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Preparation and Stereochemistry of Cobalt(III) Complexes Containing 1,1,11,11-Tetraphenyl-4,8-diaza-1,11-diphosphaundecane or (3*S*,9*S*)-3,9-Dimethyl-1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane, $(C_6H_5)_2PCH_2CHRNHCH_2CH_2CH_2NHCHRCH_2P(C_6H_5)_2$ (R=H or CH_3)

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Two new quadridentate phosphine ligands 1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane (pp-232PNNP) and (3*S*,9*S*)-3,9-dimethyl-1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane (*SS*(*C*)-pp-232PNNP), and several their cobalt(III) complexes were prepared and characterized. The *RS*(*N*) isomers of *trans*-$[CoCl_2$(pp- or *SS*(*C*)-pp-232PNNP)$]^+$ were formed by oxidation of cobalt(II) complexes of these ligands in dichloromethane with chlorine, while the *RR*,*SS*(*N*), and *RR*(*N*) isomers of the pp-232PNNP and *SS*(*C*)-pp-232PNNP complexes, respectively, were derived from the corresponding carbonato complexes and hydrochloric acid. The [Co(O-O)(pp- or SS(C)-pp-232PNNP)$]^{n+}$ (O-O= CO_3^{2-}, $C_2O_4^{2-}$, $C_5H_7O_2^-$) complexes yielded only a cis*β* isomer. The stereochemistry of the complexes was discussed on the basis of the absorption, circular dichroism and NMR spectra.

In our previous papers, we have reported a number of new cobalt(III) complexes containing the following quadridentate aminoalkylphosphine ligands; pp- and mm-222PNNP=$R_2PCH_2CH_2NHCH_2CH_2NHCH_2CH_2PR_2$ (R=C_6H_5 and CH_3),[1] *SS*(*C*)-pp- and SS(C)-mm-222PNNP= (*S*,*S*)-$R_2PCH_2CH(CH_3)NHCH_2CH_2NHCH(CH_3)CH_2PR_2$ (R=C_6H_5 and CH_3),[2] mp- and SS(C)-mp-222PNNP=$(C_6H_5)(CH_3)PCH_2CHRNHCH_2CH_2NHCHRCH_2P(CH_3)(C_6H_5)$ (R=H and CH_3),[3] and 222NPPN and SS(C)-222NPPN=$NH_2CHRCH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CHRNH_2$ (R=H and CH_3).[4] The properties such as stereoselectivity and the relation between circular dichroism spectra and the absolute configuration observed for these complexes have often been found to differ from those reported for complexes containing the corresponding tetramine ligand $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ (trien) and its derivatives.[5] To elucidate properties of cobalt(III)-polydentate phosphine complexes in more detail, further preparative studies will be necessary on related complexes. This paper deals with the preparation and characterization of cobalt(III) complexes formed with two new ligands of the PNNP type, 1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane (pp-232PNNP) and (3*S*, 9*S*)-3,9-dimethyl-1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane (*SS*(*C*)-pp-232PNNP), which form two five-and one six-membered chelate rings upon coordination.

Experimental

Quadridentate phosphine ligands pp-232PNNP and SS(C)-pp-232PNNP 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. 1,9-Dichloro-3,7-diazanonane dihydrochloride,[6] diphenylphosphine [7] and (*S*)-alaninol (2-amino-1-propanol)[8] were prepared according to the literature methods. Absorption, circular dichroism (CD), and ^{1}H and ^{13}C NMR spectra were recorded on Hitachi 323 and U3400 spectrometers, a Jasco J-40CS spectropolarimeter, and Jeol JNM PMX-60 and Hitachi R-90HS spectrometers, respectively.

Preparation of Ligands. 1,1,11,11-Tetraphenyl-4,8-diaza-1,11-diphosphaundecane (pp-232PNNP). To liquid ammonia (150 cm^3) containing metallic sodium (1.7 g, 74 mmol) in a 500 cm^3 round-bottom flask was added dropwise diphenylphosphine (12.1 g, 65 mmol) at −78 °C. After stirring for 20 min, 1,9-dichloro-3,7-diazanonane dihydrochloride (4.0 g, 14.7 mmol) was added in small portions with stirring. After 1 h, liquid ammonia was evaporated. To the residue were added water (50 cm^3) and then diethyl ether (60 cm^3) with stirring. The ethereal layer was separated and dried over $MgSO_4$ (ca. 10 g) overnight. A viscous liquid was obtained by removing the solvent and unreacted diphenylphosphine under vacuum. The oily product (ca. 4 g) thus obtained was used for the preparation of cobalt(III) complexes without further purification.

(2*S*,8*S*)-2,8-Dimethyl-3,7-diaza-1,9-nonanediol Dihydrochloride. To an ethanol solution (130 cm^3) of (*S*)-alaninol (31 g, 0.41 mol) in a 500 cm^3 round-bottom flask was added a solution of 1,3-dibromopropane (21 g, 0.106 mol) in ethanol (10 cm^3) over 30 min at 70 °C with stirring. Stirring was continued for 4 h. The solution was cooled to 0 °C and then was mixed with KOH (11.9 g, 0.212 mol) in ethanol (200 cm^3). After 1 h precipitated KBr was filtered off, and ethanol was removed under reduced pressure. The oily residue was distilled at ca. 130 Pa, giving unreacted (*S*)-alaninol (bp 68 °C, 17.95 g) and the desired material (bp 168 °C). Yield: 8.85 g (49.1 mmol, 46.5%). Since the product was very hygroscopic, it was converted into the dihydrochloride. A methanol solution (150 cm^3) of the product was mixed with concd HCl (15 cm^3) at 0 °C, and then the solvent was removed under reduced pressure. On addition of isopropyl alcohol the oily residue gave white crystals, which were filtered and recrystallized from isopropyl alcohol containing a

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small amount of water. Yield: 7.6 g. Found: C, 40.88; H, 9.09; N, 10.89%. Calcd for $C_9H_{24}N_2Cl_2O_2$: C, 41.07; H, 9.19; N, 10.64%.

