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Preparation and Stereochemistry of Cobalt(III) Complexes Containing 3,6-Diphenyl-3,6-diphosphaoctane-1,8-diamine or (2*S*,9*S*)-4,7-Diphenyl-4,7-diphosphadecane-2,9-diamine, $NH_2CHRCH_2P(C_6H_5)CH_2CH_2P(C_6H_5)$-$CH_2CHRNH_2$ (R=H, CH_3)

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Nine new cobalt(III) complexes containing 3,6-diphenyl-3,6-diphosphaoctane-1,8-diamine (NPPN), *trans*-[$CoCl_2$(*rac*(*P*)-NPPN)]$^+$, *cis*α-[Co(L)(*rac*(*P*)-NPPN)]$^{n+}$ (L=en, *n*=3; L=acac, *n*=2) and *Δ*- and *Λ*-*cis*α-[Co(L′)(*rac*(*P*)-NPPN)]$^{n+}$ (L′=*R*-pn, *n*=3; L′=*S*-ala or *S*-pro, *n*=2), and five new cobalt(III) complexes containing (2*S*,9*S*)-4,7-diphenyl-4,7-diphosphadecane-2,9-diamine (*SS*(*C*)-NPPN), *Δ*- and *Λ*-*cis*α-[Co(L)(*rac*(*P*),*SS*(*C*)-NPPN)]$^{n+}$ (L=en, *n*=3; *L*=acac, *n*=2) and *Δ*-*cis*β-[Co(acac)(*meso*(*P*),*SS*(*C*)-NPPN)]$^{2+}$, were prepared, where en, *R*-pn, acac, *S*-ala and *S*-pro denote ethylenediamine, (*R*)-1,2-propanediamine, 2,4-pentanedionate, (*S*)-alaninate and (*S*)-prolinate ions, respectively. Stereochemistries of the complexes and the chiral phosphorus donor atoms were studied on the basis of the absorption, ^{1}H and ^{13}C NMR, and CD spectra. The *rac*(*P*)-NPPN and *rac*(*P*),*SS*(*C*)-NPPN ligands formed selectively either the trans or cisα isomer, while no stable complex was obtained with the meso(P) isomers of NPPN and *SS*(*C*)-NPPN except *cis*β-[Co(acac)(*meso*(*P*),*SS*(*C*)-NPPN)]$^{2+}$ which slowly decomposes in water.

Studies on stereochemistry of optically active octahedral metal complexes containing chiral phosphorus or arsenic donor atoms have little been reported,[1-5] except a systematic study on cobalt(III) complexes containing a quadridentate arsine ligand $(CH_3)_2As(CH_2)_3As(C_6H_5)(CH_2)_3As(C_6H_5)(CH_2)_3As(CH_3)_2$ reported by Bosnich and his co-workers.[6] Since a chiral phosphorus or arsenic atom is stable to racemization,[7] a multidentate ligand containing such chiral donor atoms is expected to exhibit different stereoselectivity in complex formation from that of the corresponding amine ligand which has been studied extensively.[8]

In this paper, we report the preparation and stereochemistry of two quadridentate ligands having two chiral phosphorus donor atoms, $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$ (NPPN) and (2*S*,9*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH(CH_3)NH_2$ (*SS*(*C*)-NPPN), and their cobalt(III) complexes.

Experimental

The phosphine ligands were prepared and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents for the preparation were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption, circular dichroism (CD), and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, a JASCO J-40CS spectropolarimeter, and Jeol PMX-60, FX-100 and GX-400 spectrometers, respectively.

Preparation of Ligands. 3,6-Diphenyl-3,6-diphosphaoctane-1,8-diamine (NPPN). Method 1. This method is a modified one of Issleib and Oehme.[9] To (2-aminoethyl)-phenylphoshine[9] (4.95 g) in dry tetrahydrofuran (THF) (500 cm^3) was added dropwise a 15% hexane solution (14 g) of butyllithium over a period of 1 h with stirring. After further stirring for 1 h, 1,2-dichloroethane (1.6 g) was added dropwise, the solution was refluxed for 3 h, and then cooled. Water (2 cm^3) was added dropwise, the solvent THF was evaporated, and to the residue water (200 cm^3) and then diethyl ether (200 cm^3) were added with stirring. The ethereal layer was separated, dried over $MgSO_4$ (ca. 5 g) overnight, filtered, and evaporated to give an oily product. It was heated at ca. 100 °C under highly reduced pressure (<ca. 135 pa) to remove by-products and starting materials since the NPPN ligand is not distillable under ordinary conditions. Yield: ca. 60%. The crude product was used for preparing cobalt(III) complexes without further purification.

Method 2. A 15% hexane solution (30 g) of butyllithium was added dropwise to a dry THF solution (200 cm^3) of 1,2-bis(phenylphosphino)ethane[10] (7.34 g) over a period of 2 h with stirring. Stirring was continued for 3 h. Aziridine (3.7 g) was added dropwise at 40 °C, and the solution was refluxed for 10 h. After cooling water (1.5 cm^3) was added, and the soluiton was dried over $MgSO_4$ (ca. 10 g) overnight, filtered and evaporated to yield an oily product. It was treated by the same way as described in Method 1. Yield: ca. 60%.

(2*S*,9*S*)-4,7-Diphenyl-4,7-diphosphadecane-2,9-diamine (*SS*-(*C*)-NPPN). This ligand was prepared by the same method as Method 2 for NPPN, using (*S*)-2-methylaziridine[11] instead of aziridine. Yield: 50—60%.

Preparation of Cobalt(III) Complexes. *trans*-[$CoCl_2$(*rac*-(*P*)-NPPN)]$ClO_4 \cdot H_2O$. A methanol solution (30 cm^3) of NPPN (2.89 g, 8.02 mmol) was added dropwise to [CoCl-$(NH_3)_5]Cl_2$[12] (2.21 g) in a mixture (700 cm^3) of methanol and water (1 : 1) with stirring. After the color of the solution had been changed from violet to green (15 min), concd HCl (5 cm^3) was added and the solution was stirred for 15 min. The solvent methanol was removed under reduced pressure, and the unreacted NPPN ligand and by-products were extracted with diethyl ether (100 cm^3×2). The aqueous solution was concentrated to a small volume under reduced

pressure to yield a green precipitate (*trans*-[$CoCl_2$ (*rac*(*P*)-NPPN)]Cl). The precipitate was recrystallized from water by adding $NaClO_4 \cdot H_2O$. Yield: 1.5 g (32%). Found: C, 37.17; H, 5.27; N, 4.63%. Calcd for $C_{18}H_{28}N_2Cl_3CoO_5P_2$: C, 37.30; H, 4.78; N, 4.83%. Perchlorate salts of cobalt(III)-phosphine complexes are potentially explosive, and should be handled carefully.

