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Preparation and Stereochemistry of Cobalt(III) Complexes Containing 1,1,10,10-Tetraphenyl-4,7-diaza-1,10-diphosphadecane or 2,11-Dimethyl-5,8-diaza-2,11-diphosphadodecane, $R_2PCH_2CH_2NHCH_2CH_2NHCH_2CH_2PR_2$ ($R=C_6H_5$ or CH_3)

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New quadridentate phosphine ligands, 1,1,10,10-tetraphenyl-4,7-diaza-1,10-diphosphadecane (pp-PNNP) and 2,11-dimethyl-5,8-diaza-2,11-diphosphadodecane (mm-PNNP), were prepared from $(ClCH_2CH_2NHCH_2\text{-})_2\cdot 2HCl$ and $NaPR_2$ ($R=C_6H_5$, CH_3) and purified through their Ni(II) complexes. Seven new cobalt(III) complexes containing the phosphine ligand were prepared: $[CoX_2(\text{pp- or mm-PNNP})]^{n+}$($X_2$=(Cl)$_2$, (NCS)$_2$, $C_5H_7O_2^-$(2,4-pentanedionate ion), and CO_3^{2-}). Four complexes of $[CoX_2(\text{pp- or mm-PNNP})]^+$ (X=Cl, NCS) afforded only a trans(X,X) isomer, and $[Co(acac)(\text{pp- or mm-PNNP})]^{2+}$ and $[Co(CO_3)(\text{pp-PNNP})]^+$ complexes yielded a cisβ isomer. The geometrical structures were assigned on the basis of the NMR and visible-ultraviolet absorption spectra.

As an extension of the studies on cobalt(III)-phosphine complexes, we have prepared quadridentate phosphine ligands, $R_2PCH_2CH_2NHCH_2CH_2NHCH_2CH_2PR_2$ ($R=C_6H_5$ or CH_3) which have a set of PNNP donor atoms, and their cobalt(III) complexes. The skeleton of the ligand is an intermediate one of $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ (trien) and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (tetraphos). The $[CoCl_2(\text{trien})]^+$ complex forms all possible geometrical isomers, trans, cisα, and cisβ,[1] while the $[CoX_2(\text{tetraphos})]^+$ (X=Cl, Br) complexes[2] yield only the cisβ isomer. It is of interest to examine the stereoselectivity for complexes containing the above intermediate ligand. An analogous ligand, $(C_6H_5)_2PCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2P(C_6H_5)_2$, and its cobalt(II) and nickel(II) complexes have been prepared by Sacconi and Dei,[3] but there has been no report on the cobalt(III) complexes containing such a quadridentate PNNP-type ligand.

The following abbreviations are used for the ligands: $(C_6H_5)_2PCH_2CH_2NHCH_2CH_2NHCH_2CH_2P(C_6H_5)_2$=pp-PNNP and $(CH_3)_2PCH_2CH_2NHCH_2CH_2NHCH_2CH_2P(CH_3)_2$=mm-PNNP.

Experimental

The phosphine ligands were prepared and handled under an atmosphere of nitrogen until they formed cobalt(III) complexes. All solvents used for the preparation were deoxygenated by bubbling nitrogen for 20 min immediately before use. Tetramethyldiphosphine,[4] diphenylphosphine,[5] and $(ClCH_2CH_2NHCH_2\text{-})_2\cdot 2HCl$[6] were prepared according to the literature methods. Absorption and ^{13}C NMR specta were recorded on a Hitachi 323 spectrophotometer and a Jeol JNM-GX 400 spectrometer, respectively.

Preparation of Ligands. *1,1,10,10-Tetraphenyl-4,7-diaza-1,10-diphosphadecane (pp-PNNP).* To liquid ammonia (300 cm^3) containing metallic sodium (1.84 g, 80 mmol) in a 500 cm^3 three-necked round bottom flask with a mechanical stirrer and an ammonia gas inlet was added dropwise diphenylphosphine (14.89 g, 80 mmol) over 5 min with stirring at −78 °C. On stirring for 1 h the color of the solution changed from deep blue to orange. To the orange solution was added $(ClCH_2CH_2NHCH_2\text{-})_2\cdot 2HCl$ (5.16 g, 20 mmol) in small portions with stirring. Stirring was continued for 1 h, giving a colorless solution. After liquid ammonia had been evaporated, water (50 cm^3) and then diethyl ether (100 cm^3) were added to the residue with stirring. The ethereal layer separated from the aqueous layer was dried over $MgSO_4$ (*ca.* 5 g) overnight. A viscous liquid (8.5 g) was obtained by removing the solvent and unreacted diphenylphosphine by vacuum distillation. The liquid was mixed with a methanol solution (*ca.* 40 cm^3) of $Ni(ClO_4)_2\cdot 6H_2O$ (10 g, 27 mmol) with stirring, affording immediately a yellow precipitate. It was filtered and dissolved in hot methanol (600 cm^3), and then the solution was filtered. The filtrate was stored in a refrigerator overnight to yield yellow crystals, which were filtered, washed with water and then diethyl ether, and air-dried. Yield: 7.35 g. The filtrate was concentrated to 150 cm^3 and stored in a refrigerator to give additional crystals (0.8 g). Total yield: 8.15 g. Found: C, 47.78; H, 4.44; N, 3.63%. Calcd for $C_{30}H_{36}N_2O_9P_2Cl_2Ni$=$[Ni(\text{pp-PNNP})](ClO_4)_2\cdot H_2O$: C, 47.40; H, 4.47; N, 3.68%. The nickel complex is soluble in methanol, ethanol, and CH_2Cl_2, but not in water.

