mm-PNNP, R=C_6H_5: *SS*(C)-pp-PNNP).[2] These PNNP complexes formed selectively particular geometrical or optical isomers. Introduction of asymmetric phosphorus donor atoms into the PNNP-type ligands will cause new stereoselectivity in the complex formation, and will give useful information for studying chiral phosphine complexes, which have little been studied.[3] This paper concerns preparation and stereochemistry of two new chiral phosphine ligands, 2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane (mp-PNNP) and (4*S*,9*S*)-4,9-dimethyl-2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane (*SS*(C)-mp-PNNP), and their cobalt(III) complexes, *trans*-$[CoCl_2$(mp- or *SS*(C)-mp-PNNP)$]^+$ and *cis*β-[Co(acac)(mp- or *SS*(C)-mp-PNNP)$]^{2+}$ (acac=2,4-pentanedionate ion).

Experimental

Phosphine ligands, mp-PNNP and *SS*(C)-mp-PNNP were prepared and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for the preparation were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption, circular dichroism (CD) and ^1H NMR spectra were recorded on a Hitachi 323 spectrometer, a Jasco J-40CS spectropolarimeter and a Jeol JNM PMX-60 spectrometer, respectively.

Preparation of Ligands. 2,11-Diphenyl-5,8-diaza-2,11-diphosphadodecane (*RS*(P)- and *RR,SS*(P)-mp-PNNP). To liquid ammonia (200 cm^3) in a 500 cm^3 three-necked, round-bottom flask with a mechanical stirrer and a nitrogen inlet was added metallic sodium (1.33 g, 49.1 mmol) with stirring at −78 °C. After 1 h $PH(CH_3)(C_6H_5)$[4] (1.33 g, 49.1 mmol) was added dropwise and the mixture was stirred for 20 min. To the resulting yellow solution of $NaP(CH_3)(C_6H_5)$ was added $(ClCH_2CH_2NHCH_2-)_2\cdot 2HCl$[5] (3.16 g, 12.3 mmol) in small portions with stirring. Stirring was continued for 2.5 h, and then liquid ammonia was evaporated. Water (30 cm^3) and then diethyl ether (40 cm^3) were added to the residue with stirring. The ethereal layer was separated from the aqueous layer and dried over $MgSO_4$ (1.5 g). The solvent and unreacted $PH(CH_3)(C_6H_5)$ were removed by distillation (83 °C, 1300 Pa). The colorless oily residue (3.71 g) thus obtained was a mixture of *RS*(P)- and *RR,SS*(P)-mp-PNNP and used for preparing the cobalt(III) complexes without further purification and separation of the isomers.

(4*S*,9*S*)-4,9-Dimethyl-2,11-diphenyl-5,8-diaza-2,11-diphosphadodecane (*RS*(P)-, *RR*(P)-, and *SS*(P)-*SS*(C)-mp-PNNP). This ligand was obtained as oily substance by the same method as that for mp-PNNP in a yield of 2.70 g, using liquid ammonia (150 cm^3), metallic sodium (0.83 g, 36 mmol), $PH(CH_3)(C_6H_5)$ (4.5 g, 36 mmol), and (2*S*,7*S*)-2,7-dimethyl-1,8-dichloro-3,6-diazaoctane dihydrochloride[2] (2.95 g, 9.05 mmol).

Preparation of Complexes. *trans*-$[CoCl_2$(*RS*(P)-mp-PNNP)$]ClO_4$ (F-1), *trans*-$[CoCl_2$(*RR,SS*(P)-mp-PNNP)$]ClO_4$ (F-2), and *trans*-$[CoCl_2$(*RR,SS*(P)-mp-PNNP)$]ClO_4\cdot 1.5H_2O$ (F-3).[6] To *cis*-$[CoCl_2(en)_2]Cl$[7] (0.96 g, 3.36 mmol) (en: ethylenediamine) in methanol (50 cm^3) was added a mixture of *RS*(P)- and *RR,SS*(P)-mp-PNNP (1.0 g, 2.77 mmol) with stirring at room temperature. After 15 min concd HCl (1 cm^3) was added and the solution was stirred overnight at room temperature. The resulting solution was filtered to remove $[Co(en)_3]Cl_3$ precipitated. The filtrate was mixed with water (300 cm^3) and the unreacted phosphine ligand was extracted with diethyl ether (ca. 50 cm^3). The green aqueous layer was mixed with $NaClO_4\cdot H_2O$ (10 g) and the green complex was extracted twice with CH_2Cl_2 (50 cm^3×2). The extract was evaporated to dryness under reduced pressure and the residue was dissolved in methanol (100 cm^3). The solution was diluted with water (1 dm^3) and applied on a column (φ2.5 cm×120 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.05 mol dm^{-3} HCl, giving three green bands F-1, F-2, and F-3. The eluate

containing each green band was collected, $NaClO_4 \cdot H_2O$ (5 g) was added to it, and the complex was extracted with CH_2Cl_2 (50 cm^3). The extract was evaporated to dryness under reduced pressure and the residue was dissolved again in a small amount of methanol. On addition of excess $NaClO_4 \cdot H_2O$ the solution gave green crystals, which were filtered, washed with water and air-dried. The complex obtained from the first band (F-1) was a racemic pair of $[CoCl_2(RS(P)$-mp-PNNP$)]^+$ ($RR(N)RS(P)$ and $SS(N)SR(P)$ isomers), and those from the second (F-2) and the third (F-3) bands are two racemic pairs of $[CoCl_2(RR,SS(P)$-mp-PNNP$)]^+$ ($RR(N)SS(P)$ and $SS(N)RR(P)$, and ($RR(N)$-$RR(P)$ and $SS(N)SS(P)$ isomers) (vide infra). Yield (F-1): 245 mg. Found: C, 40.87; H, 5.19; N, 4.39%. Calcd for $C_{20}H_{30}N_2Cl_3CoO_4P_2$: C, 40.74; H, 5.13; N, 4.75%. Yield (F-2): 100 mg. Found: C, 40.67; H, 5.05; N, 4.40%. Calcd for $C_{20}H_{30}N_2Cl_3CoO_4P_2$: C, 40.74; H, 5.13; N, 4.75%. Yield (F-3): 95 mg. Found: C, 38.98; H, 5.16; N, 4.23%. Calcd for $C_{20}H_{33}N_2Cl_3CoO_{5.5}P_2$: C, 38.95; H, 5.39; N, 4.54%. All the complexes are soluble in methanol, acetone and dichloromethane, slightly in water, but not in diethyl ether and benzene.

