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Synthesis and Stereochemistry of Cobalt(III) Complexes with the New Optically Active Phosphine Ligand, *N,N'*-Bis[2-(diphenylphosphanyl)ethyl]-(1*R*,2*R*)-cyclohexane-1,2-diamine (ch-PNNP). Crystal Structure of Λ-*cis*β-[Co(acac)(ch-PNNP)]$(ClO_4)_2$

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A new optically active tetradentate phosphine ligand, *N,N'*-bis[2-(diphenylphosphanyl)ethyl]-(1*R*,2*R*)-cyclohexane-1,2-diamine (ch-PNNP), was prepared from (1*R*,2*R*)-cyclohexane-1,2-diamine and purified through the nickel(II) complex. Three new ch-PNNP complexes of cobalt(III) were prepared: *trans*-$[CoCl_2(ch\text{-}PNNP)]^+$, *trans*-$[Co(NCS)_2(ch\text{-}PNNP)]^+$ and Λ-*cis*β-[Co(acac)(ch-PNNP)]$^{2+}$. The geometrical structures of the complexes were assigned on the basis of NMR, CD and absorption spectra. The molecular structure and the absolute configuration of Λ-*cis*β-[Co(acac)(ch-PNNP)]$(ClO_4)_2$ were determined by X-ray analysis. The orthorhombic cell ($P2_12_12_1$) has $a=12.721(4)$, $b=17.073(3)$, $c=18.26(3)$ Å, $V=3966(7)$ Å^3 and $Z=4$. The X-ray analysis shows that the three chelate rings from the ch-PNNP ligand form distorted *gauche* (δλλ) conformations.

Previously one of the authors (M.A.) reported the synthesis and stereochemistry of cobalt(III) complexes with several PNNP-type tetradentate aminoalkyphosphine ligands.[1–4] Four such ligands are shown in Fig. 1 with the abbreviations used. They all contain two phosphorus and two nitrogen donors linked P–C–C–N–C–C–N–C–C–P and exhibit a specific stereoselectivity on coordination to cobalt(III). The optically active ligands, *SS*-pp-PNNP and *SS*-mm-PNNP, which have an asymmetric carbon atom between the P and N atoms, have been shown to form the *trans* (δλδ conformation) or the Λ-*cis*β isomer selectively.

By replacing the $N–CH_2–CH_2–N$ moiety in these ligands with a (1*R*,2*R*)-cyclohexane-1,2-diamine moiety, $C_6H_{10}N_2$, as in the ligand $C_6H_{10}(NHCH_2CH_2PPh_2)_2$ a λ fixation of the $N–CH_2–CH_2–N$ conformation in the complex is obtained. In the present paper we describe the synthesis of this new ligand, *N,N'*-bis[2-(diphenylphosphanyl)ethyl]-(1*R*,2*R*)-cyclohexane-1,2-diamine (ch-PNNP), and its complex formation with cobalt(III), additional ligands being Cl^-, NCS^- or pentane-2,4-dionate (acac). The crystal structure of [Co(acac)-(ch-PNNP)]$(ClO_4)_2$ was determined from single crystal X-ray diffraction. The stereochemistry and selectivity of the ch-PNNP complexes are discussed on the basis of UV/VIS absorption, circular dichroism (CD) and NMR spectra.

Experimental

Chemicals and apparatus. The phosphine ligand was prepared and handled under an atmosphere of argon (or nitrogen) using standard Schlenk-type apparatus and a syringe and needle technique until the cobalt(III) complexes were formed. All the solvents for the preparation of the ligand and the complexes were made oxygen-free by bubbling argon gas through them for 20 min before use. Absorption, circular dichroism (CD), and ^1H and ^{13}C NMR spectra were recorded on a Hitachi 228 spectrophotometer, a Jasco J-720 spectropolarimeter and a Varian XL-300 spectrometer, respectively. Mass spectra were recorded on a Hitachi M-80B mass spectrometer.