$[Ni(\text{pp-PNNP})](ClO_4)_2\cdot H_2O$ (8.15 g, 10.7 mmol) and KCN (14 g, 210 mmol) were stirred in a mixture of CH_2Cl_2 (30 cm^3) and water (100 cm^3) for 20 min, and then benzene (100 cm^3) was added to the mixture. The organic layer was separated from water, dried over $MgSO_4$ (*ca.* 3 g), and evaporated under reduced pressure to yield a viscous liquid, which solidified on standing. Yield: 4.7 g. mp 59 °C. Found: C, 71.54; H, 7.02; N, 5.40%. Calcd for $C_{30}H_{36}N_2OP_2$=pp-PNNP·H_2O: C, 71.70; H, 7.22; N, 5.57%.

2,11-Dimethyl-5,8-diaza-2,11-diphosphadodecane (mm-PNNP). To liquid ammonia (150 cm^3) containing metallic sodium (1.90 g, 83 mmol) in a 300 cm^3 three-necked flask was added dropwise tetramethyldiphosphine (5.05 g, 41 mmol) with stirring at −78 °C. The solution was stirred for 1 h. To the resulting orange solution was added $(ClCH_2CH_2NHCH_2\text{-})_2\cdot 2HCl$ (5.33 g, 21 mmol) in small portions with stirring. After stirring for 1 h, liquid ammonia was evaporated, and then water (50 cm^3) and diethyl ether (40 cm^3) were added to the residue with stirring. The ethereal layer was separated from the aqueous layer and dried over $MgSO_4$ (*ca.* 3 g) overnight.

The solvent and unreacted dimethylphosphine were removed by vacuum distillation. The colorless oily product (2.5 g) thus obtained was used for preparing cobalt(III) complexes without further purification because of a small amount. The ligand can be purified *via* the Nickel(II) complex in the same manner as for pp-PNNP.

Preparation of Complexes. trans*(Cl,Cl)-[CoCl$_2$(pp-PNNP)]ClO$_4$·H$_2$O.* To a methanol solution (20 cm^3) of $\mathrm{Co(ClO_4)_2\cdot 6H_2O}$ (830 mg, 2.27 mmol) was added pp-PNNP (1.10 g, 2.27 mmol) with stirring, affording orange crystals. Methanol was removed under vacuum, and the residue was dissolved in $\mathrm{CH_2Cl_2}$. Chlorine gas was bubbled into the $\mathrm{CH_2Cl_2}$ solution for 10 min, and then nitrogen gas for 20 min to remove excess $\mathrm{Cl_2}$. To the resulting green solution was added methanol (20 cm^3), and the solution was evaporated to a small volume under reduced pressure, yielding a green precipitate (the solution should not be evporated to dryness since perchlorates of complexes are potentially explosive in a solid state). Additional methanol (250 cm^3) was added to the concentrate. The mixture was warmed at 70 °C for 10 min and then mixed with $\mathrm{NaClO_4\cdot H_2O}$ (20 g) in methanol (20 cm^3). On cooling green crystals were obtained, filtered, washed with water and then diethyl ether, and air-dried. Yield: 1.0 g. Found: C, 49.31; H, 4.95; N, 3.80%. Calcd for $\mathrm{C_{30}H_{36}N_2O_5P_2Cl_3Co}$: C, 49.23; H, 4.96; N, 3.83%. The complex is soluble in methanol, $\mathrm{CH_2Cl_2}$, and $\mathrm{CHCl_3}$, but not in water and diethyl ether.