(2*S*,8*S*)-2,8-Dimethyl-1,9-dichloro-3,7-diazanonane Dihydrochloride. To a mixture of (2*S*,8*S*)-2,8-dimethyl-3,7-diaza-1,9-nonanediol dihydrochloride (7.6 g, 29 mmol) and chloroform (30 cm^3) was added $SOCl_2$ (22 cm^3) dropwise over 20 min at 0 °C. The mixture was stirred for 30 min at 0 °C, and then refluxed for 2 h at 70 °C. Excess $SOCl_2$ and chloroform were removed by distillation, and the residue was dissolved in hot methanol (50 cm^3). The solution was filtered and the filtrate was cooled in ice to give colorless crystals, which were filtered, washed with diethyl ether, and dried in vacuum. Yield: 1.85 g. An additional amount of products (4.85 g) was obtained from the filtrate by adding excess diethyl ether. Total yield: 6.7 g (77%). Found: C, 36.57; H, 7.22; N, 9.62%. Calcd for $C_9H_{22}N_2Cl_4$: C, 36.02; H, 7.39; N, 9.33%. The compound is very hygroscopic.

(3*S*,9*S*)-3,9-Dimethyl-1,1,11,11-tetraphenyl-4,8-diaza-1,11-diphosphaundecane (*SS*(*C*)-pp-232PNNP). To liquid ammonia (150 cm^3) containing metallic sodium (2.4 g, 104 mmol) in a 500 cm^3 round-bottom flask was added dropwise diphenylphosphine (18 g, 97 mmol), and the mixture was stirred for 1 h at −78 °C. To the resulting orange solution was added (2*S*,8*S*)-2,8-dimethyl-1,9-dichloro-3,7-diazanonane dihydrochloride (6.7 g, 22 mmol) in small portions with stirring. Stirring was continued for 2.5 h. Liquid ammonia was evaporated, and water (33 cm^3) and then diethyl ether (30 cm^3) were added to the residue with stirring. The ethereal layer was separated from the aqueous layer and dried over $MgSO_4$ (ca. 2.0 g) overnight. The solvent and unreacted diphenylphosphine were removed by distillation under vacuum. The oily residue (4.3 g) thus obtained was used for the preparation of cobalt(III) complexes without further purification.

Preparation of Cobalt(III) Complexes.[††] ***RS*(*N*)-*trans*-[CoCl$_2$(pp-232PNNP)]X(Isomer A, X=Cl, ClO$_4$). Method 1.** To $[CoCl(NH_3)_5]Cl_2$ (500 mg, 2.0 mmol) in a mixture of methanol (100 cm^3) and water (100 cm^3) was added pp-232PNNP (1.0 g, 2.0 mmol) in methanol (10 cm^3) with stirring. After 30 min concd HCl (2 cm^3) was added to the mixture, and stirring was continued overnight. The resulting green solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The green residue was dissolved in water (300 cm^3), the solution was shaken with diethyl ether (300 cm^3), and the aqueous layer was separated and evaporated to dryness under reduced pressure. From the residue the green complex was extracted with a small amount of methanol, and the extract was evaporated again to dryness under reduced pressure to give the complex. Yield: 680 mg (51%). Found: C, 56.06; H, 5.94; N, 3.93%. Calcd for $C_{31}H_{36}N_2Cl_3P_2Co$: C, 56.09; H, 5.47; N, 4.22%. The complex is soluble in water, methanol, ethanol, acetone and dichloromethane, but insoluble in diethyl ether and benzene.

Method 2. To a methanol solution (10 cm^3) of $Co(ClO_4)_2\cdot 6H_2O$ (470 mg, 1.28 mmol) was added pp-232PNNP (636 mg, 1.28 mmol) in methanol (10 cm^3). After a while the resulting orange-brown solution was evaporated to dryness under reduced pressure, and the residue was dissolved in dichloromethane (50 cm^3). Chlorine gas was bubbled into the solution for 10 min, and then excess chlorine was removed by bubbling nitrogen for 20 min. The solution was filtered, mixed with methanol (30 cm^3), evaporated to a small volume (ca. 20 cm^3) under reduced pressure, then mixed with $NaClO_4\cdot H_2O$ (7.0 g), and concentrated again to ca. 10 cm^3 under reduced pressure. (The solution should not be evaporated to dryness.) On addition of water (10 cm^3) the solution gave a green precipitate, which was filtered, washed with water and air dried. Yield: 676 mg (72.5%). Absorption and NMR spectra of this [CoCl$_2$(pp-232PNNP)]ClO$_4$ complex coincide with those of the above chloride salt. The solubility of the complex is similar to that of the chloride salt except insoluble property in water.