$\Lambda[RS(P)]\Delta[SR(P)]$-*cis*$\beta$-[Co(acac)(*RS*(P)-mp-PNNP)]$(ClO_4)_2$ and $\Lambda[SR(P)]\Delta[RS(P)]$-*cis*$\beta$-[Co(acac)(*RS*(P)-mp-PNNP)]$(ClO_4)_2 \cdot 1.5H_2O$ (see Fig. 5). A methanol solution (30 cm^3) containing *trans*-$[CoCl_2(RS(P)$-mp-PNNP$)]ClO_4$ (100 mg, 0.17 mmol) and Li(acac) (60 mg, 0.57 mmol) was stirred for 12 h at room temperature. The resulting red solution was diluted with water (200 cm^3) and applied on a column (ϕ2.5 cm×100 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.2 mol dm^{-3} NaCl, giving two red bands. The eluate containing each band was collected, evaporated to dryness under reduced pressure, and the complex in the residue was extracted with ethanol (50 cm^3). The extract was evaporated to dryness, and the residue was dissolved in water (10 cm^3). On addition of $NaClO_4 \cdot H_2O$ (ca. 1.0 g) the solution gave a red precipitate, which was filtered, washed with a small amount of cold water, and dried in vacuo. The complex obtained from the first band is the $\Lambda[RS(P)]\Delta[SR(P)]$ isomer and that from the second band the $\Lambda[SR(P)]\Delta[RS(P)]$ isomer (see Fig. 5). Yield (the $\Lambda[RS(P)]\Delta[SR(P)]$ isomer): 11 mg. Found: C, 42.03; H, 5.18; N, 4.11%. Calcd for $C_{25}H_{37}N_2Cl_2CoO_{10}P_2$: C, 41.85; H, 5.20; N, 3.91%. Yield (the $\Lambda[SR(P)]\Delta[RS(P)]$ isomer): 40 mg. Found: C, 40.18; H, 5.31; N, 3.55%. Calcd for $C_{25}H_{40}N_2Cl_2CoO_{11.5}P_2$: C, 40.34; H, 5.42; N, 3.76%.

$\Lambda[SS(P)]\Delta[RR(P)]$-*cis*$\beta$-[Co(acac)(*RR,SS*(P)-mp-PNNP)]$(ClO_4)_2$ and $\Lambda[RR(P)]\Delta[SS(P)]$-*cis*$\beta$-[Co(acac)(*RR,SS*(P)-mp-PNNP)]$(ClO_4)_2 \cdot 0.5H_2O$. These complexes were obtained from *trans*-$[CoCl_2(RR,SS(P)$-mp-PNNP$)]ClO_4$ (F-2) (95 mg, 0.161 mmol) or *trans*-$[CoCl_2(RR,SS(P)$-mp-PNNP$)]ClO_4 \cdot 1.5H_2O$ (F-3) (100 mg, 0.162 mmol) and Li(acac) (60 mg, 0.57 mmol) by the same method as that for the corresponding $RS(P)$-mp-PNNP complex. The complex obtained from the first band is the $\Lambda[SS(P)]\Delta[RR(P)]$ isomer and that from the second band the $\Lambda[RR(P)]\Delta[SS(P)]$ isomer. Yield (the $\Lambda[SS(P)]\Delta[RR(P)]$ isomer): 17 mg. Found: C, 41.71; H, 5.41; N, 3.85%. Calcd for $C_{25}H_{37}N_2Cl_2CoO_{10}P_2$: C, 41.85; H, 5.20; N, 3.91%. Yield (the $\Lambda[RR(P)]\Delta[SS(P)]$ isomer): 36 mg. Found: C, 41.36; H, 5.24; N, 3.89%. Calcd for $C_{25}H_{38}N_2Cl_2CoO_{10.5}P_2$: C, 41.34; H, 5.27; N 3.86%. All the $[Co(acac)(mp\text{-}PNNP)]^{2+}$ complexes are soluble in water, methanol, acetone and dichloromethane, but not in diethyl ether and benzene.

***trans*-[$CoCl_2$(*RS*(P)-*SS*(C)-mp-PNNP)]$ClO_4 \cdot NaClO_4 \cdot H_2O$ and a Pseudo Racemate of *trans*-[$CoCl_2$(*RR,SS*(P)-*SS*(C)-mp-PNNP)]$ClO_4 \cdot H_2O$.** To *cis*-$[CoCl_2(en)_2]Cl$ (220 mg, 0.77 mmol) in methanol (150 cm^3) was added a mixture of $RS(P)$-, $RR(P)$- and $SS(P)$-$SS(C)$-mp-PNNP (300 mg, 0.77 mmol) with stirring at room temperature. After 30 min concd HCl (2 cm^3) was added to the resulting green solution, and the mixture was stirred overnight at room temperature. The solution was filtered, and the filtrate was concentrated to 50 cm^3 under reduced pressure. To the concentrate were added $NaClO_4 \cdot H_2O$ (6.0 g) and water (200 cm^3), and the complex was extracted twice with CH_2Cl_2 (30 cm^3×2). The green extract was evaporated to dryness under reduced pressure, and the residue was dissolved in hot methanol (20 cm^3, 60 °C). To the solution was added $NaClO_4 \cdot H_2O$ (2.0 g), and the mixture was allowed to stand at room temperature to yield a green precipitate, which was filtered, washed with water and air-dried. The filtrate was preserved because it contains the other isomer. Yield: 138 mg. Found: C, 41.80; H, 5.88; N, 4.15%. Calcd for $C_{22}H_{36}N_2Cl_3CoO_5P_2$: C, 41.56; H, 5.71; N, 4.41%. This complex was assigned to a pseudo racemate of *trans*-$[CoCl_2(RR,SS(P)$-$SS(C)$-mp-PNNP$)]^+$ from the ^1H NMR spectrum. From the filtrate green crystals were formed by addition of a large excess of diethyl ether (ca. 80 cm^3), filtered, washed with water and air-dried. Yield: 100 mg. Found: C, 34.74; H, 4.56; N, 3.48%. Calcd for $C_{22}H_{36}N_2Cl_4CoNaO_9P_2$: C, 34.85; H, 4.79; N, 3.69%. This complex was assigned to the *trans*-$[CoCl_2(RS(P)$-$SS(C)$-mp-PNNP$)]^+$ isomer from the ^1H NMR spectrum. Both dichloro complexes are soluble in methanol and dichloromethane, slightly in water, but not in diethyl ether.