trans*(Cl,Cl)-[CoCl$_2$(mm-PNNP)]ClO$_4$.* To *cis*-[CoCl$_2$(en)$_2$]Cl[7] (en=ethylenediamine) (3.5 g, 12 mmol) in a mixture of water (10 cm^3) and methanol (30 cm^3) was added mm-PNNP (1.12 g, 4.75 mmol) with stirring. The solution was stirred for 3 h at room temperature and filtered to remove $\mathrm{[Co(en)_3]Cl_3}$ precipitated. The filtrate was warmed with concd HCl (4 cm^3) at 60 °C for 1 h, and then evaporated to dryness under reduced pressure. The residue was dissolved in water (200 cm^3), and the solution was applied on a column (ϕ7 cm×15 cm) of SP-Sephadex C-25 ($\mathrm{Na^+}$ form). By elution with 0.05 mol dm^{-3} HCl, a blue eluate was obtained, a red brown band remaining on the top of the column. The blue eluate was evaporated to dryness under reduced pressure, and the blue product was extracted with ethanol. The extract was evaporated again to dryness under reduced pressure, and the residue was mixed with $\mathrm{NaClO_4\cdot H_2O}$ (2.0 g) in water (10 cm^3), yielding blue crystals, which were filtered, washed with water and then diethyl ether, and air-dried. Yield: 282 mg. Found: C, 25.89; H, 5.94; N, 6.00%. Calcd for $\mathrm{C_{10}H_{26}N_2O_4P_2Cl_3Co}$: C, 25.80; H, 5.63; N, 6.02%. The complex is soluble in methanol and acetone, slightly in water, but not in diethyl ether, $\mathrm{CHCl_3}$, and $\mathrm{CH_2Cl_2}$.

cis*β-[Co(acac)(pp-PNNP)](ClO$_4$)$_2$·H$_2$O.* A methanol solution (50 cm^3) containing *trans*(Cl,Cl)-[CoCl$_2$(pp-PNNP)]ClO$_4$·H$_2$O (150 mg, 0.21 mmol) and Li(acac) (60 mg, 0.57 mmol) was stirred for 20 min at room temperature. The resulting orange-red solution was diluted with water (200 cm^3), and the solution was applied on a column (ϕ3.5 cm×70 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, two very small orange bands and a large red one were eluted successively. The eluate of the large red band was collected and concentrated to 40 cm^3 under reduced pressure. On addition of $\mathrm{NaClO_4\cdot H_2O}$ the concentrate gave a red precipitate, which was filtered, washed with a small amount of water, and air-dried. Yield: 47 mg. Found: C, 48.69; H, 4.83; N, 3.27%. Calcd for $\mathrm{C_{35}H_{43}N_2O_{11}P_2Cl_2Co}$: C, 48.91; H, 5.04; N, 3.26%. The complex is soluble in water, methanol, and $\mathrm{CH_2Cl_2}$, but not in diethyl ether.

cis*β-[Co(acac)(mm-PNNP)](ClO$_4$)$_2$·H$_2$O.* A mixture of $\mathrm{[Co(acac)_3]}$[8] (870 mg, 2.44 mmol) and mm-PNNP (580 mg, 2.45 mmol) in methanol (100 cm^3) was stirred at room temperature for 3 h. To the resulting solution was added water (200 cm^3), and then unreacted mm-PNNP and $\mathrm{[Co(acac)_3]}$ were extracted with diethyl ether three times (50 cm^3 ×3). The aqueous layer was diluted with water to 1 dm^3, and the solution was applied on a column (ϕ3.5 cm×10 cm) of SP-Sephadex C-25. After complexes with the +1 charge contained in the adsorbed product had been eluted with 0.05 mol dm^{-3} NaCl, those with the +2 charge were eluted with 0.2 mol dm^{-3} NaCl. The orange eluate collected was evaporated to dryness under reduced pressure, and the orange product was extracted with ethanol (70 cm^3). The extract was diluted with water (200 cm^3) and rechromatographed with a column (ϕ3.5 cm×100 cm) of SP-Sephadex C-25 and an eluent of 0.2 mol dm^{-3} NaCl. The column showed a very small violet and a large red band. The eluate of the red band was concentrated to 50 cm^3 under reduced pressure. The concentrate was mixed with $\mathrm{NaClO_4\cdot H_2O}$ (3 g) to yield an orange-red precipitate, which was recrystallized from hot water (60 °C), giving red crystals. Yield: 505 mg. Found: C, 29.55; H, 5.42; N, 4.55%. Calcd for $\mathrm{C_{15}H_{35}N_2O_{11}P_2Cl_2Co}$: C, 29.48; H, 5.77; N, 4.58%. The complex is soluble in water, methanol, and acetone, but not in $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, and diethyl ether.