***cis*α-[Co(en)(*rac*(*P*)-NPPN)]$(ClO_4)_3 \cdot 0.5H_2O$.** A methanol solution (100 cm^3) containing *trans*-[$CoCl_2$(*rac*(*P*)-NPPN)]Cl (300 mg, 0.578 mmol) and en (100 mg, 1.66 mmol) was stirred overnight. The resulting yellow solution was diluted with water (1 dm^3) and applied on a column (φ3 cm×60 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.15 mol dm^{-3} Na_2SO_4. The yellow eluate (major product) was collected, diluted with water, and applied again on a column (φ1 cm×10 cm) of SP-Sephadex C-25. The adsorbed yellow product was eluted with 0.5 mol dm^{-3} $NaClO_4$, and the eluate was concentrated slowly in a desiccator, yielding yellow crystals. Yield: 350 mg (89%). Found: C, 31.69; H, 4.65; N, 7.33%. Calcd for $C_{20}H_{35}N_4CoCl_3O_{12.5}P_2$: C, 31.66; H, 4.65; N, 7.38%.

***cis*α-[Co(acac)(*rac*(*P*)-NPPN)]$(ClO_4)_2$.** The complex was prepared by the same method as for the en complex, using lithium 2,4-pentanedionate (Li(acac)) instead of en. Yield: 65%. Found: C, 39.90; H, 4.86; N, 3.83%. Calcd for $C_{23}H_{33}N_2CoCl_2O_{10}P_2$: C, 40.08; H, 4.83; N, 4.06%.

Δ-*cis*α-[Co(*R*-pn)(*RR*(*P*)-NPPN)]$(ClO_4)_3 \cdot 2H_2O$ and Λ-*cis*α-[Co(*R*-pn)(*SS*(*P*)-NPPN)]$(ClO_4)_3 \cdot 1.5H_2O$. The complexes were prepared by the same method as that for the en complex, using (*R*)-1,2-propanediamine (*R*-pn) instead of en. By elution with 0.15 mol dm^{-3} Na_2SO_4 two large yellow bands (F1 (faster) and F2 (slower)) were eluted. From each band the complex was isolated by a method similar to that for the en complex. Yields, F1(Δ-*cis*α): 23% and F2 (Λ-*cis*α): 22%. Found for F1: C, 31.50; H, 4.94; N, 6.99%. Calcd for $C_{21}H_{40}N_4CoCl_3O_{14}P_2$:C, 31.54; H, 5.04; N, 7.01%. Found for F2: C, 31.69; H, 4.62; N, 7.01%. Calcd for $C_{21}H_{39}N_4CoCl_3O_{13.5}P_2$: C, 31.90; H, 4.67; N, 7.08%.

Δ-*cis*α-[Co(*S*-ala)(*RR*(*P*)-NPPN)]$(ClO_4)_2 \cdot 2.5H_2O$ and Λ-*cis*α-[Co(*S*-ala)(*SS*(*P*)-NPPN)]$(ClO_4)_2 \cdot 2H_2O$. The complexes were prepared by a method similar to that for the *R*-pn complex, using sodium (*S*)-alaninate instead of *R*-pn. Yields, F1(Δ-*cis*α): 17% and F2(Λ-*cis*α): 19%. Found for F1: C, 34.65; H, 4.60; N, 5.75%. Calcd for $C_{21}H_{37}N_3CoCl_2O_{12.5}P_2$: C, 34.87; H, 5.16; N, 5.81%. Found for F2: C, 35.01; H, 4.66; N, 5.82%. Calcd for $C_{21}H_{36}N_3CoCl_2O_{12}P_2$: C, 35.31; H, 5.08; N, 5.88%.

Δ-*cis*α-[Co(*S*-pro)(*RR*(*P*)-NPPN)]$(ClO_4)_2 \cdot 0.5H_2O$ and Λ-*cis*α-[Co(*S*-pro)(*SS*(*P*)-NPPN)]$(ClO_4)_2 \cdot 0.5H_2O$. The complexes were prepared by the same method as for the *S*-ala complexes, using sodium (*S*)-prolinate. Yields, F1 (Δ-*cis*α): 14% and F2 (Λ-*cis*α) : 10%. Found for F1: C, 38.76; H, 4.80; N, 5.78%. Calcd for $C_{23}H_{35}N_3CoCl_2O_{10.5}P_2$: C, 38.73; H, 4.95; N, 5.89%. Found for F2: C, 38.82; H, 4.99; N, 5.90%. Calcd for $C_{23}H_{35}N_3CoCl_2O_{10.5}P_2$: C, 38.73; H, 4.95; N, 5.89%.

Δ-*cis*α-[Co(en)(*RR*(*P*),*SS*(*C*)-NPPN)]$(ClO_4)_3 \cdot 0.5H_2O$ and Λ-*cis*α-[Co(en)(*SS*(*P*),*SS*(*C*)-NPPN)]$Cl_2 \cdot ClO_4 \cdot 0.5H_2O$. To [Co(en)$_3$]$(ClO_4)_3$[13] (1 g) in a mixture (100 cm^3) of water and methanol (5:3) were added a methanol solution (100 cm^3) of *SS*(*C*)-NPPN (700 mg, 1.94 mmol) and active charcoal (ca. 50 mg). The mixture was stirred overnight, filtered, diluted with water (3 dm^3) added concd HNO_3 (2 cm^3), and applied on a column (φ3 cm×60 cm) of SP-Sephadex C-25. By elution with 0.3 mol dm^{-3} Na_2[Sb_2(*d*-tartrate)$_2$], the column gave two large yellow bands (F1 (faster) and F2 (slower)) with a large orange-yellow ([Co(en)$_3$]$^{3+}$) and a few small bands. Each eluate of F1 and F2 was diluted ten times with water, poured again on a column (φ2 cm×15 cm) of SP-Sephadex C-25, and the complex was eluted with 2 mol dm^{-3} NaCl. The eluate was concentrated to a small volume under reduced pressure. On addition of excess $NaClO_4 \cdot H_2O$ the concentrate gave crystals of the complex. Yields, F1 (Δ-*cis*α): 80 mg (5%) and F2 (Λ-*cis*α): 200 mg (15%). Found for F1: C, 33.71; H, 4.77; N, 6.61%. Calcd for $C_{22}H_{39}N_4CoCl_3O_{12.5}P_2$: C, 33.58, H, 5.00; N, 7.12%. Found for F2: C, 39.13; H, 6.29; N, 8.16%. Calcd for $C_{22}H_{41}N_4CoCl_3O_{5.5}P_2$: C, 39.04; H, 6.11; N, 8.28%.