***trans*-[$CoCl_2$(*SS*(P)-*SS*(C)-mp-PNNP)]ClO_4 and *trans*-[$CoCl_2$(*RR*(P)-*SS*(C)-mp-PNNP)]$ClO_4 \cdot 0.5H_2O$.** A pseudo racemate of *trans*-$[CoCl_2(RR,SS(P)$-$SS(C)$-mp-PNNP$)]$-$ClO_4 \cdot H_2O$ (340 mg, 0.540 mmol) obtained above was converted into the chloride by stirring with Dowex 1X8 (Cl^- form, 6 g) in methanol (50 cm^3) for 6 h at room temperature. The mixture was filtered, the filtrate was diluted with water (500 cm^3), and the solution was applied on a column (ϕ2.5 cm×100 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} HCl, two green bands appeared. The eluate containing each band was collected, mixed with $NaClO_4 \cdot H_2O$ (ca. 10 g), and the complex was extracted with CH_2Cl_2. The green extract was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (20 cm^3), and $NaClO_4 \cdot H_2O$ (2 g) was added to the solution. On standing at room temperature, the solution obtained from the first band yielded green crystals of *trans*-$[CoCl_2(SS(P)$-$SS(C)$-mp-PNNP$)]ClO_4$, which were filtered, washed with water and air-dried. Yield: 80 mg. Found: C, 42.35; H, 5.45; N, 4.48%. Calcd for $C_{22}H_{34}N_2Cl_3CoO_4P_2$: C, 42.77; H, 5.55; N, 4.53%. The methanol solution containing $NaClO_4 \cdot H_2O$ obtained from the second band gave a green precipitate by addition of water. It was filtered, washed with water and air-dried. Yield: 65 mg. Found: C, 41.93; H, 5.33; N, 4.37%. Calcd for $C_{22}H_{35}N_2Cl_3CoO_{4.5}P_2$: C, 42.16; H, 5.63; N, 4.47%. The pruduct is *trans*-$[CoCl_2(RR(P)$-$SS(C)$-mp-PNNP$)]$-$ClO_4 \cdot 0.5H_2O$.

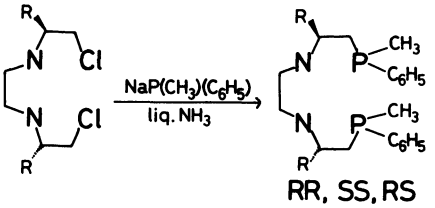
***A*-*cis*β-[Co(acac)(*SS*(P)-*SS*(C)-mp-PNNP)]$(ClO_4)_2 \cdot 1.5H_2O$ and *A*-*cis*β-[Co(acac)(*RR*(P)-*SS*(C)-mp-PNNP)]$(ClO_4)_2 \cdot H_2O$.** A methanol solution (30 cm^3) containing a pseudo racemate of *trans*-$[CoCl_2(RR,SS(P)$-$SS(C)$-mp-PNNP$)]ClO_4 \cdot H_2O$ (200 mg, 0.314 mmol) and Li(acac) (100 mg, 0.945 mmol)

was stirred for 8 h at room temperature. The resulting red solution was diluted with water (1 dm^3) and the solution applied on a column (ϕ2.5 cm×25 cm) of SE-Toyopearl. By elution with 0.1 mol dm^{-3} Na_2SO_4, two red bands appeared. The eluate of each band was collected, concentrated to nearly dryness under reduced pressure, and the complex was extracted with ethanol (50 cm^3). The extract was evaporated to dryness under reduced pressure, and the residue was dissolved in water (10 cm^3). On addition of $NaClO_4 \cdot H_2O$ (1.5 g) in water (5 cm^3), the solution gave a red precipitate, which was filtered, washed with a small amount of cold water and air-dried. The complex obtained from the first band is *Λ-cisβ*-[Co(acac)(*SS*(P)-*SS*(C)-mp-PNNP)]$(ClO_4)_2 \cdot 1.5H_2O$ and that from the second band *Λ-cisβ*-[Co(acac)-(*RR*(P)-*SS*(C)-mp-PNNP)]$(ClO_4)_2 \cdot H_2O$. These complexes were also prepared separately from trans-dichloro complexes of *SS*(P)- and *RR*(P)-*SS*(C)-mp-PNNP. Yield (the *SS*(P)-isomer): 59 mg. Found: C, 42.15; H, 6.05; N, 3.66%. Calcd for $C_{27}H_{44}N_2Cl_2CoO_{11.5}P_2$: C, 41.98; H, 5.74; N, 3.63%. Yield (the *RR*(P)-isomer): 45 mg. Found: C, 42.48; H, 6.04; N, 3.69%. Calcd for $C_{27}H_{43}N_2Cl_2CoO_{11}P_2$: C, 42.48; H, 5.68; N, 3.67%. The complexes are soluble in water, methanol and dichloromethane, but not in diethyl ether and benzene.

Λ[*RS*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)](ClO$_4$)$_2$ and Λ[*SR*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)](ClO$_4$)$_2$·1.5H$_2$O (see Fig. 5). These complexes were prepared from *trans*-$[CoCl_2(RS(P)\text{-}SS(C)\text{-mp-PNNP})]ClO_4 \cdot NaClO_4 \cdot H_2O$ (285 mg, 0.376 mmol) and Li(acac) (40 mg, 0.377 mmol) according to a method similar to that for the corresponding *RR*(P)- and *SS*(P)-*SS*(C)-mp-PNNP complexes. In column chromatography, the Λ[*RS*(P)]-isomer was eluted faster than the Λ[*SR*(P)]-isomer. Yield (the Λ[*RS*(P)]-isomer): 31 mg. Found: C, 43.76; H, 5.73; N, 3.80%. Calcd for $C_{27}H_{41}N_2Cl_2CoO_{10}P_2$: C, 43.51; H, 5.54; N, 3.76%. Yield (the Λ[*SR*(P)]-isomer): 20 mg. Found: C, 42.00; H, 5.75; N, 4.16%. Calcd for $C_{27}H_{44}N_2Cl_2CoO_{11.5}P_2$: C, 41.98; H, 5.74; N, 3.63%. The complexes are soluble in water, methanol and dichloromethane, but not in diethyl ether and benzene.

Results and Discussion

Quadridentate ligands having chiral phosphorus donor atoms, mp-PNNP and *SS*(C)-mp-PNNP were prepared according to methods similar to those for 1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (pp-PNNP)[1] and (3*S*,8*S*)-3,8-dimethyl-1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (*SS*(C)-pp-PNNP),[2] respectively (Scheme). The ligands have two chiral phosphorus atoms. The mp-PNNP ligand exists in two diastereomers, *RR*,*SS*(P) (racemic) and