cis*β-[Co(CO$_3$)(pp-PNNP)]Cl·NaCl·H$_2$O.* To a methanol solution (100 cm^3) of *trans*(Cl,Cl)-[CoCl$_2$(pp-PNNP)]ClO$_4$·H$_2$O (500 mg, 0.68 mmol) were added $\mathrm{(NH_4)_2CO_3}$ (200 mg, 2.08 mmol) and active charcoal (100 mg). The mixture was stirred for 8 h at room temperature, and then filtered. The filtrate was diluted with water (1 dm^3), and the solution was applied on a column (ϕ3.5 cm×40 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.05 mol dm^{-3} NaCl. The eluate of the first main red band was collected and concentratred to 30 cm^3 under reduced pressure. The concentrate was mixed with NaCl (*ca.* 10 g) and stored in a refrigerator to yield red crystals, which were filtered, washed with a small amount of water and then diethyl ether, and air-dried. Yield: 74 mg. Found: C, 52.15; H, 4.92; N, 3.55%. Calcd for $\mathrm{C_{31}H_{36}N_2O_4P_2Cl_2CoNa}$: C, 52.05; H, 5.07; N, 3.92%. An additional amount of the complex was obtained as the perchlorate by adding excess $\mathrm{NaClO_4\cdot H_2O}$ to the filtrate. Yield: 53 mg. Found: C, 52.52; H, 4.64; N, 3.79%. Calcd for $\mathrm{C_{31}H_{34}N_2P_2O_7ClCo}$=[Co(CO$_3$)(pp-PNNP)](ClO$_4$): C, 52.97; H, 4.87; N, 3.99%. Both the chloride and perclorate are soluble in water, methanol, and $\mathrm{CH_2Cl_2}$, but not in diethyl ether.

trans*(NCS,NCS)-[Co(NCS)$_2$(pp-PNNP)]Cl·4H$_2$O.* A methanol solution (20 cm^3) containing *trans*(Cl,Cl)-[CoCl$_2$(pp-PNNP)]ClO$_4$·H$_2$O (100 mg, 0.14 mmol) and KNCS (70 mg, 0.7 mmol) was stirred at 50 °C for 30 min. The resulting red solution was diluted with a mixture of water (50 cm^3) and methanol (30 cm^3), and the solution was applied on a column (ϕ3.5 cm×50 cm) of SP-Sephadex C-25. By elution with a 0.05 mol dm^{-3} NaCl methanol–water (1:3) solution, the eluate of the first red band was collected. The complex in the eluate was extracted with chloroform two times (30 cm^3×2), and the extract was evaporated to dryness under reduced pressure. The residue was dissolved again in methanol (5 cm^3), and the solution was mixed with NaCl (2 g) in water (20 cm^3), giving a red precipitate. Red crystals were obtained by dissolving the precipitate in a mixture of methanol and water (1:1) and by evaporating the solution slowly at room temperature. Yield: 23 mg. Found: C, 50.35; H, 5.32; N, 7.63%. Calcd for $C_{32}H_{42}N_4O_4P_2S_2ClCo$: C, 50.10; H, 5.51; N, 7.30%. The complex is soluble in methanol, acetone, $CHCl_3$, and CH_2Cl_2, but not in water and diethyl ether.

trans*(NCS,NCS)-[Co(NCS)$_2$(mm-PNNP)]Cl·1/2(NaCl)·H$_2$O.* A methanol solution (50 cm^3) containing *trans*(Cl,Cl)-[$CoCl_2$(mm-PNNP)]ClO_4 (140 mg, 0.30 mmol) and KNCS (140 mg, 1.44 mmol) was stirred at 60 °C for 40 min. The resulting red solution was diluted with water (1 dm^3), and applied on a column (ϕ3.5 cm×50 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} NaCl, orange and blue bands were obtained. The eluate of the orange band was collected and evaporated to dryness under reduced pressure, and the complex was extracted from the residue with ethanol (100 cm^3). The extract was evaporated to dryness under reduced pressure, and the residue was again dissolved in water (5 cm^3). The solution was mixed with NaCl (1.5 g) at 50 °C, and stored in a refrigerator to yield red crystals, which were filtered, washed with a small amount of cold water, and air-dried. Yield 71 mg. Found: C, 29.21; H, 5.64; N, 11.46%. Calcd for $C_{12}H_{28}N_4OP_2S_2Cl_{1.5}Na_{0.5}Co$: C, 29.17; H, 5.71; N, 11.34%. The complex is soluble in water, methanol, and ethanol, but not in diethyl ether and $CHCl_3$.