Δ-*cis*α-[Co(acac)(*RR*(*P*),*SS*(*C*)-NPPN)]$(ClO_4)_2 \cdot H_2O$, Λ-*cis*α-[Co(acac)(*SS*(P),*SS*(*C*)-NPPN)]$(ClO_4)_2$, and Δ-*cis*β-[Co(acac)(*RS*(P),*SS*(*C*)-NPPN)][$B(C_6H_5)_4$]$_2 \cdot 3H_2O$. To [Co(acac)$_3$][14] (400 mg, 1.12 mmol) in methanol (200 cm^3) were added a methanol solution (50 cm^3) of *SS*(*C*)-NPPN (550 mg, 1.53 mmol) and active charcoal (ca. 50 mg). The mixture was stirred overnight, filtered, diluted with water (3 dm^3) added concd HNO_3 (2 cm^3), and applied on a column (φ3 cm×150 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.15 mol dm^{-3} Na_2[Sb_2(*d*-tartrate)$_2$], yielding three large bands (orange F1 (fast), orange F2 (middle), and orange-red F3 (slow)). Each eluate of F1, F2, and F3 was diluted ten times with water acidified with HCl (pH ca. 3.0), and applied again on a column (φ2 cm×15 cm) of SP-Sephadex C-25. The adsorbed complex was eluted with 1 mol dm^{-3} Na_2SO_4. Either eluate obtained from F1 and F2 was evaporated to dryness under reduced pressure, and the complex was extracted with methanol. The extract gave orange crystals on addition of excess $NaClO_4 \cdot H_2O$. The complex contained in eluate F3 was isolated by adding sodium tetraphenylborate and purified by column (φ2.5 cm×60 cm) chromatography using Toyopearl TSK-GEL and methanol. Yields, F1 (Δ-*cis*α): 95 mg (9%), F2 (Λ-*cis*α): 70 mg (6%) and F3 (Δ-*cis*β): 195 mg (11%). Found for F1 : C, 40.51; H, 5.09; N, 4.07%. Calcd for $C_{25}H_{39}N_2CoCl_2O_{11}P_2$: C, 40.83; H, 5.35; N, 3.81%. Found for F2: C, 41.53; H, 5.29; N, 4.36%. Calcd for $C_{25}H_{37}N_2CoCl_2O_{10}P_2$: C, 41.86; H, 5.20; N, 3.91%. Found for F3: C, 72.15; H, 6.65; N, 2.28%. Calcd for $C_{73}H_{83}N_2B_2CoO_5P_2$: C, 72.41; H, 6.91; N, 2.31%. Complex F3 decomposes slowly in neutral water, so that it should be treated always in slightly acidic conditions.

Derivation of the en Complexes of *SS*(*C*)-NPPN from the acac Complexes. To isomer F1 (10 mg) of the acac complex in a small amount of methanol was added concd HCl (2 cm^3) and the solution was allowed to stand overnight, the color changing gradually from orange to red. The red solution was diluted ten times with water and applied on a column (φ1 cm×15 cm) of SP-Sephadex C-25. The adsorbed red complex was eluted with 0.3 mol dm^{-3} HCl. To the red eluate was added a methanol solution of excess en, the color being changed instantly from red to yellow. The yellow eluate was diluted ten times with water and applied on a column (φ1 cm×15 cm) of SP-Sephadex C-25. The adsorbed yellow complex was eluted with 0.4 mol dm^{-3} NaCl. The absorption and CD spectra of the yellow eluate coincide with those of isomer F1 of the en complex prepared from

$[Co(en)_3]^{3+}$ and *SS(C)*-NPPN. By the same method, isomer F2 of the en complex was derived from isomer F2 of the acac complex. However, any en complex of *SS(C)*-NPPN could not be obtained from isomer F3 of the acac complex. A methanol solution of F3 turned red by adding concd HCl, but the product gradually decomposed to Co(II) species on addition of excess en.

Optical Resolution of the NPPN Complexes. Partial resolutions of *cisα*-[Co(en)(*rac(P)*-NPPN)]$^{3+}$ and *cisα*-[Co(acac)(*rac(P)*-NPPN)]$^{2+}$ were achieved by an SP-Sephadex C-25 column-chromatographic method using a column (ϕ3 cm×120 cm), and 0.2 mol dm^{-3} and 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$ as an eluent, respectively. In each resolution the first and last several fractions of the band showed a constant $\Delta\varepsilon/\varepsilon$ value. The fractions with a constant $\Delta\varepsilon/\varepsilon$ value were collected, diluted five times with water and applied on a column (ϕ1 cm×10 cm) of SP-Sephadex C-25. The column was washed with water and the complex was eluted with 0.3 mol dm^{-3} NaCl. The effluent was used for CD measurements, and the concentration of the complex was determined by reference to the ε values of the racemate.

Results and Discussion

NPPN Complexes. We have prepared the NPPN ligand from $(C_6H_5)HPCH_2CH_2PH(C_6H_5)$ and aziridine (Method 2) and also from $NH_2CH_2CH_2PH(C_6H_5)$ and $ClCH_2CH_2Cl$ by Method 1 which is a modified method of Issleib and Oehme.[9] Both methods gave similar yields. The ligand could not be purified by vacuum distillation because it had a high boiling point and decomposed at a high temperature.[9] Thus, the crude product was used without purification for preparing the cobalt(III) complexes.

By reaction of NPPN with $[CoCl(NH_3)_5]Cl_2$, only one isomer of $[CoCl_2(NPPN)]^+$ was isolated, no dichloro complex being formed by oxidizing [Co(NPPN)]$^{2+}$ with Cl_2[15] or O_2.[16] The absorption spectrum of $[CoCl_2(NPPN)]^+$ is similar in pattern to that of *trans(Cl,Cl)*, *cis(P,P)*-$[CoCl_2(ebpp)_2]^+$ (ebpp= $NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$) whose structure has been determined by X-ray analysis (Fig. 1).[2] Although the NPPN complex exhibits strong Co–Cl and Co–P charge-transfer bands[2,15,17] at fairly lower energies, the spectrum indicates that the complex has a trans(Cl,Cl) configuration. For *trans(Cl,Cl)*-$[CoCl_2(NPPN)]^+$, there are two possible diastereomers arising from the combination of chiral phosphorus atoms of the ligand; racemic(RR,SS) and meso(RS)[18] (Fig. 2). The isolated *trans(Cl,Cl)*-$[CoCl_2(NPPN)]^+$ complex can be assigned to have the racemic NPPN ligand, since the complex affords only *cisα*-[Co(L)(NPPN)]$^{n+}$ (L=en, acac) by reaction with L. The meso NPPN ligand can not coordinate to a metal ion in the cisα form, but only in the cisβ form. The filtrate obtained after *trans(Cl,Cl)*-$[CoCl_2(rac(P)\text{-NPPN})]^+$ had been removed contained another green complex which seemed to be *trans(Cl,Cl)*-$[CoCl_2(meso(P)\text{-NPPN})]^+$. However, the complex was rather unstable and decomposed during the course of isolation to give cobalt(II) species and an oily material. The instability of this complex may be attributable to its strained structure, in which the central five-membered P–Co–P chelate ring is forced