***RR*,*SS*(*N*)-*trans*-[CoCl$_2$(pp-232PNNP)]Cl (Isomer B).** A solution of [Co(C_2O_4 or CO_3)(pp-232PNNP)]X (X=PF_6, $B(C_6H_5)_4$) (0.13 mmol) (see below) in a mixture of methanol (25 cm^3), water (25 cm^3) and concd HCl (5 cm^3) was warmed at 40 °C for 15 min. The resulting green solution was diluted with a mixture of methanol (500 cm^3) and water (500 cm^3), and applied on a column (ϕ 3 cm×10 cm) of SP-Sephadex C-25. The column was washed with water, and the adsorbed product was eluted with 1 mol dm^{-3} HCl in a mixture of methanol and water (1 : 1). The green eluate was evaporated to dryness under reduced pressure to give the complex, which was collected, washed with a small amount of water and then diethyl ether. Yield: 82 mg (97%). Found: C, 56.04; H, 5.75; N, 4.20%. Calcd for $C_{31}H_{36}N_2Cl_3P_2Co$: C, 56.09; H, 5.47; N, 4.22%. The solubility of the complex is similar to that of the corresponding RS(N) isomer.

***cis*β-[Co(C$_2$O$_4$)(pp-232PNNP)]PF$_6$.** To $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ (500 mg, 1.0 mmol) in a mixture of water (50 cm^3) and methanol (5 cm^3) was added pp-232PNNP (500 mg, 1 mmol) in methanol (2 cm^3), and the mixture was stirred overnight. The resulting red solution was evaporated under reduced pressure to remove methanol, and then shaken with diethyl ether (100 cm^3). The separated aqueous layer was diluted with water (1 dm^3) and applied on a column (ϕ 3cm×30 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.05 mol dm^{-3} NaCl, and the eluate of the main red band was concentrated to 20 cm^3 and filtered. The filtrate was mixed with NH_4PF_6 (200 mg) in water (5 cm^3), yielding a red precipitate, which was filtered, washed with a small amount of cold water, and air dried. Yield: 410 mg (52%). Found: C, 50.07; H, 4.74; N, 3.61%. Calcd for $C_{33}H_{36}N_2O_4F_6P_3Co$: C, 50.14; H, 4.59; N, 3.54%. The complex is soluble in methanol, ethanol, acetone, dichloromethane, and acetonitrile, slightly soluble in water, but insoluble in diethyl ether.

***cis*β-[Co(CO$_3$)(pp-232PNNP)]B(C$_6$H$_5$)$_4$.** To $K[Co(CO_3)_2(C_5H_5N)_2]$[9] (400 mg, 1.0 mmol) in methanol (50 cm^3) was added pp-232PNNP (500 mg, 1.0 mmol) in methanol (5 cm^3), and the mixture was stirred for 6 h. The resulting red solution was diluted with water (1.5 dm^3), filtered, and the filtrate was applied on a column (ϕ 3 cm×30 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.1 mol dm^{-3} NaCl, and the eluate of the main red band was concentrated to ca. 20 cm^3 under reduced pressure. The concentrate was filtered, and the filtrate was mixed with $NaB(C_6H_5)_4$ (350 mg) in water (5 cm^3), yielding a red precipitate, which was filtered, washed with water, and air dried. Yield: 470 mg (50%). Found: C, 71.84; H, 6.25; N, 2.55%. Calcd for $C_{56}H_{56}N_2O_3BP_2Co$: C, 71.80; H, 6.03; N, 2.99%. The complex is soluble in acetone and acetonitrile, slightly soluble in methanol and dichloromethane, but insoluble in water.

[††] Caution; All of the perchlorate salts of cobalt(III)-phosphine complexes are potentially explosive, and should be handled carefully.

***cis*β-[Co(acac)(pp-232PNNP)](ClO_4)$_2$·4.5H_2O (acac=Acetylacetonate Ion).** An ethanol solution (60 cm^3) containing *RS(N)*- or *RR,SS(N)-trans*-[$CoCl_2$(pp-232PNNP)]X (X=Cl, ClO_4) (0.28 mmol) and Li(acac) (35 mg, 0.33 mmol) was warmed at 30 °C for 1 h. The resulting red solution was diluted with water (300 cm^3) and applied on a column (ϕ 2 cm×40 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, the eluate of the main red band was collected , evaporated to dryness under reduced pressure, mixed with ethanol (50 cm^3), and the mixture was filtered. The filtrate was again evaporated to dryness under reduced pressure, and the residue was dissolved in water (50 cm^3). On addition of $NaClO_4 \cdot H_2O$ (0.5 g) in water (5 cm^3) the solution gave a red precipitate, which was filtered, washed with cold water then a small amount of ethanol, and air dried. Yield: 55 mg (23%). Found: C, 49.52; H, 5.78; N, 3.28%. Calcd for $C_{36}H_{52}N_2Cl_2O_{10.5}P_2Co$: C, 49.55; H, 6.01; N, 3.21%. The complex is soluble in methanol, ethanol and dichloromethane, slightly soluble in water, but insoluble in diethyl ether and benzene.

The hexafluorophosphate *cis*β-[Co(acac)(pp-232PNNP)](PF_6)$_2$ was obtained by addition of NH_4PF_6 instead of $NaClO_4 \cdot H_2O$. Found: C, 45.77; H, 4.63; N, 2.97%. Calcd for $C_{36}H_{43}N_2O_2F_{12}P_4Co$: C, 45.68; H, 4.58; N, 2.96%. The solubility of this complex is similar to that of the perchlorate.