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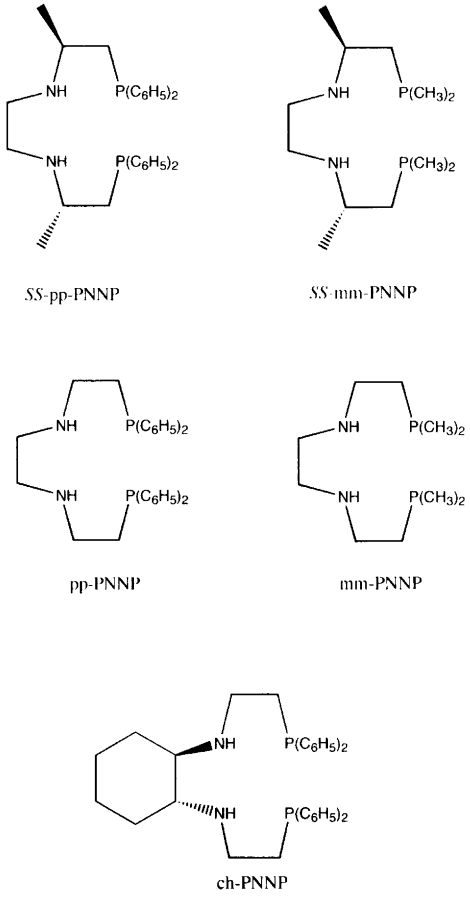
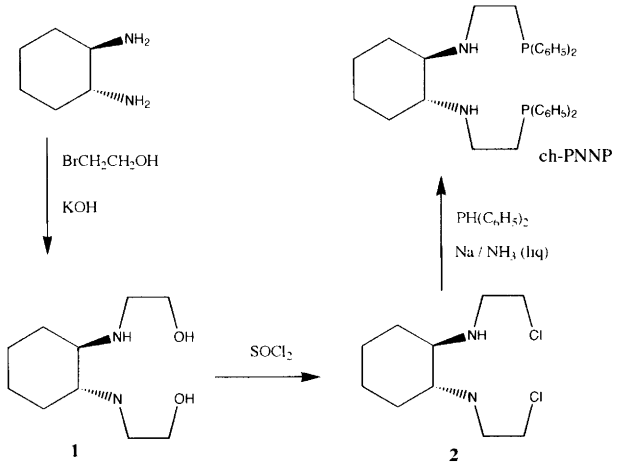


Fig. 1. PNNP-type tetradentate ligands.

Liquid SIMS spectra (glycerol matrix) were recorded on this instrument equipped with attachments for secondary ion mass spectroscopy.

Syntheses. **Caution!** In the following procedures handling of the perchlorates must be done with care.[5] Syntheses on a larger scale should be avoided or done with the utmost care. Special care must be taken on the evaporation of reaction mixtures. Avoid scraping and (local) heat, and dilute acid mixtures of organic solvents and perchlorate as soon as possible. We did not experience explosions when these precautions were taken.

The ch-PNNP ligand. The synthesis of this ligand is illustrated in Scheme 1. To a mixture of (1*R*,2*R*)-cyclohexane-1,2-diamine[6] (79.85 g, 0.713 mol) and water (50 cm^3) in a 500 cm^3 three-necked round-bottom flask was added $BrCH_2CH_2OH$ (178.20 g, 1.426 mol) dropwise over 30 min with stirring. The mixture was stirred for 3 h at 70 °C, and then evaporated under reduced pressure to remove water. The oily residue was dissolved in methanol (ca. 200 cm^3), mixed with KOH (80.2 g, 1.43 mol) at 0 °C, and stirred for 2 h. The precipitated KBr was filtered off, and the filtrate was evaporated under reduced pressure to give a viscous liquid, which was stored in a vacuum desiccator over P_4O_{10} for a



Scheme 1.

week. The liquid was distilled under vacuum (ca. 150 Pa) to separate $NH_2C_6H_{10}NHCH_2CH_2OH$ (b.p. 135 °C, 28.4 g) and **1** (Scheme 1) (b.p. 175 °C). Yield of **1**: 37.5 g (0.185 mol, 25.9%). ^{13}C NMR (solvent: D_2O, ref: dioxane): 24.16; 29.85; 47.10; 59.82; 60.46 ppm. MS: m/e = 203 ($M+H^+$).

To a mixture of compound **1** (10.5 g, 52 mmol) and chloroform (50 cm^3) in a 500 cm^3 three-necked round-bottom flask $SOCl_2$ (18 g, 0.15 mol) was added dropwise under cooling in an ice-bath. Then the mixture was refluxed for 1.5 h with stirring, cooled in an ice-bath, and evaporated under reduced pressure to remove chloroform and $SOCl_2$. The residue was dissolved in hot propane-2-ol (ca. 100 cm^3) and allowed to stand in a refrigerator. The solution gave colourless (or pale brown) crystals of **2** (Scheme 1) which were filtered off and dried in a vacuum desiccator. Yield of **2**: 4.5 g (28%). Found: C, 38.39; H, 7.31; N, 8.97%. Calc. for $C_{10}H_{22}N_2Cl_4$: C, 38.48; H, 7.10; N, 8.97%. MS: found: m/e = 239.1081, calc. for $C_{10}H_{21}N_2(^{35}Cl)_2 = (^{35}ClCH_2CH_2NH)_2C_6H_{10} + H^+$: m/e = 239.1081.