Results and Discussion

Preparation. Multidentate ligands containing both nitrogen and phosphorus donor atoms have been usually prepared by reaction of ω-chloroalkylamines with phosphides.[9] Sacconi and Dei[3] prepared a linear-quadridentate ligand, $(C_6H_5)_2PCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2P(C_6H_5)_2$ which has a set of PNNP donor atoms, from $(ClCH_2CH_2N(CH_3)CH_2-)_2\cdot 2HCl$ and $KP(C_6H_5)_2\cdot(dioxane)_2$. We have prepared pp-PNNP and mm-PNNP by a similar method using $NaP(C_6H_5)_2$ and $NaP(CH_3)_2$, respectively, generated from $PH(C_6H_5)_2$ or $(CH_3)_2PP(CH_3)_2$ and metallic sodium in liquid ammonia. These quadridentate ligands were not purified by vacuum distillation because of a high boiling point. The purification was achieved through their Ni(II) complexes. Pure pp-PNNP solidified on standing at room temperature, whereas mm-PNNP remained oily. Yields of the ligands seemed to depend largely on the purity of reactants and the presence of moisture. The pp-PNNP ligand was also prepared from (2-aminoethyl)diphenylphosphine(edpp) and 1,2-dibromoethane, but the separation of the ligand from unreacted edpp was somewhat troublesome. In the air pp-PNNP is rather stable, but mm-PNNP is readily oxidized.

The [$CoCl_2$(pp-PNNP)]$^+$ complex was prepared by oxidizing the Co(II)–pp-PNNP complex with chlorine in a moderate yield. However, the corresponding mm-PNNP complex was not obtained by this method, but done by reaction of the ligand with [$CoCl_2$(en)$_2$]$^+$ in a fairly poor yield. The oxidizing method by chlorine is not effective either for a trialkylphosphine complex, *trans*(Cl,Cl)-[$CoCl_2$(edmp)$_2$]$^+$ (edmp=(2-aminoethyl)-dimethylphosphine),[10] although the corresponding (2-aminoethyl)diphenylphosphine(edpp) complex is obtained easily by this method.[11] Green [$CoCl_2$(pp-PNNP)](ClO_4)·H_2O was used for preparing other complexes of [CoX_2(pp-PNNP)]$^{n+}$ (X=NCS^-, X_2=CO_3^{2-}, and acac). Although several geometrical isomers are possible for the pp-PNNP complex, only one isomer was formed for each complex as confirmed by column chromatography and ^{13}C NMR spectra. On the contrary, the corresponding NCS^- and acac complexes of edpp, [CoX_2(edpp)$_2$]$^{n+}$, form two geometrical isomers, trans(NCS, NCS)cis(P,P) and cis(NCS,NCS)trans(P,P),[12] and trans(P,P) and trans(P,N),[11] respectively, by similar reactions with [$CoCl_2$(edpp)$_2$]$^+$. The mm-PNNP complexes also yielded only one isomer. The [Co(NCS)$_2$(mm-PNNP)]$^+$ complex was obtained by the reaction of [$CoCl_2$(mm-PNNP)]$^+$ with KNCS in a 48% yield. The reaction between [$CoCl_2$(mm-PNNP)]$^+$ and Li(acac) yielded [Co(acac)(mm-PNNP)]$^{2+}$ in a poor yield (7%), but that between mm-PNNP and [Co(acac)$_3$] gave the complex in a better yield (36%). This is quite in contrast to the reactions of pp-PNNP with [Co(acac)$_3$] and of [$CoCl_2$(pp-PNNP)]$^+$ with Li(acac) resulting in 8 and 27% yields, respectively. Synthetic methods for Co(III)–phosphine complexes should be designed carefully by considering the kind of phosphine ligands.[13] The reaction between [$CoCl_2$(mm-PNNP)]$^+$ and $(NH_4)_2CO_3$ at room temperature scarcely proceeded, and decomposition occurred at a higher temperature. The reaction of [$CoCl_2$(mm-PNNP)] with a large excess of $(NH_4)_2CO_3$ gave a trace amount of an orange complex assignable to [$CoCO_3$(mm-PNNP)]$^+$. However, it was not isolated because of a extremely low yield. Attempts to prepare [Co(en)(pp-PNNP or mm-PNNP)]$^{3+}$ from the dichloro complex and en were all unsuccessful.

Stereochemistry. There are three possible geometrical isomers for X=Cl^- and NCS^-, and two for X_2=CO_3^{2-} and acac in the [CoX_2(PNNP)]-type complex. The geometrical structures were assigned on the basis of the NMR and ligand field absorption spectra. The ^{13}C NMR and absorption spectral data are summarized in Tables 1 and 2, respectively.