***RS(N)-trans*-[$CoCl_2$(SS(C)-pp-232PNNP)]ClO_4·1.5H_2O (Isomer C).** This complex was prepared from Co(ClO_4)$_2$·6H_2O (410 mg, 1.12 mmol) and *SS*(*C*)-pp-232PNNP (590 mg, 1.12 mmol) by a method similar to Method 2 for the corresponding pp-232PNNP complex. Yield: 250 mg (29%). Found: C, 50.47; H, 5.16; N, 3.45%. Calcd for $C_{33}H_{43}N_2O_{5.5}P_2Co$: C, 50.62; H, 5.54; N, 3.58%. The solubility of the complex is similar to that of the corresponding pp-232PNNP complex.

***RR(N)-trans*-[$CoCl_2$(SS(C)-pp-232PNNP)]ClO_4·1.5H_2O (Isomer D).** A solution of *Λ-cis*β-[Co(CO_3)(SS(C)-pp-232PNNP)]ClO_4·0.5($NaClO_4$) (50 mg, 0.062 mmol) (see below) in a mixture of methanol (20 cm^3) and concd HCl (2.5 cm^3) was warmed at 50 °C for 5 min to give a green solution. On addition of $NaClO_4 \cdot H_2O$ (5g) in water (20 cm^3) the solution gave a green precipitate, which was filtered, washed with cold water, and air dried. Yield: 44 mg (91%). Found: C, 50.74; H, 5.26; N, 3.69%. Calcd for $C_{33}H_{43}N_2Cl_3O_{5.5}P_2Co$: C, 50.62; H, 5.54; N, 3.58%. The solubility of the complex is similar to that for the corresponding *RS*(*N*) isomer.

***Λ-cis*β-[Co(CO_3)(SS(C)-pp-232PNNP)]ClO_4·0.5($NaClO_4$).** A mixture of *RS*(*N*)-*trans*-[$CoCl_2$(*SS*(*C*)-pp-232PNNP)]ClO_4·1.5H_2O (200 mg, 0.26 mmol), (NH_4)$_2CO_3$ (133 mg, 1.4 mmol) and active charcoal (ca. 50 mg) in methanol (40 cm^3) was stirred for 2 h at room temperature. Active charcoal was filtered off, the filtrate was diluted with water (1 dm^3) and applied on a column (ϕ 2.5 cm×100 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} NaCl the eluate of the main red band was collected and concentrated to ca. 40 cm^3 under reduced pressure. The concentrate was filtered, and the filtrate was mixed with $NaClO_4 \cdot H_2O$ (3.0 g) to yield a pink precipitate, which was filtered, washed with cold water, and air dried. Yield: 55 mg (27%). Found: C, 51.00; H, 5.14; N, 3.68%. Calcd for $C_{34}H_{40}N_2Cl_{1.5}O_9P_2Na_{0.5}Co$: C, 50.65; H, 5.00; N, 3.47%. The complex is soluble in water, methanol, ethanol and acetone, but insoluble in diethyl ether and benzene. The complex can also be prepared from K[Co(CO_3)$_2$(C_5H_5N)$_2$] and the ligand by a method similar to that for the corresponding pp-232PNNP complex.

***Λ-cis*β-[Co(acac)(SS(C)-pp-232PNNP)](PF_6)$_2$·2($NaPF_6$)·2H_2O.** A methanol solution (50 cm^3) containing *RS*(*N*)-trans-[$CoCl_2$(*SS*(*C*)-pp-232PNNP)]ClO_4·1.5H_2O (200 mg, 0.26 mmol) and Li(acac) (30 mg, 0.28 mmol) was stirred for 1 h at room temperature. The resulting red solution was diluted with water (1 dm^3) and applied on a column (ϕ 2.5 cm×100 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.4 mol dm^{-3} NaCl, the main red eluate was collected, concentrated to nearly dryness under reduced pressure, and the residue was mixed with methanol (ca. 100 cm^3) to extract the complex. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in a small amount of water. On addition of NH_4PF_6 (ca. 100 mg) the solution gave a red precipitate, which was filtered, washed with a small amount of cold water and air dried. Yield: 174 mg (50.6%). Found: C, 33.85; H, 3.53; N, 2.20%. Calcd for $C_{38}H_{51}N_2F_{24}O_4P_6Na_2Co$: C, 33.89; H, 3.52; N, 2.08%. The complex is soluble in water, methanol, ethanol, acetone and dichloromethane, but insoluble in diethyl ether and benzene.