The last step in Scheme 1 was performed as follows. To liquid ammonia (100 cm^3) containing metallic sodium (0.69 g, 20 mmol) in a 300 cm^3 three-necked round-bottom flask with a mechanical stirrer diphenylphosphine (5.6 g, 30 mmol) was added dropwise over 5 min under stirring at −78 °C. After stirring for 1 h the colour of the solution changed from deep blue to orange. Compound **2** (1.81 g, 7.5 mmol) was added in small portions to the stirred orange solution. Stirring was continued for 1 h, giving a colourless solution. After evaporation of liquid ammonia water (50 cm^3) and then diethyl ether (50 cm^3) were added to the residue under stirring. The ether layer was separated from the aqueous layer and dried over anhydrous Na_2SO_4 (ca. 2 g) overnight. A viscous liquid was obtained by removing the solvent and diphenyl phosphine under vacuum. The ch-PNNP product (ca 3.0 g) was used for preparing nickel(II) and cobalt(III) complexes without further purification. MS: m/e = 539 (ch-PNNP+H^+, CI). The

crude product of ch-PNNP could be purified via the nickel(II) complex as follows. To a methanol solution (15 cm^3) containing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.25 g, 0.68 mmol) crude ch-PNNP (0.363 g) was added under stirring. The yellow solution was stirred for 20 min and then mixed with $NaClO_4 \cdot H_2O$ (5.0 g). On addition of water (18 cm^3) the solution gave a yellow precipitate of $[Ni(ch\text{-}PNNP)](ClO_4)_2$, which was filtered off, washed with water and air-dried. Yield: 393 mg (73 %). Found: C, 51.03; H, 5.42; N, 3.43%. Calc. for $C_{34}H_{40}N_2P_2Cl_2O_8Ni$: C, 51.29; H, 5.06; N, 3.52%. Liquid SIMS: $m/e = 597$ ($[Ni(ch\text{-}PNNP)]^+$).

A methanol solution (5 cm^3) containing $[Ni(ch\text{-}PNNP)](ClO_4)_2$ (70 mg, 0.088 mmol) was mixed with KCN (25 mg) and water (5 cm^3) and stirred for 1 h to librate ch-PNNP, which was extracted with diethyl ether (30 cm^3). The extract (ether layer) was dried over anhydrous Na_2SO_4 overnight and then filtered. The filtrate was evaporated under reduced pressure to give an oily product. MS: found: $m/e = 539.2733$, calc. for $C_{34}H_{41}N_2P_2$ ($M+H^+$): $m/e = 539.2745$. ^{13}C NMR (δ from TMS, in chloroform-d): 29.49(d, $J = 12$ Hz; P-CH_2), 43.74(d; N-CH_2), 61.41(CH), 24.98(CH_2), 31.56(CH_2).

trans-*[$CoCl_2$(ch-PNNP)](ClO_4)*. To a methanol solution (20 cm^3) containing $Co(ClO_4)_2 \cdot 6H_2O$ (0.701 g, 1.92 mmol) ch-PNNP (1.605 g, 1.97 mmol) was added under stirring. The solution gave orange crystals. Methanol was removed under reduced pressure, and the residue was dissolved in dichloromethane (50 cm^3). Chlorine gas was bubbled into the solution for 4 min, and then argon gas for 10 min to remove excess Cl_2. The resulting green solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in hot methanol (ca. 100 cm^3) and then mixed with $NaClO_4 \cdot H_2O$ (10 g) in methanol (10 cm^3). The solution was stored in a refrigerator (5 °C) to give green crystals, which were collected, washed with water, and then air-dried. Yield: 835 mg (55%). Found: C, 53.08; H, 5.55; N, 3.39%. Calc. for $C_{34}H_{40}N_2P_2Cl_3O_4Co$: C, 53.18; H, 5.25; N, 3.65%. MS: $m/e = 667$ ($[CoCl_2(ch\text{-}PNNP)]^+$, liquid SIMS). The complex is soluble in methanol, acetone, dichloromethane and dimethyl sulfoxide, but not in water and diethyl ether.