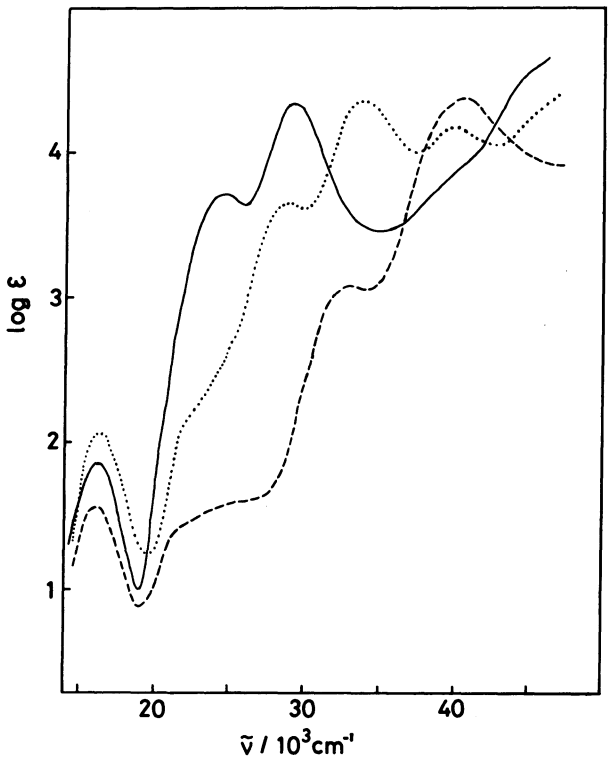


Fig. 1. Absorption spectra of *trans*-$[CoCl_2(rac(P)\text{-NPPN})]^+$ (——), *trans*-$[CoCl_2(en)_2]^+$ (------), and *trans*-$[CoCl_2(ebpp)_2]^+$ (·····).[2]

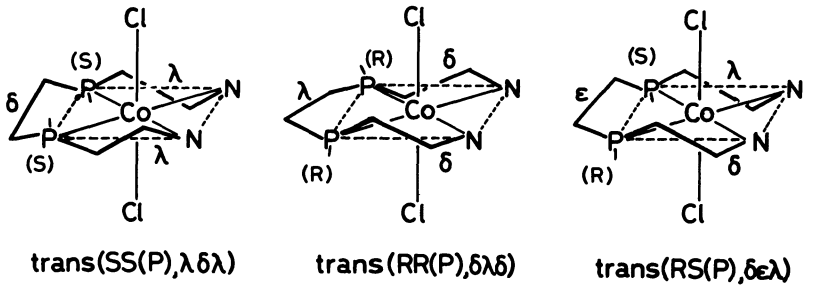


Fig. 2. Three possible isomers of *trans*-$[CoCl_2(NPPN)]^+$.

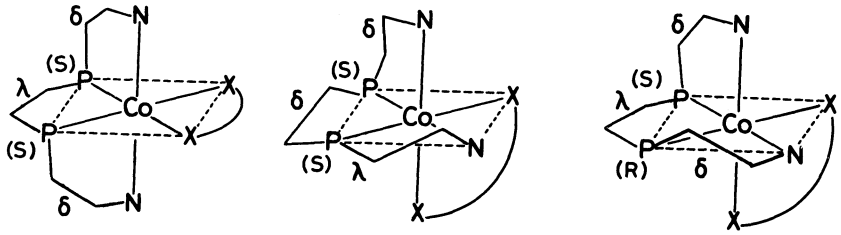


Fig. 3. Three possible isomers of $[Co(L)(NPPN)]^{n+}$.

to take an envelope conformation (Fig. 2), although such an envelope conformation was found in *trans*-$[Co(NH_3)_2(trien)]^{3+}$ (trien=$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$).[20] The *trans*(*Cl,Cl*)-$[CoCl_2$ (*rac*(*P*)-NPPN)$]^+$ complex is very stable and does not change in water over several days. Thus only the *rac*(*P*)-NPPN ligand can form stable *trans*(*Cl,Cl*)-$[CoCl_2$-(NPPN)$]^+$.

As stated previously, either reaction of *trans*(*Cl,Cl*)-$[CoCl_2(NPPN)]^+$ with L (L=en, acac) afforded one geometrical isomer of $[Co(L)(NPPN)]^{n+}$. In each reaction product, a very small band (yellow for en and orange for acac) was observed on column chromatography, but they were not characterized because of a very small amount. For $[Co(chelate)(NPPN)]^{n+}$, three geometrical isomers are possible and each isomer has its antipode (Fig. 3). The $[Co(chelate)(meso(P)\text{-}NPPN)]^{n+}$ complex can not form the cisα isomer, since two terminal P–N chelate arms point to the same apical site with respect to the P–Co–P plane. The ^{13}C NMR spectra of the en and acac complexes exhibit eight and ten carbon signals, respectively. Thus these complexes can be assigned to the cisα isomer which has C_2 symmetry. The reason for preferential formation of the cisα isomer in $[Co(L)(rac(P)\text{-}NPPN)]^{n+}$ is not clear at the moment. Molecular models show that the cisβ isomer of the *rac*(*P*)-NPPN complex involves fairly large steric interactions between the phenyl group on the central phosphorus atom of three meridionally coordinated atoms N–P–P and all of three chelate rings formed by NPPN. The instability of the cisβ isomer of the *rac*(*P*)-NPPN complex seems to come from such a steric factor.

The chirality of phosphorus atoms (RR or SS) of *rac*(*P*)-NPPN has a mutual relation with the chirality of $[Co(chelate)(rac(P)\text{-}NPPN)]^{n+}$ (Δ or Λ); *SS*(*P*)-NPPN can form Λ-cisα and Δ-cisβ isomers, while *RR*(*P*)-NPPN Δ-cisα and Λ-cisβ isomers (Fig. 3). Figure 4 shows absorption and circular dichroism spectra of the faster-moving *cis*α-$[Co(en)(rac(P)\text{-}NPPN)]^{3+}$ isomer in column chromatography. The CD spectrum of this isomer is quite similar to that of *Λ-cis*α-$[Co(en)(SS(P),SS(C)\text{-}NPPN)]^{3+}$ (vide post) whose

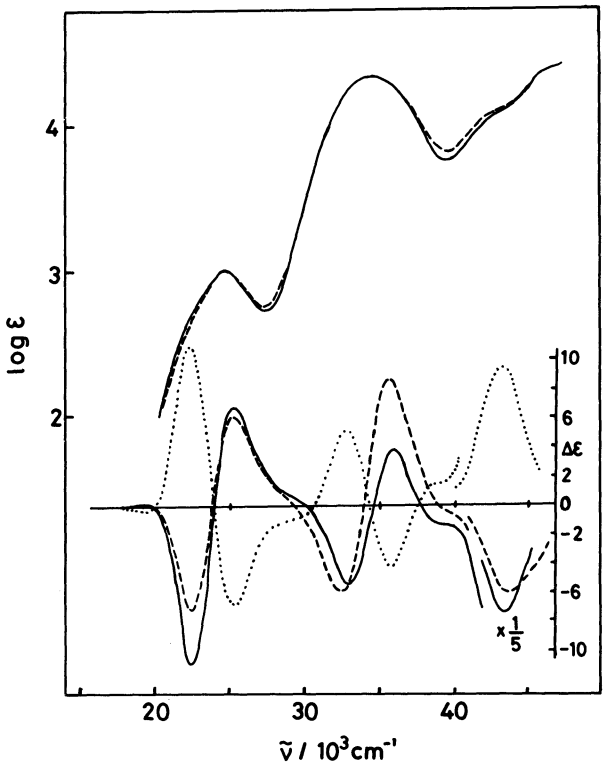


Fig. 4. Absorption and CD spectra of *cis*α-$[Co(L)(NPPN)]^{3+}$: *cis*α-$[Co(en)(NPPN)]^{3+}$ (——) (faster-eluting fractions (see Experimental)), *cis*α-$[Co(R\text{-}pn)(NPPN)]^{3+}$ (F1) (·····), *cis*α-$[Co(R\text{-}pn)(NPPN)]^{3+}$ (F2) (------).