R = H : mp-PNNP

R = CH_3: SS(C)-mp-PNNP

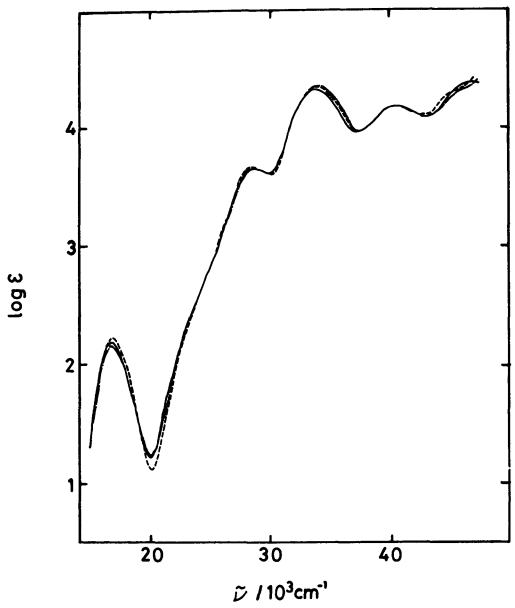
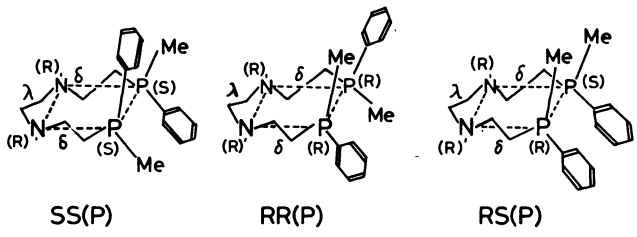


Fig. 1. Absorption spectra of *trans*-$[CoCl_2(RS(P)\text{-mp-PNNP})]^+$ (F-1) (——), *trans*-$[CoCl_2(RR,SS(P)\text{-mp-PNNP})]^+$ (F-2) (-·—·-), and *trans*-$[CoCl_2(RR,SS\text{-}(P)\text{-mp-PNNP})]^+$ (F-3) (----).



trans-RR(N)-[CoCl$_2$(mp-PNNP)]$^+$

Fig. 2. Three possible diastereomers of *trans*-$[CoCl_2$(mp- or *SS*(C)-mp-PNNP)$]^+$.

RS(P) (meso), and the *SS*(C)-mp-PNNP ligand in three optically active diastereomers, *RR*(P)-*SS*(C), *SS*(P)-*SS*(C), and *RS*(P)-*SS*(C). The separation of these diastereomers was not attempted for the free lignds because they are easily oxidized in the air, but done successfully through complexation with Co(III). The Co(III) complexes with these chiral phosphine ligands were prepared by methods similar to those for the previous PNNP complexes.[1,2]

The $[CoCl_2$(mp-PNNP)$]^+$ complex was separated into three green isomers, F-1, F-2, and F-3 by SP-Sephadex C-25 column chromatography. Figure 1 shows absorption spectra of these isomers. The spectra are essentially the same and show a pattern characteristic of the *trans*(Cl,Cl), *cis*(P,P)-$[CoCl_2N_2P_2]$-type complex.[8,9] Thus all of the isomers can be assigned to have the *trans*(Cl,Cl) configuration. For *trans*-$[CoCl_2$(mp-PNNP)$]^+$, there are three possible isomers as shown in Fig. 2. All the isomers exist in a pair of enantiomers, in which the two chiral nitrogen

atoms have the same absolute configutation (*RR* or *SS*) and all the chelate rings take a gauche conformation (δ or λ). The *RS*(N) isomers, in which the N–N chelate ring takes an envelop (ε) conformation as found for 3,6-diazaoctane-1,8-diamine (trien) complex,[10] are also probable. However, they can be excluded by considering stereoisomers of the trans-dichloro complexes of *SS*(C)-mp-PNNP and of the acac complexes derived from the *trans*-dichloro complexes (vide infra). In ^{1}H NMR spectra, isomer F-1 shows a P-CH_3 signal at 1.92(t) ppm, while isomers F-2 and F-3 give the signals at a remarkably high field, 1.37(t) and 1.32(t) ppm, respectively. As shown in Fig. 2, the methyl groups of the two isomers containing *RR,SS*(P)-mp-PNNP are disposed to the same direction as the phenyl group on the other P atom to face with each other. The high field shift of the mehtyl groups of isomers F-2 and F-3 will be attributable to the shielding effect of this phenyl group. The isomer containing *RS*(P)-mp-PNNP has no such a shielded methyl group. Thus isomers F-2 and F-3 can be assigned to the complexes containing *RR,SS*(P)-mp-PNNP, and isomer F-1, which shows the P–CH_3 signal at a lower field, to the complex containing *RS*(P)-mp-PNNP. Grocott and Wild[11] assigned the configurations of donor atoms of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue in Ru(II) complexes on the basis of similar high field shifts of the methyl group. All of the isomers do not show optical activity. Thus isomer F-1 is assigned to a racemate of the *RR*(N)-*RS*(P)- and *SS*(N)-*SR*(P)-mp-PNNP complexes. Assignment of the *RR*(N)-*SS*(P)-, *SS*(N)-*RR*(P)-mp-PNNP, and the *RR*(N)-*RR*(P)-, *SS*(N)-*SS*(P)-mp-PNNP complexes in Fig. 2 to the two isomers, F-2 and F-3 can not be made at present. Both isomers were obtained in nearly the same yield. There will be little difference in stability between them. To assign the isomers, the circular dichroism (CD) spectra will be needed. Attempts to resolve the isomers were unsuccessfull.

The $[CoCl_2(SS(C)\text{-mp-PNNP})]^+$ complex also yielded three green isomers. These isomers will correspond to the above three isomers of *trans*-$[CoCl_2(\text{mp-PNNP})]^+$, since the absorption spectra of six isomers are very similar (Fig. 3). The chelate ring of the N–P moiety of *SS*(C)-mp-PNNP will be stabilized in a δ-gauche conformation with the equatorial methyl group, and the ligand will form a $\delta\lambda\delta$ conformation preferentially. Hence all of the isomers are expected to be optically pure and the structures should be those given in Fig. 2.

The three isomers of *trans*-$[CoCl_2(SS(C)\text{-mp-PNNP})]^+$ were separated by fractional crystallization and column chromatography. A pseudo racemate of the *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP complexes was precipitated from a methanol solution containing the three isomers by the addition of excess $NaClO_4 \cdot H_2O$. The precipitate gives the P–CH_3 signal at a higher field (around 1.30(m) ppm). From the methanol solution filtered off the precipitate, the *RS*(P)-*SS*(C)-mp-PNNP complex was obtained by adding large excess diethyl ether. The product shows the P–CH_3 signal at 1.84(t) ppm. Thus the complexes containing *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP, and *RS*(P)-*SS*(C)-mp-PNNP can be easily separated by the solubility difference in methanol. The separation of the *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP complexes was achieved by SP-Sephadex C-25 column chromatography using 0.05 mol dm^{-3} HCl as an eluent; the *SS*(P)-*SS*(C)-mp-PNNP complex was eluted faster than the other complex. The absolute configurations of the two isomers were assigned from the CD spectra described below. The P–CH_3 signals of the *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP complexes were observed at 1.30(t) and 1.38(t) ppm, respectively.