trans-*[$Co(NCS)_2$(ch-PNNP)]$Cl \cdot 3.5H_2O$*. To a methanol solution (100 cm^3) containing *trans*-$[CoCl_2(ch\text{-}PNNP)]ClO_4$ (148.7 mg, 0.194 mmol) KNCS (563 mg, 5.79 mmol) was added under stirring. The mixture was stirred at room temperature overnight. The colour of the solution gradually turned red. The red solution was diluted with excess water and passed through a column of SP–Sephadex C-25. The red product, adsorbed on the SP–Sephadex gel, was eluted with 0.05 M NaCl (methanol : water = 1 : 3) giving a red elution band. The eluate of the red band was collected, concentrated under reduced pressure, and then the red product was extracted with several portions of dichloromethane. The extract was evaporated to dryness under reduced pressure, and dissolved in a small amount of methanol. Excess aqueous sodium chloride solution (2 M) was added to give a red precipitate, which was filtered off, washed with water and air-dried. Yield: 112.4 mg (0.138 mmol, 71%). Found: C, 53.27; H, 5.77; N, 6.81. Calc. for $C_{36}H_{47}N_4O_{3.5}S_2P_2ClCo$ (=812.25): C, 53.23; H, 5.83; N, 6.81.

Λ-cisβ-*[Co(acac)(ch-PNNP)](ClO_4)$_2 \cdot H_2O$*. To a methanol solution containing *trans*-$[CoCl_2(ch\text{-}PNNP)]ClO_4$ (83 mg, 0.12 mmol) lithium pentane-2,4-dionate (20 mg, 0.19 mmol) and activated charcoal (ca. 10 mg) were added under stirring. The solution turned red within 5 min. The mixture was stirred for 1 h at room temperature, and then filtered. The charcoal was washed with several portions of hot methanol (ca. 50 cm^3). The filtrate and the washings were combined, diluted with water (ca. 500 cm^3), and applied to a column (150 cm × 2.5 cm^{Φ}) of SP–Sephadex C-25. The adsorbed product was eluted with 0.2 M NaCl, giving a large red band and a very small dark orange band, successively. The eluate of the large red band was collected and concentrated to ca. 100 cm^3 under reduced pressure. The red product was extracted with chloroform (3 × 30 cm^3), and the extract was evaporated to dryness under reduced pressure. The red residue was dissolved in water (10 cm^3), filtered and then mixed with $NaClO_4 \cdot H_2O$ (1 g) in water (5 cm^3). The mixture was allowed to stand in a refrigerator to give red crystals, which were collected, washed with cold water and air-dried. Yield: 41 mg (37%). Found: C, 51.27; H, 5.41; N, 3.07%. Calc. for $C_{39}H_{49}N_2Cl_2CoO_{11}P_2$: C, 51.27; H, 5.41; N, 3.07%. The complex is soluble in dichloromethane, chloroform, acetone, dimethyl sulfoxide and hot methanol, but not in diethyl ether. A methanol solution of the complex was allowed to evaporate slowly to give single crystals for X-ray work.

The eluate of the second, dark-orange band was collected and evaporated to dryness under reduced pressure. An orange complex was extracted with methanol but not isolated because of its small amount. Liquid SIMS spectra of this product showed two main peaks at $m/e =$ 713 and 612, which can be assigned to species containing oxidized ch-PNNP.

X-Ray powder diffraction patterns. A Stoe Stadi P powder diffractometer was used to record the diagram of the title complex using Cu$K\alpha_1$ radiation selected by a curved germanium monochromator. The diffraction pattern from the sample recorded in a transmission mode were measured with a position-sensitive detector covering 7° in 2θ. The software[7] Visual X^{POW} supplied with the instrument was used to analyse the diffraction pattern, which was found to be in agreement with the results obtained from the single crystal X-ray diffraction. The cell parameters found by powder diffraction (25 °C) are $a = 12.966(3)$, $b = 17.459(4)$, $c = 18.117(4)$ Å, $\alpha = \beta = \gamma = 90°$, giving a volume of 4101(2) $Å^3$ and a density of

1.451 g cm^{-3} (Z = 4) compared with 1.448 g cm^{-3} found by flotation.

Crystal structure determination. A crystal, representative of the sample, was selected for the data collection, which was performed with an Enraf-Nonius CAD4 diffractometer using a graphite monochromated Mo$K\alpha$ radiation. The crystal was cooled to 122.0(3) K. The cell parameters were determined and refined from 20 reflections in the θ-range 17.34–17.95°. Further details are found in Table 1.