absolute configuration has been determined by X-ray analysis.[21] Thus the isomer is assigned to the Λ-cisα isomer and the phosphorus atoms to the S configuration. By reaction of *trans*-$[CoCl_2(rac(P)\text{-}NPPN)]^+$ with *R*-pn, two isomers of $[Co(R\text{-}pn)(rac(P)\text{-}NPPN)]^{3+}$ (F1 and F2) were obtained in similar yields. The isomers were completely separated by SP-Sephadex column chromatography. Both isomers show identical absorption spectrum and the spectrum is nearly the same as that of *cis*α-$[Co(en)(rac(P)\text{-}NPPN)]^{3+}$. The CD spectra of isomers F1 and F2 are also very similar to those of the faster- and slower-

moving isomers of the en complex, *Δ-cisα*-[Co(en)(*RR*(*P*)-NPPN)]$^{3+}$ and *Λ-cisα*-[Co(en)(*SS*(*P*)-NPPN)]$^{3+}$ respectively (Fig. 4). Thus isomers F1 and F2 of the *R*-pn complex can be assigned to *Δ-cisα*-[Co(*R*-pn)(*RR*(*P*)-NPPN)]$^{3+}$ and *Λ-cisα*-[Co(*R*-pn)(*SS*(*P*)-NPPN)]$^{3+}$, respectively. It is noted that the Λ-isomer of these diamine complexes of *rac*(*P*)-NPPN shows a negative main CD band in the first d–d band region. The result is in contrast to the CD pattern for usual chelate complexes of Co(III), although the CD spectra of the present NPPN complexes involve the vicinal effect of chiral phosphorus atoms that can not be evaluated.

Similarly two isomers (F1 and F2) were obtained for each amino acidato complex [Co(L)(*rac*(*P*)-NPPN)]$^{2+}$ (L=*S*-ala, *S*-pro). From comparisons of the absorption and CD spectra with those of the above diamine complexes (Fig. 5), isomer F1 can be assigned to *Δ-cisα*-[Co(L)(*RR*(*P*)-NPPN)]$^{2+}$ and isomer F2 to *Λ-cisα*-[Co(L)(*SS*(*P*)-NPPN)]$^{2+}$. Spectral data for the NPPN complexes are listed in Table 1.

***SS*(*C*)-NPPN Complexes.** The *SS*(*C*)-NPPN ligand was prepared from $(C_6H_5)HPCH_2CH_2PH(C_6H_5)$ and (*S*)-2-methylaziridine by a method similar to Method 2 for NPPN. The *trans*-[$CoCl_2$(*SS*(*C*)-NPPN)]$^+$ complex was yielded from *SS*(*C*)-NPPN and [$CoCl(NH_3)_5$]Cl_2 by the same method as for the NPPN complex, but the yield was very poor. The N–P chelate ring of *SS*(*C*)-NPPN in a complex will be stabilized in a δ-gauche conformation because of the equatorial preference of the methyl group on the (*S*)-carbon atom. Molecular models indicate that when the N–P chelate ring takes a λ-conformation, the methyl group becomes axial and has steric interactions with the phenyl group disposed nearly axially and also with the chloride ion at the apical position of the complex. Of these possible isomers of the *trans*-dichloro complex shown in Fig. 2, only the

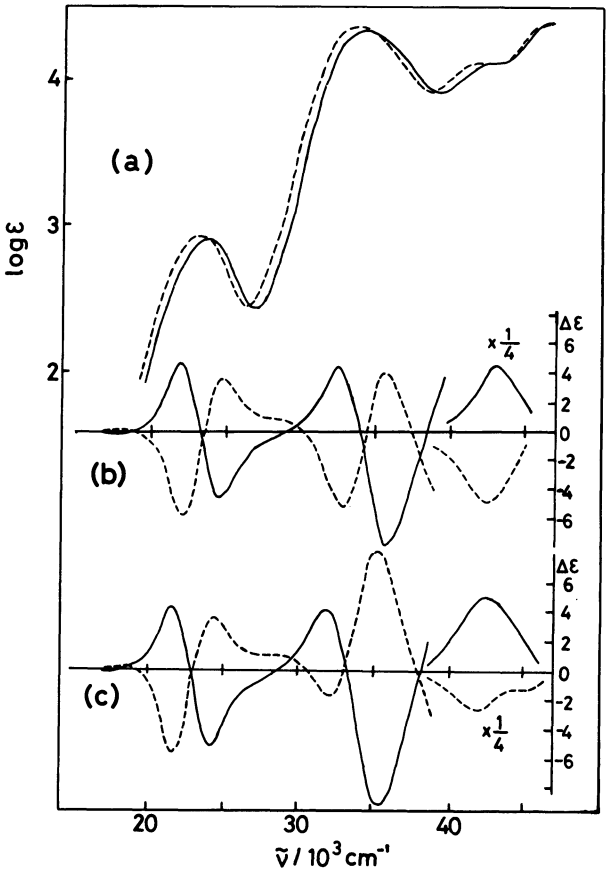


Fig. 5. (a) Absorption spectra of *cisα*-[Co(L)(NPPN)]$^{2+}$ (F2); L=*S*-ala (——), L=*S*-pro (------). (b) CD spectra of *cisα*-[Co(*S*-ala)(NPPN)]$^{2+}$; F1 (——), F2 (------). (c) CD spectra of *cisα*-[Co(*S*-pro)(NPPN)]$^{2+}$; F1 (——), F2 (------).