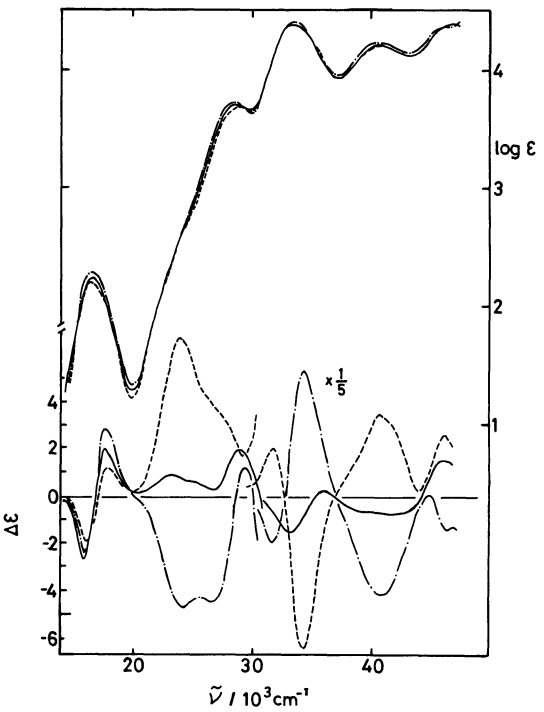


Fig. 3. Absorption and CD spectra of *trans*-$[CoCl_2(RS(P)\text{-}SS(C)\text{-mp-PNNP})]^+$ (——), *trans*-$[CoCl_2(SS(P)\text{-}SS(C)\text{-mp-PNNP})]^+$ (----), and *trans*-$[CoCl_2(RR(P)\text{-}SS(C)\text{-mp-PNNP})]^+$ (-·—·-).

Figure 3 compares CD spectra of the three isomers of *trans*-$[CoCl_2(SS(C)\text{-mp-PNNP})]^+$. The spectra show similar patterns in the region of 15000 to 20000 cm^{-1} (Ia absorption band region[2]). In the higher energy region, however, the *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP complexes exhibit fairly strong CD nearly enantiomeric to each other, while the *RS*(P)-*SS*(C)-mp-PNNP complex shows rather weak CD. The similarity in the three spectra in the Ia band region indicates that these dichroisms arise mainly from the vicinal effects of the (*R,R*)-nitrogen donor atoms and the $\delta\lambda\delta$ conformation which are common chiralities among the three complexes. Figure 4 shows the CD spectrum of

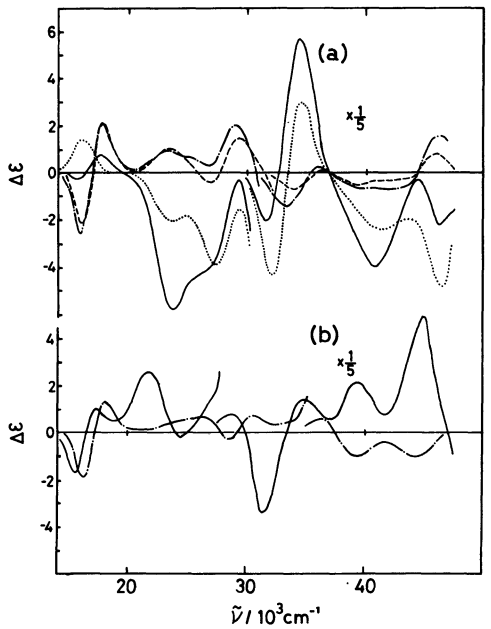
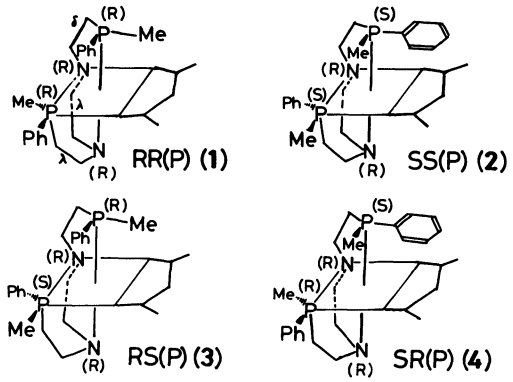


Fig. 4. a) Calculated vicinal effects of asymmetric phosphorus donors, $\Delta\varepsilon[RR(P)]$ (——) and $\Delta\varepsilon[RR(N),SS(C),\delta\lambda\delta]$ (----), and CD spectra of *trans*-$[CoCl_2(R\text{-ebpp})_2]^+$ (·····) and *trans*-$[CoCl_2(RS(P)\text{-}SS(C)\text{-mp-PNNP})]^+$ (-·—·-). b) CD spectra of *trans*-$[CoCl_2(SS(C)\text{-pp-PNNP})]^+$ (——) and *trans*-$[CoCl_2(SS(C)\text{-mm-PNNP})]^+$ (-·—·-).

trans(Cl,Cl), *cis*(P,P)-$[CoCl_2(R\text{-ebpp})_2]^+$ (*R*-ebpp=(*R*)-(2-aminoethyl)butylphenylphosphine) whose absolute configuration was determined by the X-ray method.[8] The complex exhibits rather strong negative bands in the region of 22000 to 28000 cm^{-1} and strong bands with opposite signs in the region of 30000 to 37000 cm^{-1}. The CD patterns of the *RR*(P)-*SS*(C)- and *SS*(P)-*SS*(C)-mp-PNNP complexes are similar and enantiomeric to that of the *R*-ebpp complex in these regions, respectively. From a comparison of these spectra, the isomer which was eluted faster in column chromatography is assigned to the *SS*(P)-*SS*(C)-mp-PNNP complex, and the other to the *RR*(P)-*SS*(C)-mp-PNNP complex.

When the additivity of the vicinal effects due to the chiral P, C, and N atoms and the chiral chelate conformation is assumed, the effect of the two chiral P atoms can be estimated by the equation, $\Delta\varepsilon[RR(P)]=1/2\{\Delta\varepsilon[RR(N), RR(P), SS(C), \delta\lambda\delta\text{-isomer}]-\Delta\varepsilon[RR(N), SS(P), SS(C), \delta\lambda\delta\text{-isomer}]\}$ (1), and the effect of the sum of the chiral two N and two C atoms and the $\delta\lambda\delta$ conformation by the equation, $\Delta\varepsilon[RR(N), SS(C), \delta\lambda\delta]=1/2\{\Delta\varepsilon[RR(N), RR(P), SS(C), \delta\lambda\delta\text{-isomer}]+\Delta\varepsilon[RR(N), SS(P), SS(C), \delta\lambda\delta\text{-isomer}]\}$ (2). The calculated curves of effects (1) and (2) are given in Fig. 4. The curve of effect (1) ($\Delta\varepsilon[RR(P)]$) is similar in pattern to the spectrum of *trans*(Cl,Cl), *cis*(P,P)-$[CoCl_2(R\text{-ebpp})_2]^+$, in which the chiral source is only at the P atom, since the chiral conformational effect seems to be very small.[8] The curve of effect (2) ($\Delta\varepsilon[RR(N), SS(C),\delta\lambda\delta]$) is nearly the same as the spectrum of *trans*-$[CoCl_2(RS(P)\text{-}SS(C)\text{-mp-PNNP})]^+$ in which the effect of the chiral P atoms should be cancelled. The curve is also very similar to those of *trans*-$[CoCl_2(SS(C)\text{-mm-PNNP}$ or $SS(C)\text{-pp-PNNP})]^+$ [2] which have the same chiralities (*RR*(N), *SS*(C), $\delta\lambda\delta$).[2] The results indicate that the additivity of the vicinal effects due to various chiral sources holds in CD spectra of these trans-dichloro-phosphine complexes.