The ^{13}C NMR spectra of [CoX_2(pp- or mm-PNNP)]$^+$ (X=Cl^- and NCS^-) indicate the complexes to be either the trans or cisα isomer which have C_2 symmetry (Fig. 1). Each of these complexes shows two kinds of phenyl or methyl signals (Table 1). Since both trans and cisα isomers are chiral (the trans isomer having chiral nitrogen donor atoms), the two phenyl or methyl groups on a phosphorus atom are diastereomeric to each other, and should be magnetically unequivalent. Thus geometrical structures of the complexes can not be assigned unequivocally from the NMR spectra. In Fig. 2 are compared the absorption spectra of [$CoCl_2$(pp- or mm-PNNP)]$^+$ and [Co(NCS)$_2$(pp-PNNP)]$^+$ with those of the corresponding bis(edpp) and bis(edmp) complexes. Molecular structures of [$CoCl_2$(edpp)$_2$]$^+$ and

TABLE 1. ^{13}C NMR SPECTRAL DATA, δ/ppm$^{a)}$ (J/Hz$^{b)}$)

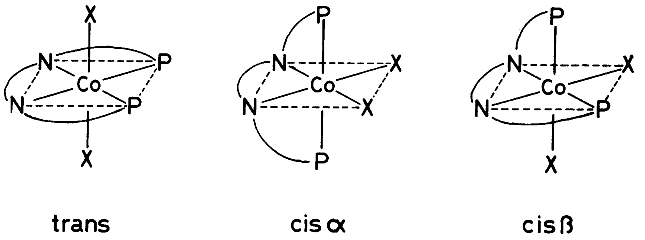
Complexes (solvent)	acac			PNNP							
	CH_3	CH	CO	P-CH_3	P-CH_2	N-$CH_2$$^{c)}$	N-$CH_2$$^{d)}$	P-C_1	*o*-P	*m*-P	*p*-P
$[CoCl_2(pp\text{-}PNNP)]^+$	—	—	—	—	36.66t(28)	49.90s	54.11s	131.13t(46)	135.18t(13)	129.16t(9)	132.02s
(CD_3OD)								135.21t(31)	135.63t(8)	129.30t(10)	132.10s
$[Co(NCS)_2(pp\text{-}PNNP)]^+$	—	—	—	—	34.54t(28)	49.98s	55.36s	136.06t(46)	134.27t(9)	130.43t(10)	133.08s
(CD_3OD)								e)	134.72t(8)	130.74t(10)	132.98s
$[CoCl_2(mm\text{-}PNNP)]^+$	—	—	—	13.04t(35)	36.38t(28)	47.84s	53.83s	—	—	—	—
(CD_3OD)				13.16t(32)							
$[Co(NCS)_2(mm\text{-}PNNP)]^+$	—	—	—	12.35t(32)	36.16t(31)	48.18s	54.53s	—	—	—	—
(D_2O)				13.23t(31)							
$[Co(acac)(pp\text{-}PNNP)]^{2+}$	26.93s	101.38s	189.95s	—	28.97d(29)	48.19s	51.36s	121.02d(43)	131.41d(7)	129.83d(12)	132.20s
(D_2O)	27.61d(5)		192.11s		30.15d(29)	48.36s	51.91s	127.70d(45)	131.94d(7)	129.98d(11)	132.77s
$[CoCO_3(pp\text{-}PNNP)]^+$	—	—	—	—	29.43d(28)	f)	52.38s	125.70d(43)	132.43d(8)	130.31(9)	132.32s
(CD_3OD)					33.40d(32)	49.84s	53.23s	127.52d(44)	133.05d(8)	130.50d(11)	133.13s
$[Co(acac)(mm\text{-}PNNP)]^{2+}$	26.82s	100.52s	190.97s	8.93d(34)	31.54d(28)	46.90s	50.53s	—	—	—	—
(D_2O)	27.61d(5)		192.12s	9.35d(34)	33.45d(28)	47.02s	50.62s				
				11.13d(28)							
				12.66d(31)							

a) Internal reference: TMS and dioxane for CD_3OD and D_2O solutions, respectively. b) The J values for triplet signals are given by the width between the outer peaks. c) P-C-$\underline{C}$-N. d) N-$\underline{C}$-$\underline{C}$-N. e) Overlapped with other peaks. f) Overlapped with solvent peaks.