Table 1. Absorption (AB) and CD Spectral Data for [Co(L)(NPPN)]$^{n+}$

L		AB ($\tilde{\nu}$/10³ cm^{-1} (log ε))	CD ($\tilde{\nu}$/10³ cm^{-1} (Δε))
Cl_2		16.3(1.82), 24.7(3.67), 29.2(4.29)	
en[a]		24.7(3.02), 34.4(4.35)	19.6(+0.40), 22.4(−10.63), 25.3(+6.57), 32.9(−5.05), 35.8(+5.42), 43.3(−19.77)
acac[a]		22.1(2.87), 35.1(4.44)	19.6(+0.32), 23.0(−3.53), 27.0(+1.88), 31.2(−15.29), 35.7(+41.59), 40.3(+31.83)
R-pn	F1	24.6(3.02), 34.2(4.38)	19.6(−0.32), 22.4(+10.97), 25.3(−6.62), 32.9(+5.07), 35.7(−4.16), 43.1(+19.72)
	F2	24.8(3.03), 34.5(4.35)	19.5(+0.20), 22.3(−7.12), 25.3(+6.16), 32.4(−5.89), 35.6(+8.57), 43.5(−11.87)
S-ala	F1	23.8(2.93), 34.1(4.34)	17.5(−0.04), 21.9(+4.68), 24.6(−4.60), 32.5(+4.44), 35.7(−7.62), 42.6(+19.36)
	F2	23.8(4.93), 34.1(4.32)	17.5(+0.05), 22.0(−5.80), 24.8(+3.50), 32.8(−5.24), 35.6(+3.96), 42.4(−18.99)
S-pro	F1	23.3(2.96), 33.6(4.39)	17.2(−0.03), 21.6(+4.35), 24.2(−4.14), 31.9(+4.30), 35.3(−9.27), 42.2(+20.70)
	F2	23.3(2.93), 33.6(4.36)	17.8(+0.05), 22.1(−5.85), 24.3(+3.51), 32.1(−1.72), 35.1(+8.26), 41.7(−10.64)

a) CD data are observed for faster eluting fraction.

trans(RR(P),$\delta\lambda\delta$) isomer[22] has no axial methyl group. The poor yield of *trans*-[$CoCl_2$(*SS*(*C*)-NPPN)]$^+$ will be attributable to such a stereochemical requirement of the complex, neither SS(P)- nor RS(P)-isomer of *SS*(*C*)-NPPN forming the stable *trans*-dichloro complex.

Two isomers (F1 and F2) of [Co(en)(*SS*(*C*)-NPPN)]$^{3+}$ were obtained by the reaction of *SS*(*C*)-NPPN with $[Co(en)_3]^{3+}$. As stated previously, the structure of isomer F2 was determined by X-ray analysis to *Λ-cisα*-[Co(en)(*SS*(*P*),*SS*(*C*)-NPPN)]$^{3+}$ where three chelate rings of *SS*(*C*)-NPPN take $\delta\lambda\delta$ conformations (Fig. 3(a)), and the two methyl groups have an equatorial disposition with respect to the N–P chelate ring. The other isomer F1 can be assigned to Δ-cis*α*, since the isomer exhibits nine carbon signals in the ^{13}C NMR spectrum, and shows absorption spectrum very similar to that of isomer F2, but the CD spectrum is nearly enantiomeric to that of isomer F2 (Fig. 6). In the Δ-cis*α* structure, both phosphorus atoms have necessarily the R configuration, and the stable conformation of *RR*(*P*),*SS*(*C*)-NPPN would be $\lambda\delta\lambda$ enantiomeric to those of the Λ-cis*α* isomer (F2). When the P–N chelate ring takes a λ-gauche conformation, the methyl group is disposed axially and approaches very close to one of the methylene groups of the central P–P chelate ring. However, the terminal P–N chelate ring in the cis*α* configuration is rather flexible and can take other conformation than λ-gauche such as an envelope-type to release the crowding. Such an envelope conformation of a similar P–N chelate ring has been found in *Λ-cisβ*-[Co(acac){(*S*,*S*)-$(CH_3)_2PCH_2$-$CH(CH_3)NHCH_2CH_2NHCH(CH_3)CH_2P(CH_3)_2$}]$^{2+}$.[23] Thus we have assigned isomer F1 to *Δ-cisα*-[Co(en)(*RR*(*P*),*SS*(*C*)-NPPN)]$^{3+}$.

No indication of formation of [Co(en)(*RS*(*P*),*SS*(*C*)-NPPN)]$^{3+}$ was observed in column chromatography. The *RS*(*P*),*SS*(*C*)-NPPN ligand can form only the cis*β* isomer as stated previously. However, molecular models indicate that the puckered chelate ring of en has steric interactions with two phenyl groups of *RS*(*P*),*SS*(*C*)-NPPN arranged in the cis*β* configuration. Thus the en complex with *RS*(*P*),*SS*(*C*)-NPPN will be unstable by such a steric factor.

The reaction of *SS*(*C*)-NPPN with [Co(acac)$_3$] afforded three isomers of [Co(acac)(*SS*(*C*)-NPPN)]$^{2+}$ (F1, F2, and F3). The ^{13}C NMR spectra suggest the cis*α* configuration for isomers F1 and F2, and the cis*β* configuration for F3. Table 2 lists the NMR data. The assignments were made on the basis of the previous work on analogous complexes.[1,24] The absorption spectra of isomers F1 and F2 are similar, while the CD spectra are nearly enantiomeric to each other (Fig. 7). Isomers F1 and F2 of the acac complex

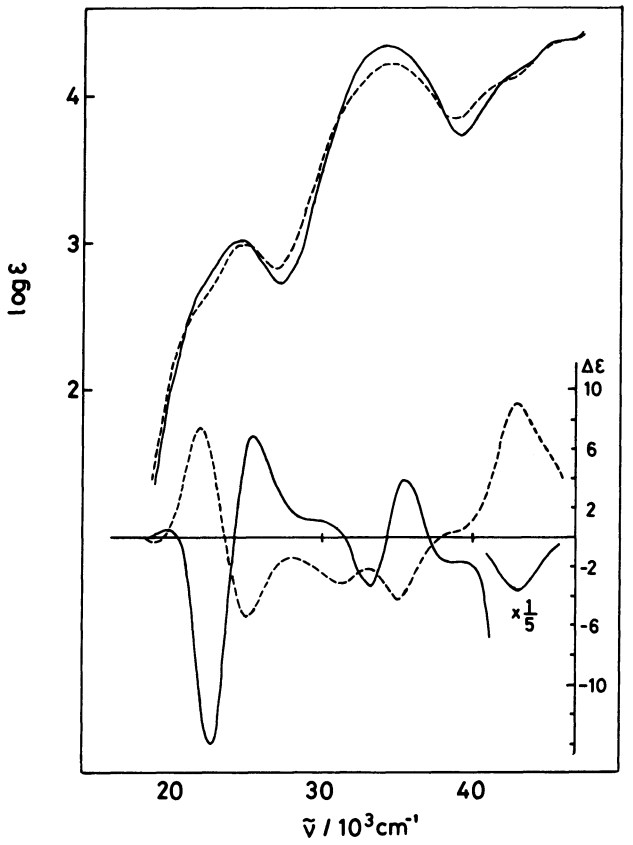


Fig. 6. Absorption and CD spectra of *cisα*-[Co(en)-(*SS*(C)-NPPN)]$^{3+}$; F1 (------), F2 (——).