Λ-cisβ-RR(N)-[Co(acac)(mp-PNNP)]$^{2+}$

Fig. 5. Four diastereomers of *cisβ*-[Co(acac)(mp- or *SS*(C)-mp-PNNP)]$^{2+}$.

The [Co(acac)(mp-PNNP or *SS*(C)-mp-PNNP)]$^{2+}$ complexes were obtained from the corresponding trans-dichloro complexes and Li(acac). All of the acac complexes can be assigned to the *cisβ*-isomer from the ^1H NMR and absorption spectra (Table 1). The *cisα*-isomer which has two mutually trans P donor atoms will be unstable because of the strong trans influence of the phosphine ligand.[1,2,12]

The *cisβ*-[Co(acac)(mp-PNNP)]$^{2+}$ complex has four possible isomers as shown in Fig. 5. All the isomers have their antipodes. The notation *RS*(P) and *SR*(P) are used for two isomers of the *RS*(P)-mp-PNNP (meso) complex; the first symbol *R* or *S* denotes the absolute configuration of the P atom at the apical coordination position with respect to the acac ligand. Each of *trans*-$[CoCl_2(RS(P)\text{-mp-PNNP})]^+$ (F-1) and *trans*-$[CoCl_2(RR,SS(P)\text{-mp-PNNP})]^+$ (F-2 and F-3) yielded two isomers by reaction with Li(acac), and the isomers were separated by SP-Sephadex C-25 column chromatography. Of these isomers, one *RS*(P)-mp-PNNP and one *RR,SS*(P)-mp-PNNP complexes show the methine proton signal of acac at a remarkably high field, δ 5.00 and 5.08, respectively, while the other *RS*(P)-mp-PNNP and *RR,SS*(P)-mp-PNNP complexes give the signal at δ 5.90 and 5.97, respectively. As seen in Fig. 5, in the $\Lambda[SR(P)](\Delta[RS(P)])$ and $\Lambda[SS(P)]$-$(\Delta[RR(P)])$ isomers, one of the two phenyl groups is disposed over the acac ring and will shield the methine proton to make its signal shift to a high field. Thus the isomers whose methine proton signals show the high field shift can be assigned to the $\Lambda[SR(P)](\Delta[RS(P)])$ and $\Lambda[SS(P)](\Delta[RR(P)])$ configurations, and the other

Table 1. Absorption Spectral Data in the Visible to Near Ultraviolet Region (Solvent: CH_3OH, at 298K)

Complex	$\tilde{\nu}/10^3\,cm^{-1}$ (log ε)			
trans-[$CoCl_2$(*RS*(P)-mp-PNNP)]$^+$ (F-1)	16.64(2.18),	28.78(3.67),	33.73(4.34),	40.57(4.19)
trans-[$CoCl_2$(*RR,SS*(P)-mp-PNNP)]$^+$ (F-2)	16.81(2.17),	28.99(3.67),	33.96(4.36),	40.65(4.19)
trans-[$CoCl_2$(*RR,SS*(P)-mp-PNNP)]$^+$ (F-3)	16.75(2.22),	28.65(3.67),	33.90(4.36),	40.65(4.20)
Λ[*RS*(P)]*Δ*[*SR*(P)]-*cisβ*-[Co(acac)(*RS*(P)-mp-PNNP)]$^{2+}$	20.50(2.83),	26(2.9)*,	29(3.8)*,	33.50(4.40)
Λ[*SR*(P)]*Δ*[*RS*(P)]-*cisβ*-[Co(acac)(*RS*(P)-mp-PNNP)]$^{2+}$	21.07(2.89),	26(2.9)*,	29(3.6)*,	33.44(4.39)
Λ[*RR*(P)]*Δ*[*SS*(P)]-*cisβ*-[Co(acac)(*RR,SS*(P)-mp-PNNP)]$^{2+}$	20.75(2.82),	26(2.9)*,	29(3.7)*,	33.50(4.37)
Λ[*SS*(P)]*Δ*[*RR*(P)]-*cisβ*-[Co(acac)(*RR,SS*(P)-mp-PNNP)]$^{2+}$	20.70(2.90),	26(2.9)*,	28.5(3.7)*,	33.22(4.41)
trans-[$CoCl_2$(*RS*(P)-*SS*(C)-mp-PNNP)]$^+$	16.56(2.23),	28.57(3.69),	33.39(4.37),	40.65(4.19)
trans-[$CoCl_2$(*SS*(P)-*SS*(C)-mp-PNNP)]$^+$	16.67(2.19),	28.78(3.68),	33.61(4.39),	40.73(4.19)
trans-[$CoCl_2$(*RR*(P)-*SS*(C)-mp-PNNP)]$^+$	16.60(2.27),	28.45(3.72),	33.54(4.39),	40.57(4.22)
Λ-cisβ-[Co(acac)(*SS*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	20.50(2.85),	25.5(2.9)*,	33.3(4.36)	
Λ-cisβ-[Co(acac)(*RR*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	21.00(2.70),	29(3.6)*,	33.5(4.30)	
Λ[*RS*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	20.3(2.78),	29.5(3.8)*,	33.8(4.39)	
Λ[*SR*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	20.92(2.39),	25.5(2.9)*,	33.5(4.32)	

* Shoulder.