TABLE 2. ABSORPTION SPECTRAL DATA. (Solvent: CH_3OH, at 298K)

Complexes	$\nu_{max}/10^3\,cm^{-1}$ ($\log \varepsilon$)		
trans(Cl,Cl)-$[CoCl_2(pp\text{-}PNNP)]^+$	16.25(2.08),	21.5(2.4)*,	26.5(3.5)*,
	31.4(4.21),	39.0(4.1)*,	44.5(4.5)*
trans(NCS,NCS)-$[Co(NCS)_2(pp\text{-}PNNP)]^+$	18.62(2.63),	25.5(3.8)*,	32.47(4.19)
trans(Cl,Cl)-$[CoCl_2(mm\text{-}PNNP)]^+$	16.95(2.19),	24.5(2.3)*,	29.59(3.48)
	37.59(4.26),	40.0(4.22)*	
trans(NCS,NCS)-$[Co(NCS)_2(mm\text{-}PNNP)]^+$	20.16(2.95),	28.37(3.49),	32.10(3.67),
	40.57(4.23)		
cisβ-$[Co(acac)(pp\text{-}PNNP)]^{2+}$	19.50(2.90),	29.0(3.9)*,	31.75(4.39),
	45.0(4.58)*		
cisβ-$[Co(CO_3)(pp\text{-}PNNP)]^+$	19.72(2.68),	25(2.6)*,	32.15(4.35)
cisβ-$[Co(acac)(mm\text{-}PNNP)]^{2+}$	20(2.54)*,	22.75(2.68),	29.5(3.40)*
	39.5(4.38)		

* Shoulder absorption.



trans cisα cisβ

Fig. 1. Geometrical isomers of the $[CoX_2(PNNP)]$-type complex.

$[Co(NCS)_2(edpp)_2]^+$ given in Fig. 2 have been determined to trans(Cl,Cl)cis(P,P)[10] and trans(NCS,NCS)-cis(P,P),[12] respectively, by X-ray analysis, and that of $[CoCl_2(edmp)_2]^+$ assigned to trans(Cl,Cl)cis(P,P) by comparing the absorption spectrum with those of the corresponding isomers of edpp and ebpp ((2-aminoethyl)butylphenylphosphine) complexes.[10] From a comparison of these spectra, $[CoCl_2$(pp- and mm-PNNP)$]^+$ and $[Co(NCS)_2(pp\text{-}PNNP)]^+$ can be assigned to the trans isomer. The spectrum of $[Co(NCS)_2(mm\text{-}PNNP)]^+$ is somewhat different from that of $[Co(NCS)_2(pp\text{-}PNNP)]^+$. However, the mm-PNNP complex shows a very similar ^{13}C NMR spectrum to that of $[CoCl_2(mm\text{-}PNNP)]^+$, indicating the trans isomer.

The *trans*(X,X)-$[CoX_2$(pp- or mm-PNNP)$]^+$ complex can have two diastereomers, racemic (*RR* and *SS*) and meso (*RS*) forms for the chiral nitrogen donor atoms. Both the NMR spectra and column chromatograms indicate that each of the trans isomers yielded only one of these two diastereomers selectively. When the complexes are the racemic form, the structures can be assigned by optical resolution. However, attempts to resolve the complexes by column chromatography using Sephadex LH-20 or SP-Sephadex C-25 were unsuccessful. The ^{13}C NMR spectra of $[Co(NCS)_2$(pp- or mm-PNNP)$]^+$ indicate that the two NCS^- groups are magnetically equivalent, although the observed signals (pp-PNNP: 143.25 ppm, mm-PNNP: 144.72 ppm) were very weak. Thus the complexes can be assigned to the racemic form (C_2 symmetry), since the two NCS^- groups in the meso form (C_s symmetry) should be magnetically unequivalent.

The ^{13}C NMR spectra of $[Co(acac)$(pp- or mm-PNNP)$]^{2+}$ and $[Co(CO_3)(pp\text{-}PNNP)]^+$ clearly indicate that the complexes are the cisβ isomer which has only C_1 symmetry (Table 1). The arrangement of donor atoms in the cisβ isomer is the same as that in trans(P,N) isomers of the corresponding edpp and edmp complexes. In the ^{13}C NMR spectra of [Co-