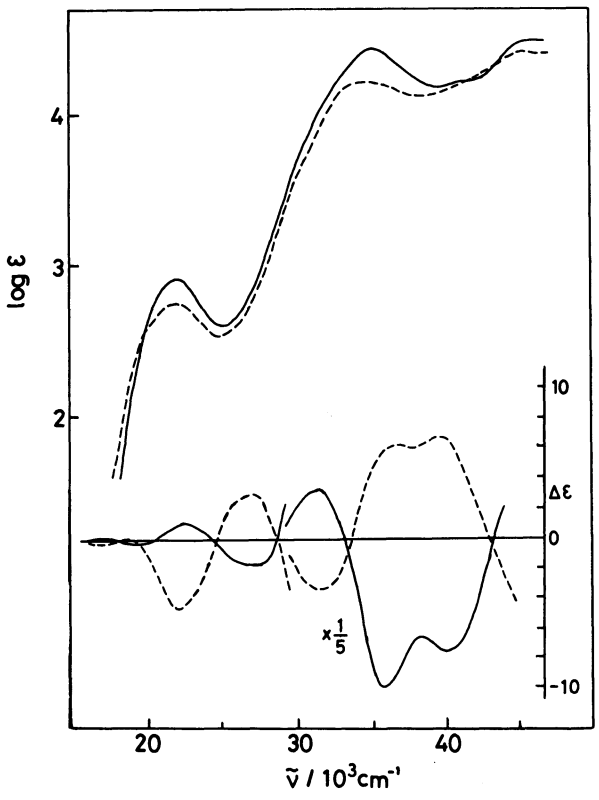
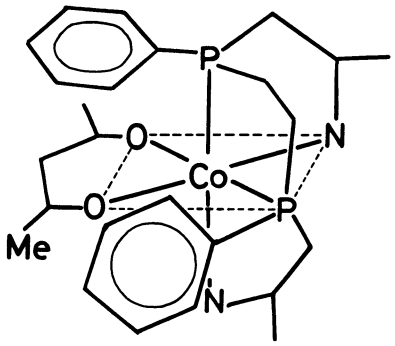


Fig. 7. Absorption and CD spectra of *cisα*-[Co(acac)-(*SS*(*C*)-NPPN)]$^{2+}$; F1 (------), F2 (——).

Table 2. ^{13}C NMR Spectral Data (δ/ppm (J/Hz))

Complexe (Solvent)	acac			en	NPPN or *SS(C)*-NPPN								
	CH_3	CH	CO	N-CH_2	PCH_2-(P)	PCH_2-(N)	NCH_2	N-CH	C-CH_3	P-C_1	*o*-	*m*-	*p*-
[Co(acac)(*rac*-NPPN)]$^{2+}$(D_2O)	28.16 s	98.91 s	191.44 s	—	22.96 d (40)	32.62 d (27)	43.20 s	—	—	124.47 t (48)	132.95 s	130.45 s	134.19 s
[Co(en)(*rac*-NPPN)]$^{3+}$(D_2O)	—	—	—	45.59 s	24.61 t (39)	30.94 t (26)	44.02 s	—	—	126.64 t (45)	131.87 t (11)	131.67 t (10)	135.16 s
[Co(acac)(*SS(C)*-NPPN)]$^{2+}$ F1 (D_2O)	28.27 t (5)	99.42 s	—[a]	—	21.54 t (39)	36.65 t (26)	—	50.49 s	20.81 t (15)	125.15 t (15)	133.10 t (7)	130.42 t (11)	134.12 s
[Co(acac)(*SS(C)*-NPPN)]$^{2+}$ F2 (D_2O)	28.51 s	99.08 s	—[a]	—	23.54 t (40)	39.43 t (24)	—	53.78 s	22.08 t (15)	123.94 q (48)	133.20 t (7)	130.61 t (11)	134.17 s
[Co(acac)(*SS(C)*-NPPN)]$^{2+}$ F3 (D_2O)	26.47 s	99.93 s	189.98 s	—	25.64dd (33.5)	35.02 d (29)	—	50.14 s	23.17 d (13)	121.9 d (49)	131.84 d (7)	130.11 d (11)	132.70 s
	27.27 d (4)		191.05 s		31.4dd (33.8)	38.46 d (26)		54.24 s	23.38 d (16)	124.1 d (46)	133.60 d (9)	130.40 d (11)	133.78 s
[Co(en)(*SS(C)*-NPPN)]$^{3+}$ F1 (CD_3CN)	—	—	—	45.56 s	22.23 t (40)	34.33bs	—	53.53 s	21.59 s	124.42 t (44)	— 131.71 b	—	134.97 s
[Co(en)(*SS(C)*-NPPN)]$^{3+}$ F2 (D_2O)	—	—	—	45.86 s	25.18 t (38)	37.48 t (27)	—	54.30 s	21.82 s	123.59 t (46)	131.87 s	131.53 s	134.94 s

a) Not obsd. Internal reference: dioxane.



Δ-cisß(RS(P))

Fig. 8. A schematic structure of *Δ-cisβ*-[Co(acac)-(*RS(P),SS(C)*-NPPN)]$^{2+}$ (F3).

afford isomers F1 (Δ-*cisα*) and F2 (Λ-*cisα*) of the en complex, respectively (see Experimental). Thus isomer F1 of the acac complex is assigned to *Δ-cisα*-[Co(acac)(*RR(P),SS(C)*-NPPN)]$^{2+}$ and isomer F2 to *Λ-cisα*-[Co(acac)(*SS(P),SS(C)*-NPPN)]$^{2+}$.

Isomer F3 of the acac complex, which was suggested to be the cisβ isomer from the ^{13}C NMR spectrum, does not afford any en complex by reaction with en (see Experimental). The result suggests that isomer F3 is the complex containig *RS(P),SS(C)*-NPPN, since the en complex of *RS(P),SS(C)*-NPPN was not formed by the reaction of *SS(C)*-NPPN with $[Co(en)_3]^{3+}$ as described above. A schematic structure of *cisβ*-[Co(acac)(*RS(P),SS(C)*-NPPN)]$^{2+}$ is given in Fig. 8. The assignment of this structure for isomer F3 is supported by the ^1H NMR spectrum. The isomer shows the methine proton signal of acac at a higher field (δ=5.17) than those of isomers F1 (δ=5.93) and F2 (δ=5.80), and also exhibits one of the two methyl proton signals of acac at a remarkably higher field (1.23 and 2.15 ppm) than those of isomers F1 (δ=2.23) and F2 (δ=2.21). The high field shifts of the methine and methyl proton signals of isomer F3 are attributable to the shielding effect of the phenyl groups approached very closely to those protons, as seen in Fig. 8. Such a high field shift of methyl signal is not expected for *cisβ*-[Co(acac)(*RR(P),SS(C)*- or *SS(P),SS(C)*-NPPN)]$^{2+}$ complex. For *cisβ*-[Co(acac)(*RS(P),SS(C)*-NPPN)]$^{2+}$, the Δ isomer will be much more stable than the Λ isomer, since two methyl groups of *RS(P),SS(C)*-NPPN are equatorial in the former, while axial in the latter (Fig. 8). The CD spectrum of isomer F3 suggests a Δ configuration. The isomer shows a similar CD pattern to that of isomer F1 (Δ-cisα) in the first d–d band region; both isomers give a negative and a positive CD band from the lower energy side in this region (Figs. 7 and 9). Thus isomer F3 can be assigned to *Δ-cisβ*-[Co(acac)