Data reduction was performed with the program package DREADD.[8] The diffraction pattern showed orthorhombic symmetry and systematically absent reflections conform with the space group $P2_12_12_1$. Analysis of the data revealed that the scan range employed had been to large owing to the relatively long b- and c-axis. Therefore we based the data reduction on the 61 central steps out of the 96 steps stored in the reflection profile. All reflections were corrected for background, Lorentz and polarization effects. The analysis of the standard reflections showed an average decrease of the intensities with exposure time of 5.8 %. Intensities of these reflections were used to obtain a third-order polynomium that were used as a rescale function for all reflections. The Gaussian integration method was used to perform the correction for absorption, the transmission factors varying between 0.903 and 0.938. The reflections related by the symmetry of the crystal class were averaged.

The structure was solved by the Patterson method using SHELXS86,[9] which gave the starting position of the cobalt atom. All other non-hydrogen atoms were found in the difference Fourier map. The refinement was performed using SHELXL93,[10] which minimizes $\Sigma w(|F_o|^2-|F_c|^2)^2$. The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms could be localized in the difference electron density and their positional parameters were included in the refinement, apart from H5A–H5C where the C–H distance was constrained to be 0.98 Å. The isotropic displacement parameters for the hydrogen atoms were constrained to be 1.2 times the isotropic displacement parameter of the connected atom, apart from the hydrogen atoms on the acac ligand where the isotropic displacement parameters were set to 1.5 times the parameter of carbon. The absolute structure was determined from the refined Flack parameter. The final atomic parameters are listed in Table 2. Structure factors, anisotropic displacement parameters and hydrogen atom coordinates are available from the authors.

Table 1. Crystal data, data collection and refinement.

Formula	$C_{39}H_{47}Cl_2CoN_2O_{10}P_2$
M_r	895.56
Crystal size/mm	0.34 × 0.28 × 0.14
Crystal form	Block
Crystal colour	Red
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions/Å	a = 12.721(4)
	b = 17.073(3)
	c = 18.26(3)
Volume/Å^3	3966(7)
Z	4
D_{calc}/g cm^{-3}	1.500
Radiation	Mo$K\alpha$ (λ = 0.71073 Å)
T/K	122.0(3)
Scan mode	ω–2θ
Scan range θ/°	1.63–26.97
Index ranges	$0 \leftarrow h \leftarrow 16$, $-21 \leftarrow k \leftarrow 21$, $-23 \leftarrow l \leftarrow 23$
Reflections collected	11287
Independent reflections	8627 (R_{int} = 0.0325)
Intensity average decay	5.8%
μ/mm^{-1}	0.709
Absorption correction	Gaussian integration method
Max. and min. transmission	0.938 and 0.903
Refinement method	Full-matrix least-squares on F^2
Data/parameters	8612/637
Goodness-of-fit on F^2	1.441
Weights	$w = 1/[\sigma^2(F_o^2)]$
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0612, wR_2 = 0.1349
Absolute structure parameter	−0.02(2)
Largest difference peak and hole/e Å^{-3}	0.970 and −0.575

Results and discussion

The ch-PNNP ligand and the stereochemistry of its octahedral complexes. Figure 1 shows four tetradentate PNNP ligands for which the stereochemistry of their cobalt(III) complexes has been investigated earlier.[1,2] Two of these ligands contain optically active components in their N···P branches. We here present the new ch-PNNP ligand, which is the first example of a PNNP ligand with an optically active unit located to the N···N part. The (1*R*,2*R*)-cyclohexane-1,2-diamine is a readily available source of optical activity, and the two-fold symmetry and the λ fixation of the chelate ring in the complexes with a ligand derived from this diamine has simplified the interpretation of the results of the present investigations. The optically active ligands *SS*-pp-PNNP and *SS*-mm-PNNP also form octahedral complexes in which the N–C–C–N chelate conformation preferably is λ due to preference for equatorial direction of the C–CH_3 bonds.[2] This makes it possible directly to compare these complexes with those containing ch-PNNP. The synthesis of ch-PNNP and various cobalt(III) complexes is given in the Experimental section, and Fig. 2 shows all the isomers topologically expected for a mononuclear octahedral ch-PNNP complex.

For *trans*(X,X)-[CoX_2(ch-PNNP)]$^{n+}$ only one isomer can be expected in which the two N···P chelate rings have δ-conformation, the N···N chelate ring being fixed in λ-conformation.

For *cis*(X,X)-[CoX_2(ch-PNNP)]$^{n+}$ there are four possibilities: The Λ-*cis*α and Δ-*cis*α isomers seem to be disfavoured because of the *trans* positions of the two

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (in Å^2).