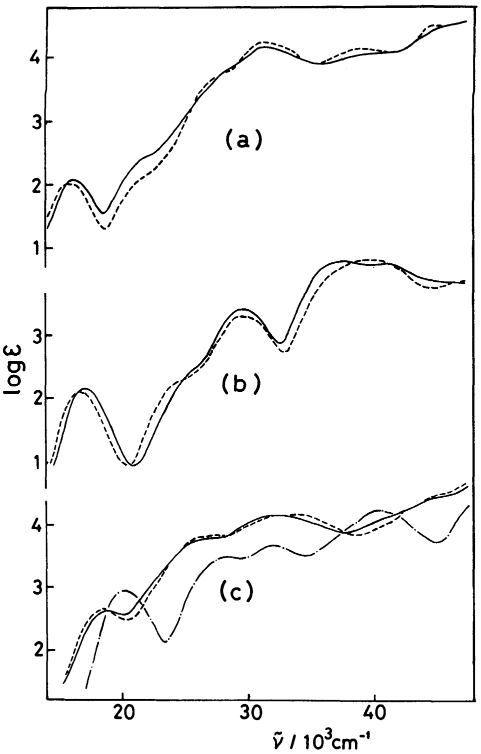


Fig. 2. Absorption spectra of trans(X,X) complexes. (a): *trans*-[CoCl$_2$(pp-PNNP)]$^+$ (——) and *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(edpp)$_2$]$^+$ (------), (b): *trans*-[CoCl$_2$(mm-PNNP)]$^+$ (——) and *trans*(Cl,Cl), *cis*(P,P)-[CoCl$_2$(edmp)$_2$]$^+$ (------), (c): *trans*-[Co(NCS)$_2$(pp-PNNP)]$^+$ (——), *trans*(NCS,NCS), *cis*(P,P)-[Co(NCS)$_2$(edpp)$_2$]$^+$ (------), and *trans*-[Co(NCS)$_2$(mm-PNNP)]$^+$ (—·—·—).

(acac)(pp- or mm-PNNP)]$^{2+}$, one of two methyl groups of acac which resonates at a lower magnetic field exhibits a coupling with the phosphorus atom trans to the oxygen donor atom of acac. The same coupling has been observed for the *trans*(P,N)-[Co(acac)(edpp)$_2$]$^{2+}$.[11]

The absorption spectra of [Co(acac or CO$_3$)(pp-PNNP)]$^{n+}$ also resemble remarkably those of respective *trans*(P,N)-[Co(acac or CO$_3$)(edpp)$_2$]$^{n+}$. (Fig. 3) The absorption spectral pattern of [Co(acac)(pp- and mm-PNNP)]$^{2+}$ are different from each other over the whole region. The pp-PNNP complex shows the single first absorption band at 19500 cm^{-1}, and the pattern is also similar to that of [Co(acac)(en)(dppe)]$^{2+}$(dppe=1,2-bis(diphenylphosphino)ethane).[11] On the other hand, the mm-PNNP complex exhibits a peak at 22750 cm^{-1} and a shoulder at *ca.* 20000 cm^{-1} in the first absorption region, and the pattern of which is quite similar to that of [Co(acac)(en)(dmpe)]$^{2+}$ (dmpe=1,2-bis(dimethylphosphino)ethane).[14] The ligand field strengths of mm-PNNP and dmpe may be much stronger than those of pp-PNNP and edpp to cause a splitting of the first absorption band of the complex.

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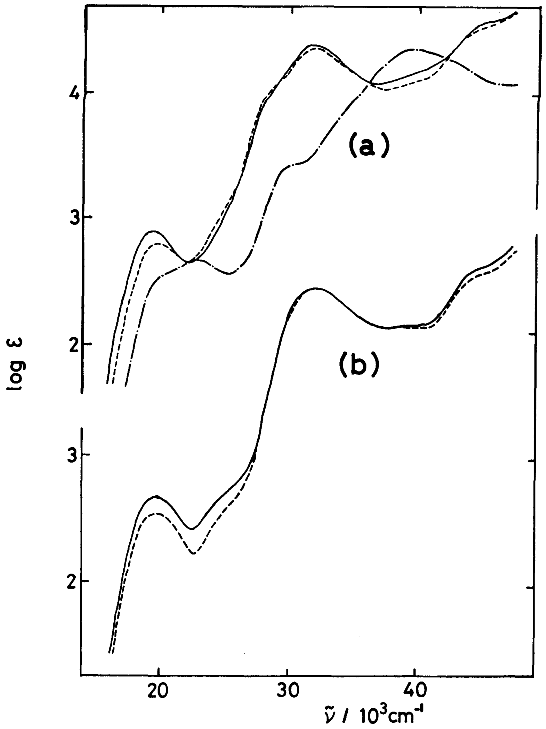

Fig. 3. Absorption spectra of *cisβ*-[Co(O–O)(PNNP)]-type Complexes. (a): *cisβ*-[Co(acac)(pp-PNNP)]$^{2+}$ (——), *trans*(P,N)-[Co(acac)(edpp)$_2$]$^{2+}$ (------), and *cisβ*-[Co(acac)(mm-PNNP)]$^{2+}$ (—·—·—), (b): *cisβ*-[Co(CO$_3$)(pp-PNNP)]$^+$ (——) and *trans*(P,N)-[Co(CO$_3$)(edpp)$_2$]$^+$ (------).

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