Results and Discussion

Preparation of Ligands. The quadridentate ligands pp-232PNNP and *SS*(*C*)-pp-232PNNP were prepared by methods similar to those for pp-222PNNP[1] and *SS*(*C*)-pp-222PNNP,[2] respectively. The yields of these ligands seem to depend largely on the purity of reactants and the presence of moisture.[1] The lower yield of *SS*(*C*)-pp-232PNNP may be attributable to moisture contained in the very hygroscopic starting material

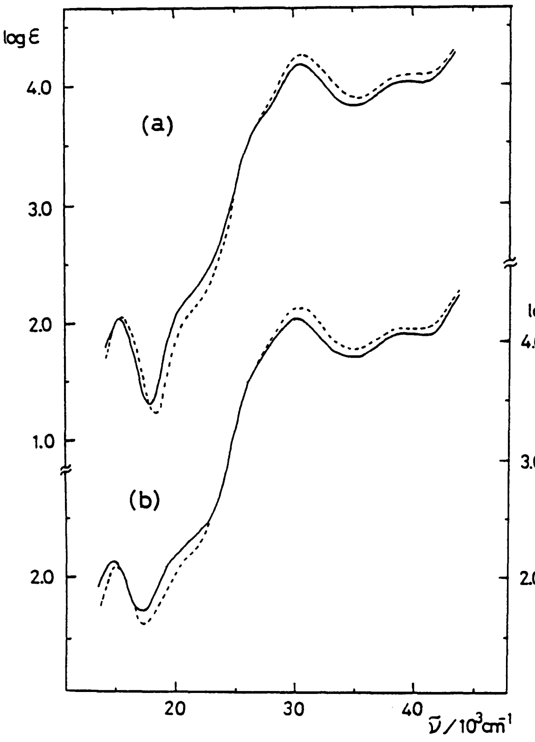


Fig. 1. Absorption spectra, (a) *RS(N)* (——) and *RR,SS(N)* (------) isomers of *trans*-[$CoCl_2$(pp-232PNNP)]$^+$, (b) *RS(N)* (——) and *RR(N)* (------) isomers of *trans*-[$CoCl_2$(SS(C)-pp-232PNNP)]$^+$.

Table 1. Absorption and CD Spectral Data for pp-232PNNP or SS(C)-pp-232PNNP Complexes (Solvent: CH_3OH)

Complex	AB $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
RS(N)-trans-$[CoCl_2(\text{pp-232PNNP})]^+$	15.4(2.05), 21(2.2)*, 26(3.5) 30.7(4.25), 39.5(4.08)	
RR,SS(N)-trans-$[CoCl_2(\text{pp-232PNNP})]^+$	15.6(2.06), 21(2.0)*, 26.8(3.6)*, 30.8(4.28)	
cis β-$[Co(C_2O_4)(\text{pp-232PNNP})]^+$	19.50(2.60), 24.6(2.8)*, 31.6(4.36)	
cis β-$[Co(acac)(\text{pp-232PNNP})]^{2+}$	19.23(2.78), 24(3.0)*, 28(4.1)*, 31.44(4.38)	
RS(N)-trans-$[CoCl_2(\text{SS(C)-pp-232PNNP})]^+$	15.5(2.16), 20.5(2.2)*, 27(3.8)*, 30.5(4.21), 39.5(4.07)	15.0(+1.69), 16.5(−0.78), 20.6(−2.41), 26.3(−1.01), 28.6(−2.15), 31.0(+6.60), 33.8(−7.60), 39.3(−10.4), 42.3(+1.0), 44.3(−4.4)
RR(N)-trans-$[CoCl_2(\text{SS(C)-pp-232PNNP})]^+$	15.5(2.11), 21(2.1)*, 23(3.6)*, 30.5(4.29), 39.5(4.13)	16.0(+1.00), 20.8(−2.32), 26.3(−2.09), 31.0(+12.8), 34.0(−8.85), 39.5(−11.4)
Λ-cis β-$[Co(CO_3)(\text{SS(C)-pp-232PNNP})]^+$	19.5(2.55), 24.5(2.5)*, 31.5(4.20)	18.3(+3.28), 20.8(−2.98), 26.3(−0.39), 30.5(−2.28), 33.3(+2.56), 40.0(−7.31), 44.5(+14.6)
Λ-cis β-$[Co(acac)(\text{SS(C)-pp-232PNNP})]^{2+}$	19.5(2.75), 27.5(3.9)*, 31.4(4.33)	18.0(+5.59), 21.0(−4.18), 27.8(−10.5), 31.0(+31.9), 35.0(−8.84), 38.5(−19.1), 45.0(+27.8)

*: Shoulder absorption.

(2*S*,8*S*)-2,8-dimethyl-1,9-dichloro-3,7-diazanonane dihydrochloride. The ligands could not be purified by distillation because of their high boiling points.