Table 2. CD Spectral Data in the Visible to Near Ultraviolet Region (Solvent: CH_3OH, at 298K)

Complex	$\tilde{\nu}/10^3\,cm^{-1}$ ($\Delta\varepsilon$)		
trans-[$CoCl_2$(*RS*(P)-*SS*(C)-mp-PNNP)]$^+$	16.0(−2.84), 29.5(+1.97),	17.8(+2.01), 33.3(−7.79)	23.9(+0.83),
trans-[$CoCl_2$(*SS*(P)-*SS*(C)-mp-PNNP)]$^+$	16.3(−2.01), 31.8(+9.83),	18.0(+1.15), 34.5(−32.5)	24.0(+6.58),
trans-[$CoCl_2$(*RR*(P)-*SS*(C)-mp-PNNP)]$^+$	16.0(−2.37), 26.7(−4.57),	17.8(+2.85), 29.5(+1.25),	24.3(−4.81), 31.8(+10.1)
Λ-cisβ-[Co(acac)(SS(P)-SS(C)-mp-PNNP)]$^{2+}$	19.5(+9.04), 32.6(+15.5)	22.5(−2.6),	29.3(−19.7),
Λ-cisβ-[Co(acac)(*RR*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	19.0(+4.05), 32.5(+19.4)	21.8(−2.87),	28.8(−16.9),
Λ-[*RS*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	19.3(+3.77), 29.1(−13.4),	21.6(−2.48), 32.9(+25.8)	24.5(+2.34),
Λ-[*SR*(P)]-*cisβ*-[Co(acac)(*RS*(P)-*SS*(C)-mp-PNNP)]$^{2+}$	19.3(+9.28), 32.5(+22.8)	21.5(−1.3)*,	29.0(−20.1)

* Shoulder.

isomers to the *Λ*[*RS*(P)](*Δ*[*SR*(P)]) and *Λ*[*RR*(P)](*Δ*-[*SS*(P)]) configurations which have a methyl group over the acac ring. Similar high field shifts of the methine proton of acac have been reported for several phenyl-substituted phosphine–acac complexes.[9,13] Attempts to resolve the isomers by SP-Sephadex C-25 column chromatography with $Na_2[Sb_2(d\text{-tartrate})_2]$ were unsuccessfull, although the *Λ*[*RR*(P)]*Δ*[*SS*(P)] and *Λ*[*SR*(P)]*Δ*[*RS*(P)] isomers were partially resolved.

Each of *trans*-[$CoCl_2$(*RR,SS*(P)-*SS*(C)-mp-PNNP)]$^+$ (a pseudo racemate) and *trans*-[$CoCl_2$(*RS*(P)-*SS*(C)-mp-PNNP)]$^+$ yielded two isomers of the acac complex by reaction with Li(acac). The isomers were separated by SE-Toyopearl column chromatography. The two isomers, the *RR*(P)- and *SS*(P)-SS(C)-mp-PNNP complexes were also prepared separately from the trans-dichloro-*RR*(P)-*SS*(C)-mp-PNNP and -*SS*(P)-*SS*(C)-mp-PNNP complexes, respectively. All the isomers are optically pure and show a large positive and a small negative CD bands in the first absorption band region, indicating the *Λ* configuration (vide infra). The ^1H NMR spectra show all the isomers to have the *cisβ* structure. The selective formation of the *Λ*-*cisβ* isomers was also observed for analogous acac complexes of *SS*(C)-mm-PNNP and *SS*(C)-pp-PNNP.[2] The X-ray structure analysis on [Co(acac)(*SS*(C)-mm-PNNP)]$^{2+}$ revealed that the complex has the *Λ*-*cisβ*, *RR*(N), *SS*(C) configuration, distorted gauche ($\delta\lambda\lambda$) conformations for the three chelate rings formed by PNNP, and the axial methyl group on carbon of the *λ*-(P–N) chelate ring.[2] The skeletal structures of all the isomers of [Co(acac)(*SS*(C)-mp-PNNP)]$^{2+}$ will be the same as those found in this *SS*(C)-mm-PNNP complex.

The *SS*(P)-*SS*(C)-mp-PNNP complex and one of two isomers of the *RS*(P)-mp-PNNP complex exhibit the methine proton signal of acac at a high field, *δ* 5.20 and 5.00, respectively. The methine protons in these isomers should be shielded by the phenyl group disposed over the acac chelate ring. The methine protons of the *RR*(P)-*SS*(C)-mp-PNNP complex (*δ* 5.85) and of the other isomer of the *RS*(P)-*SS*(C)-mp-PNNP complex (*δ* 5.93) do not show such a high field shift. The results confirm that the configurational structures of the four isomers are those given in Fig. 5. Each absorption spectrum of the isomers given in Fig. 6 is very similar to that of the corresponding isomer of the

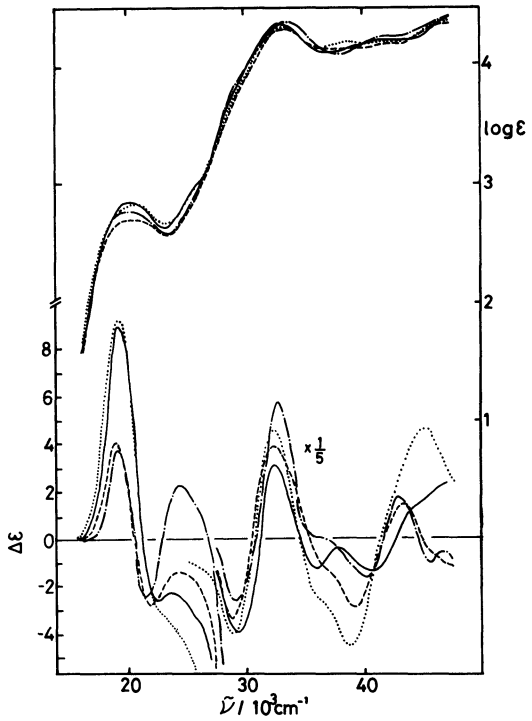


Fig. 6. Absorption and CD spectra of *Λ-cisβ*-[Co(acac)(*SS*(C)-mp-PNNP)]$^{2+}$: *SS*(P)-isomer (——), *RR*(P)-isomer (----), *SR*(P)-isomer (·····), and *RS*(P)-isomer (-·—·-).

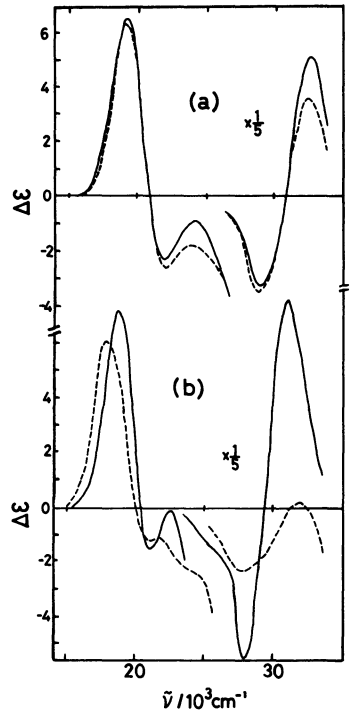


Fig. 7. a) Calculated curves for the effect of the sum, *Λ*, *SS*(C), *RR*(N), and *δλλ* (Δε[*Λ*,*SS*(C),*RR*(N), *δλλ*]): 1/2{Δε[isomer(**3**)]+Δε[isomer(**4**)]} (——) and 1/2{Δε[isomer(**1**)]+Δε[isomer(**2**)]} (----). b) CD spectra of *Λ-cisβ*-[Co(acac)(*SS*(C)-pp-PNNP)]$^{2+}$ (——) and *Λ-cisβ*-[Co(acac)(*SS*(C)-mm-PNNP)]$^{2+}$ (----).

mp-PNNP complex, especially in the first absorption band region, where the spectral patterns are fairly different among the isomers.