Table 3. Absorption (AB) and CD Spectral Data for *SS(C)*-NPPN Complexes

Complexe	AB ($\bar{\nu}/10^3$ cm^{-1} (log ε))	CD ($\bar{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$))
Δ-cisα-[Co(acac)(*SS(C)*-NPPN)]$^{2+}$	22.0(2.78), 34.5(4.28), 45.5(4.51)	16.8(−0.07), 18.7(+0.03), 22.1(−4.74), 26.9(+3.03), 31.9(−5.05), 37.0(+8.60), 39.9(+9.50)
Λ-cisα-[Co(acac)(*SS(C)*-NPPN)]$^{2+}$	22.0(2.96), 35.0(4.52), 45.5(4.56)	16.8(+0.04), 19.3(−0.13), 23.0(+1.34), 27.5(−1.61), 31.5(+3.40), 36.0(−10.0), 40.4(−7.57)
Δ-cisβ-[Co(acac)(*SS(C)*-NPPN)]$^{2+}$	19.9(2.7),[a] 22.7(3.08), 37.2(4.32)	20.0(−5.90), 24.0(+3.69), 29.3(+13.9), 33.0(−5.40), 36.0(+2.16), 38.2(−6.84), 43.5(+3.68)
Δ-cisα-[Co(en)(*SS(C)*-NPPN)]$^{3+}$	24.6(3.06), 34.5(4.31)	19.0(−0.18), 21.9(+7.53), 25.0(−5.54), 31.5(−4.30), 35.0(−6.04), 43.0(12.7)
Λ-cisα-[Co(en)(*SS(C)*-NPPN)]$^{3+}$	24.5(3.02), 34.5(4.33)	19.8(+0.45), 22.5(−14.0), 25.4(+6.78), 33.2(−3.34), 35.5(+3.97), 43.0(−17.8)

a) Shoulder absorption.

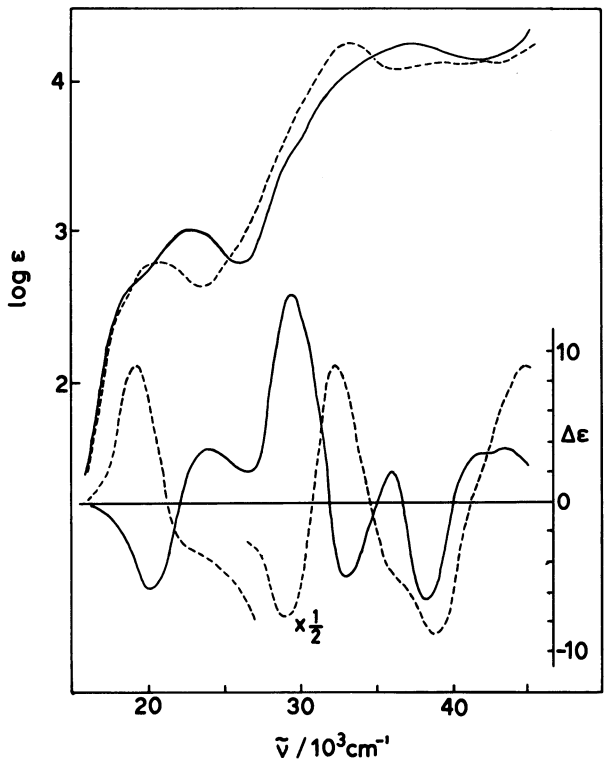


Fig. 9. Absorption and CD spectra of *Δ-cisβ*-[Co(acac)(*RS(P),SS(C)*-NPPN)]$^{2+}$ (F3) (——) and *Λ-cisβ*-[Co(acac){*SR(P),SS(C)*-(CH$_3$)(C$_6$H$_5$)PCH$_2$CH(CH$_3$)NHCH$_2$CH$_2$NHCH(CH$_3$)CH$_2$P(CH$_3$)(C$_6$H$_5$)}]$^{2+}$ (------).[4]

(*RS(P),SS(C)*-NPPN)]$^{2+}$. As stated above, this structure is very crowded and will involve steric interactions between the acac ligand and the phenyl groups of *RS(P),SS(C)*-NPPN. In fact, the isomer in aqueous solution changes slowly from orange to red in color, although the red complex could not be isolated.

The first d–d band of isomer F3 (cisβ) splits into two components (Fig. 9), while those of isomers F1 and F2 (cisα) do not (Fig. 7). If it is assumed that the ligand field strengths of donor atoms are P>N>O, a large band-splitting is expected for the cisβ isomer than for

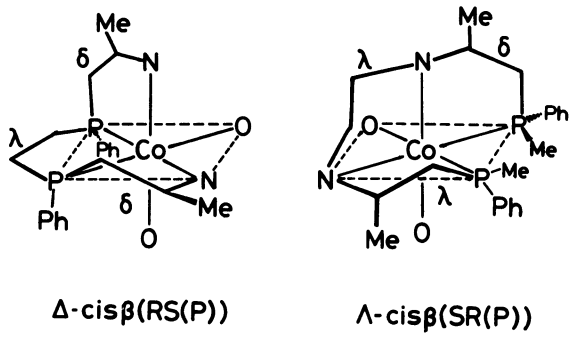


Fig. 10. Molecular models of *Δ-cisβ*-[Co(acac)(*RS(P),SS(C)*-NPPN)]$^{2+}$ (F3) and *Λ-cisβ*-[Co(acac){*SR(P),SS(C)*-(CH$_3$)(C$_6$H$_5$)PCH$_2$CH(CH$_3$)NHCH$_2$CH$_2$NHCH(CH$_3$)CH$_2$P(CH$_3$)(C$_6$H$_5$)}]$^{2+}$.

the cisα isomer from Yamatera's rule.[25] Figure 9 compares the CD spectrum of isomer F3 with that of *Λ-cisβ*-[Co(acac){*RS(P),SS(C)*-(CH$_3$)(C$_6$H$_5$)PCH$_2$CH(CH$_3$)NHCH$_2$CH$_2$NHCH(CH$_3$)CH$_2$P(CH$_3$)(C$_6$H$_5$)}]$^{2+}$,[4] which has a chelate ring between the two N atoms in place of the P–P chelate ring in isomer F3. Both complexes have the same geometrical arrangement for the coordinating donor atoms, cis(P,P)cis(N,N)cis(O,O), but are antipodal to each other with respect to the arrangement of donor atoms and of chelate rings as seen in Fig. 10. These two complexes show CD spectra nearly enantiomeric to each other except those in the higher energy region.

The absorption and CD spectral data of the *SS(C)*-NPPN complexes are listed in Table 3.

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