***trans*-Dichloro Complexes.** For each quadridentate ligand, two kinds of green $[CoCl_2(L)]^+$ (L= pp-232PNNP or SS(C)-pp-232PNNP) were obtained by different preparative methods; one is oxidation of the Co(II)-L complex in CH_2Cl_2 with chlorine, and the other is reaction of $[Co(CO_3$ or $C_2O_4)L]^+$ with hydrochloric acid. Each method yielded only one kind of green complex. Absorption spectra of these complexes shown in Fig. 1 are very similar to that of *trans(Cl,Cl),cis(P,P)*-$[CoCl_2(edpp)_2]^+$ (edpp=$NH_2CH_2CH_2P(C_6H_5)_2$) whose structure has been determined by X-ray analysis.[10,11] Thus the two complexes of each pp-232PNNP and *SS*(*C*)-pp-232PNNP can be assigned to isomers of the *trans(Cl,Cl)* complex. Table 1 lists the data of absorption and CD spectra. For *trans*-$[CoCl_2(\text{pp-232PNNP})]^+$, a small difference in absorption spectra is observed between one isomer (A) obtained from oxidation with chlorine and the other isomer (B) derived from the CO_3^{2-} or $C_2O_4^{2-}$ complex. The ^{13}C NMR spectra show a more clear difference for these two isomers. Isomer A in CD_3CN shows signals at δ 28.5 ($-CH_2-\underline{C}H_2-CH_2-$), δ 30.7 ($P-CH_2-$: triplet), and δ 49.6 and 52.4 ($-\underline{C}H_2-NH-\underline{C}H_2-$), while isomer B in the same solvent gives the corresponding signals at δ 23.8, 28.3, and 45.5 and 51.5. The chemical shifts of signals due to the phenyl groups are also different between the isomers. In *trans*-$[CoCl_2(\text{pp-232PNNP})]^+$ there are three possible isomers arising from the absolute configuration of the nitrogen atoms, the *RS*(*N*), *RR*(*N*) and *SS*(*N*) isomers, the latter two being a pair of enantiomers (Fig. 2). Thus two isomers A and B will be the *RS*(*N*) and *RR*,*SS*(*N*) isomers, although the assignment for the isomers can not be made from the absorption and NMR spectra. However, it is assumed that isomer B which was prepared from *cis*β-$[Co(CO_3$ or $C_2O_4)L]^+$ (see below) and hydrochloric acid is the *RR*,*SS*(*N*)isomer, since molecular models suggest that the cisβ complex is more stable in the *RR*,*SS*(*N*) isomer than the *RS*(*N*) one, and the configuration of the nitrogen atom will be retained in strongly acidic solution. Thus the other isomer A can be assigned to the *RS*(*N*) isomer. The *trans*-$[CoCl_2(232tet)]^+$ complex (232tet=3,7-diazanonane-1,9-diamine) which has the same skeletal structure as the pp-232PNNP complex yields the same *RR*,*SS*(*N*) and *RS*(*N*) isomers, and the former is obtained from *cis*β-$[Co(CO_3)(232tet)]^+$.[12] All *cis*-$[CoX_2(232tet)]^{n+}$ complexes so far known have a *RR*,*SS*(*N*) structure, no *RS*(*N*)-*cis*β and *cis*α isomers being reported. The pp-232PNNP complex seems to show the same stereoselectivity as the 232tet complex.

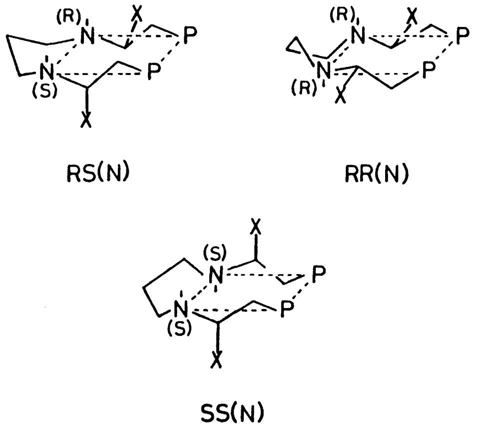


Fig. 2. Three possible isomers for *trans*-$[CoCl_2(\text{pp-232PNNP})]^+$ (X=H) and *trans*-$[CoCl_2(\text{SS(C)-pp-232PNNP})]^+$ ($X=CH_3$).

Possible isomers of *trans*-$[CoCl_2(SS(C)$-pp-

232PNNP)]$^+$ are three diastereomers with the *RS*(*N*), *RR*(*N*), and *SS*(*N*) configurations (Fig. 2). The *RR*(*N*) and *SS*(*N*) isomers have a C_2 axis, while the *RS*(*N*) isomer belongs to C_1 symmetry. Isomer C prepared by oxidation with chlorine shows two kinds of the methyl signal at δ 1.47 and 1.83 in the ^{1}H NMR spectrum in $CDCl_3$. On the other hand, the other isomer D derived from *cisβ*-[Co(CO_3)(*SS*(*C*)-pp-232PNNP)]$^+$ exhibits only one methyl signal at δ 1.83. Thus isomer C can be assigned to the *RS*(*N*) isomer, and isomer D to either *RR*(*N*) or *SS*(*N*) isomer. In the *RS*(*N*) isomer one of the two methyl groups is equatorial to the chelate ring, while the other is axial (Fig. 2). The axial methyl group comes fairly close to the phenyl ring and will receive its shielding effect. The methyl signal at the high field (δ 1.47) can be assigned to this axial methyl group, and the signal at δ 1.83 to the equatorial methyl group. Isomer D which shows the methyl signal at δ 1.83 should be the *RR*(*N*) isomer in which two methyl groups have an equatorial disposition. The *SS*(*N*) isomer has two axial methyl groups and will be less stable than the *RR*(*N*) isomer.[13] The assinment of *RR*(*N*) for isomer D indicates that its starting [Co(CO_3)(*SS*(*C*)-pp-232PNNP)]$^+$ complex has a *Λ-cisβ-RR*(*N*) configuration. As shown later this carbonate complex exhibits CD spectrum typical of a *Λ* configuration. Similar *RR*(*N*) and *RS*(*N*) isomers have been obtained for a structurally related tetramine complex *trans*-[$CoCl_2$((2*S*,10*S*)-Me_2-232tet)]$^+$ ((2*S*,10*S*)-Me_2-232tet= (2*S*,10*S*)-4,8-diazaundecane-2,10-diamine).[14]

As described before, the two isomers (A and B, or C and D) of each pp-232PNNP or *SS*(*C*)-pp-232PNNP dichloro complex show a small difference in absorption spectra, but the differences between the isomers are very similar for both pp-232PNNP and *SS*(*C*)-pp-232PNNP complexes as seen in Fig. 1. This result supports the assignments of *RR,SS*(*N*) and *RS*(*N*) configurations for two pp-232PNNP complexes based on only stereochemical consideration.