Figure 6 shows the CD spectra of four isomers of the *SS*(C)-mp-PNNP complex. The spectra have similar patterns and show a large positive and a small negative bands in the first absorption band region. Thus all the isomers will have the same skeletal configuration, *Λ-cisβ*. However, the positive CD bands of the *SS*(P)- and *SR*(P)-*SS*(C)-mp-PNNP complexes are much larger than those of the *RR*(P)- and *RS*(P)-*SS*(C)-mp-PNNP complexes. The former two complexes have a phenyl group disposed over the acac chelate ring, whereas the latter two complexes a methyl group in place of the phenyl group. The *SR*(P)- and *RS*(P)-*SS*(C)-mp-PNNP complexes show the positive CD band largely different in strength. These results indicate that the magnitude of the vicinal effect of the chiral P atom at one coordination position is remarkably different from that at the other chemically unequivalent coordination position. When the two effects are similar, the *SR*(P)-and *RS*(P)-*SS*(C)-mp-PNNP complexes will give similar CD spectra by cancellation of the effects due to the (*S*)- and (*R*)-P atoms.

Isomers (**1**) to (**4**) in Fig. 5 have common chiralities, *Λ*, *SS*(C), *RR*(N) and *δλλ*, and the following chiralities for the P atoms; (**1**) *R*(P_a), *R*(P_p), (**2**) *S*(P_a), *S*(P_p), (**3**) *R*(P_a), *S*(P_p), and (**4**) *S*(P_a), *R*(P_p), where P_a and P_p denote

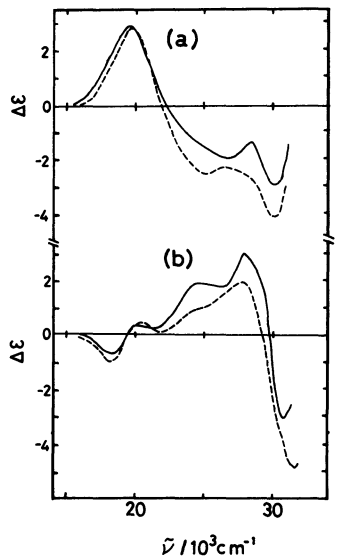


Fig. 8. a) Calculated vicinal effects of (*S*)-P atom at the apical position (Δε[*S*(P_a)]): 1/2{Δε[isomer(**4**)]−Δε[isomer(**1**)]} (——) and 1/2{Δε[isomer(**2**)]−Δε[isomer(**3**)]} (----). b) Calculated vicinal effect of (*S*)-P atom at the planar position (Δε[*S*(P_p)]): 1/2{Δε[isomer(**3**)]−Δε[isomer(**1**)]} (——) and 1/2{Δε-[isomer(**2**)]−Δε[isomer(**4**)]} (----).

P atoms at the apical and planar coordination positions, respectively with respect to the acac ligand. The effect of the sum of common chiralities, *Λ*, *SS*(C),

RR(N) and $\delta\lambda\lambda$ can be estimated by $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$]=1/2{$\Delta\varepsilon$[isomer(**1**)]+$\Delta\varepsilon$[isomer(**2**)]} (3a) or $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$]=1/2{$\Delta\varepsilon$[isomer(**3**)]+$\Delta\varepsilon$[isomer(**4**)]} (3b). Figure 7(a) shows two curves of $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$] calculated from (3a) and (3b). The vicinal effect of the apical (*S*)-P atom can be estimated by $\Delta\varepsilon$[*S*(P_a)]=1/2{$\Delta\varepsilon$[isomer(**2**)]−$\Delta\varepsilon$[isomer(**3**)]} (4a) or $\Delta\varepsilon$[*S*(P_a)]=1/2{$\Delta\varepsilon$[isomer(**4**)]−$\Delta\varepsilon$[isomer(**1**)]} (4b), and the effect of the planar (*S*)-P atom by $\Delta\varepsilon$[*S*(P_p)]=1/2{$\Delta\varepsilon$[isomer(**3**)]−$\Delta\varepsilon$[isomer(**1**)]} (5a) or $\Delta\varepsilon$[*S*(P_p)]=1/2{$\Delta\varepsilon$[isomer(**2**)]−$\Delta\varepsilon$[isomer(**4**)]} (5b). The curves of $\Delta\varepsilon$[*S*(P_a)] calculated from (4a) and (4b) are given in Fig. 8(a), and those of $\Delta\varepsilon$[*S*(P_p)] from (5a) and (5b) in Fig. 8(b). The two curves for each chiral effect are very similar, and the results indicate that the additivity of the three effects, $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$], $\Delta\varepsilon$[*S*(P_a)] and $\Delta\varepsilon$[*S*(P_p)] holds for the CD spectra of four isomers of [Co(acac)(*SS*(C)-mp-PNNP)]$^{2+}$.

The $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$] curve in Fig. 7(a) shows a large positive and a small negative bands in the first absorption band region. This pattern has been observed for a number of *Λ*-complexes of Co(III). Thus it is suggested that the effects of *SS*(C), *RR*(N) and $\delta\lambda\lambda$ are fairly small compared with the *Λ* configurational effect. Figure 7(b) shows CD spectra of *Λ*-*cis*-β-[Co(acac)(L)]$^{2+}$ (L=*SS*(C)-mm-PNNP, *SS*(C)-pp-PNNP).[2] The spectra are very similar to the $\Delta\varepsilon$[*Λ*, *SS*(C), *RR*(N), $\delta\lambda\lambda$] curve, although the *SS*(C)-mm-PNNP complex shows a somewhat different spectrum in the high energy region. The difference will be attributable to the difference in substituent on the P atom, methyl or phenyl. The absolute configuration (*Λ*, *Λ*) of the [Co(acac)(PNNP)]$^{2+}$-type complex can be safely assigned from the CD sign in the first absorption band region.

The curves of $\Delta\varepsilon$[*S*(P_a)] and $\Delta\varepsilon$[*S*(P_p)] in Fig. 8(a) and 8(b) are those for chiral donor P atoms with the same *S* configuration. However, the curves are quite different and almost enantiomeric to each other. In the first absorption band region, the $\Delta\varepsilon$[*S*(P_a)] curve shows a band much larger than that in the $\Delta\varepsilon$[*S*(P_p)] curve. The vicinal effect of the chiral P donor atom depends largely on its coordination position in [Co(acac)((*SS*(C)-mp-PNNP)]$^{2+}$. To our knowledge, there has been no report on such a coordination position dependence for the vicinal effect of a chiral donor atom. Care must be taken when the absolute configuration of a chiral donor atom is assigned by CD spectroscopy.

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