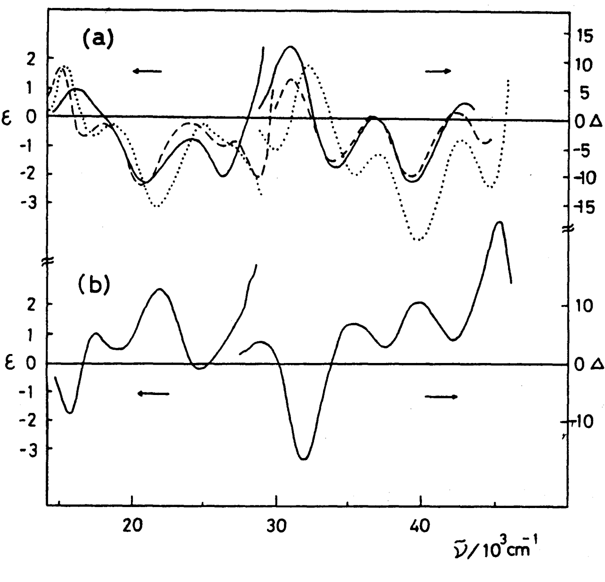
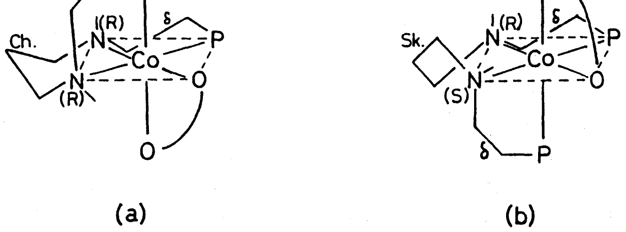


Fig. 3. CD spectra, (a) *RS(N)* (----) and *RR(N)* (——) isomers of *trans*-[$CoCl_2$(SS(C)-pp-232PNNP)]$^+$, and *trans*-[$CoCl_2$(S-pdpp)$_2$]$^+$ (······), (b) *RR(N)-trans*-[$CoCl_2$(SS(C)-pp-222PNNP)]$^+$.

Figure 3(a) shows CD spectra of *RR*(*N*) and *RS*(*N*) isomers of *trans*-[$CoCl_2$(*SS*(*C*)-pp-232PNNP)]$^+$. The spectra are rather similar except the region around 15000 cm^{-1} (the I_a absorption band region). The chiral sources of the isomers indicated by molecular models are as follows; the *RR*(*N*) isomer has two (*R*)-nitrogen and two (*S*)-carbon atoms, and δ-gauche, λ-skew and δ-gauche conformations for the five-, six-, and five-membered chelate rings, respectively, while the *RS*(*N*) isomer has one (*R*)- and one (*S*)-nitrogen and two (*S*)-carbon atoms, and δ-gauche, chair and λ-gauche conformations. The chiral sources are thus different between the isomers, but their CD spectra are similar and quite resemble that of *trans*(*Cl,Cl*)*cis*(*P,P*)-[$CoCl_2$-(S-pdpp)$_2$]$^+$ (*S*-pdpp=(*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$) shown in Fig. 3(a) whose chiral sources are two (*S*)-carbon and two δ-gauche chelate rings.[11] On the other hand, the CD spectrum of a related complex *RR*(*N*)-*trans*-[$CoCl_2$(*SS*(*C*)-pp-222PNNP)]$^+$ [2] is nearly enantiomeric to those of the present isomers as shown in Fig. 3(b), although the chiral sources of this complex (two(*R*)-nitrogen and two (*S*)-carbon atoms, and δ-, λ- and δ-gauche conformations) are similar to those of the *RR*(*N*) isomer of the *SS*(*C*)-pp-232PNNP complex. No reasonable explanation can be given for these CD spectra at present. The complexes of the *trans*(*Cl,Cl*)-type have no chirality in the arrangement (*Δ,Λ*) of chelate rings around the metal ion, and their CD will be induced by a chiral field produced by chiral atoms and/or chiral conformations of ligands (vicinal effect). Little CD work has been reported for the vicinal effect of polydentate ligands.

O-O Chelate Complexes. All the complexes of [Co(O-O)(pp- or *SS*(*C*)-pp-232PNP)]$^{n+}$ were assigned to the cisβ isomer from the ^{1}H NMR spectra. For example, [Co(acac)(pp-232PNNP)]$^{2+}$ shows two kinds of methyl signals of acac at δ 1.84 and 2.29 in D_2O, indicating the cisβ structure (C_1 symmetry). Each of [Co(CO_3 or acac)(*SS*(*C*)-pp-232PNNP)]$^{n+}$ yielded only one optical isomer stereoselectively. These isomers



(a) (b)

Fig. 4. Two possible isomers, (a) *Λ-RR(N)* and (b) *Δ-RS(N)*, for *cisβ*-[Co(CO_3 or acac)(SS(C)-pp-232PNNP)]$^{n+}$

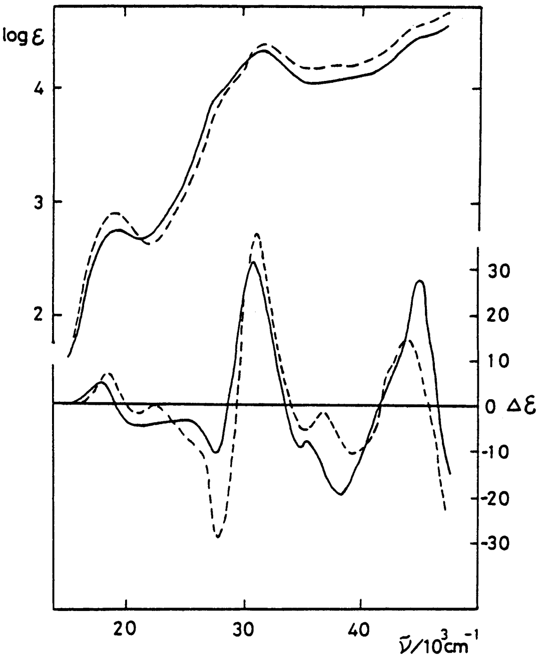


Fig. 5. Absorption and CD spectra of $(+)_{589}$-*Λ-cisβ*-[Co(acac)(SS(C)-pp-232PNNP)]$^{2+}$ (——) and $(+)_{589}$-*Λ-cisβ*-[Co(acac)(SS(C)-pp-222PNNP)]$^{2+}$ (------).

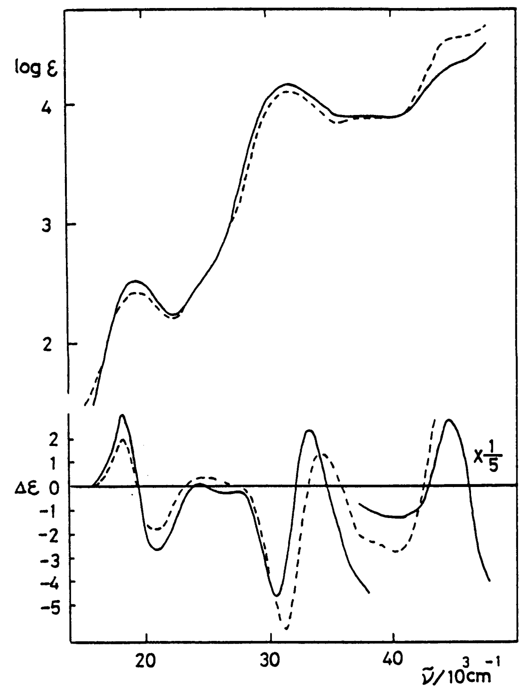


Fig. 6. Absorption and CD spectra of $(+)_{589}$-*Λ-cisβ*-[Co(CO$_3$)(SS(C)-pp-232PNNP)]$^{+}$ (——) and $(+)_{589}$-*Λ-cisβ*-[Co(CO$_3$)(SS(C)-pp-222PNNP)]$^{+}$ (------).

give two doublet methyl signals of the phosphine ligand at δ 1.67 ($^4J_{PH}$= 5 Hz) and at a fairly high field δ 0.85 ($^4J_{PH}$= 5 Hz).

Figure 4 shows structures of two probable cisβ isomers in which both methyl groups of the phosphine ligand have an equatorial disposition. The other two cisβ isomers will be unstable because of two axial methyl groups. Of the two probable isomers, the *Λ-cisβ-RR*(*N*) one has one methyl group disposed very close to one phenyl ring on the phosphorus atom. The signal at δ 0.85 can be assigned to the methyl group shielded by the phenyl group, and both carbonato and acac complexes can be assigned to the *Λ-cisβ-RR*(*N*) isomer. The *Λ* configuration of the isomers is confirmed by the CD spectra. Figures 5 and 6 compare CD spectra of the acac and carbonato complexes, respectively with those of the corresponding *Λ-cisβ-RR*(*N*) isomers of the *SS*(*C*)-pp-222PNNP complexes.[2] The absolute configurations of the latter complexes have been assigned from a comparison of CD spectra with that of *Λ-cisβ-RR*(*N*)-[Co(acac)(SS(C)-Me$_2$-mm-222PNNP)]$^{2+}$ (*SS*(*C*)-Me$_2$-mm-222PNNP=(4*S*,9*S*)-2,4,9,11-tetramethyl-5,8-diaza-2,11-diphosphadodecane) whose absolute configuration has been determined by the X-ray method.[2] In contrast to CD spectra of the *trans(Cl,Cl)*-type complexes, the *SS(C)*-pp-232PNNP and *SS*(*C*)-pp-222PNNP complexes show CD spectra very similar to each other over the whole region and give CD patterns characteristic of a *Λ* configuration in the first absorption band region. From *Λ-cisβ-RR*(*N*)-[Co(CO$_3$)(*SS*(*C*)-pp-232PNNP)]$^+$ the *RR*(*N*)-*trans*-(*Cl,Cl*) complex was derived by reaction with hydrochloric acid. The [Co(CO$_3$)(pp-232PNNP)]$^+$ complex should also have the *cisβ-RR,SS(N)* structure, since it affords the *RR,SS(N)-trans(Cl,Cl)* complex by the same reaction. Thus cis-complexes containing the pp-232PNNP-type ligand yield selectively the cisβ-isomer with (*R,R*)- or (*S,S*)-nitrogen atoms and the six-membered chelate ring of a chair conformation. The same selectivity has been observed for the corresponding 232-tetramine complexes.[14]

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