Atom	*x*	*y*	*z*	U_{eq}[a]
Co	0.7959(1)	0.1382(1)	0.2385(1)	0.013(1)
P1	0.6721(1)	0.0786(1)	0.1669(1)	0.014(1)
P2	0.7611(1)	0.0929(1)	0.3512(1)	0.016(1)
O1	0.9099(3)	0.1964(2)	0.2800(2)	0.016(1)
O2	0.8790(3)	0.0506(2)	0.2129(2)	0.018(1)
N1	0.8282(3)	0.1968(3)	0.1460(2)	0.015(1)
N2	0.7091(4)	0.2310(2)	0.2649(2)	0.014(1)
C11A	0.5354(4)	0.1062(3)	0.1780(3)	0.018(1)
C12A	0.4890(4)	0.1087(3)	0.2469(3)	0.020(1)
C13A	0.3829(4)	0.1287(3)	0.2550(3)	0.024(1)
C14A	0.3224(5)	0.1426(4)	0.1941(4)	0.034(2)
C15A	0.3668(5)	0.1387(5)	0.1260(4)	0.041(2)
C16A	0.4723(5)	0.1215(4)	0.1181(3)	0.028(1)
C11B	0.6696(4)	−0.0267(3)	0.1555(3)	0.015(1)
C12B	0.7538(5)	−0.0629(3)	0.1187(3)	0.021(1)
C13B	0.7503(5)	−0.1430(4)	0.1050(3)	0.027(1)
C14B	0.6667(5)	−0.1870(4)	0.1278(3)	0.030(1)
C15B	0.5837(5)	−0.1523(3)	0.1637(3)	0.026(1)
C16B	0.5841(5)	−0.0720(3)	0.1772(3)	0.024(1)
C21A	0.8775(4)	0.0798(3)	0.4077(3)	0.017(1)
C22A	0.9235(5)	0.1436(4)	0.4427(3)	0.024(1)
C23A	1.0169(5)	0.1346(4)	0.4812(3)	0.027(1)
C24A	1.0635(5)	0.0623(4)	0.4859(3)	0.031(2)
C25A	1.0175(5)	−0.0021(4)	0.4529(3)	0.026(1)
C26A	0.9240(5)	0.0058(4)	0.4136(3)	0.022(1)
C21B	0.6865(4)	0.0043(3)	0.3664(3)	0.020(1)
C22B	0.7123(5)	−0.0638(3)	0.3283(3)	0.026(1)
C23B	0.6622(6)	−0.1334(4)	0.3443(4)	0.037(2)
C24B	0.5842(6)	−0.1353(5)	0.3975(4)	0.039(2)
C25B	0.5566(5)	−0.0676(4)	0.4349(4)	0.035(2)
C26B	0.6089(5)	0.0027(4)	0.4208(3)	0.028(1)
C31	0.7596(4)	0.2683(3)	0.1419(3)	0.018(1)
C32	0.7435(5)	0.2989(3)	0.2200(3)	0.017(1)
C33	0.6665(5)	0.3670(4)	0.2197(3)	0.025(1)
C34	0.7025(6)	0.4324(4)	0.1668(3)	0.028(1)
C35	0.7250(5)	0.4004(4)	0.0902(3)	0.030(1)
C36	0.8030(5)	0.3324(4)	0.0929(3)	0.024(1)
C1	1.0819(5)	0.2306(4)	0.3137(4)	0.027(1)
C2	1.0058(4)	0.1715(3)	0.2845(3)	0.017(1)
C3	1.0395(4)	0.0984(4)	0.2621(3)	0.021(1)
C4	0.9781(4)	0.0423(3)	0.2283(3)	0.019(1)
C5	1.0227(5)	−0.0346(4)	0.2049(4)	0.039(2)
C1P	0.7116(5)	0.1129(3)	0.0756(3)	0.017(1)
C1N	0.8214(4)	0.1484(3)	0.0789(3)	0.019(1)
C2P	0.6877(5)	0.1760(3)	0.3892(3)	0.021(1)
C2N	0.7146(5)	0.2490(3)	0.3461(3)	0.018(1)
Cl1	0.3865(1)	0.1296(1)	0.5012(1)	0.035(1)
O11	0.4144(6)	0.1301(4)	0.4252(3)	0.083(2)
O12	0.4751(6)	0.1579(3)	0.5397(4)	0.084(2)
O13	0.3661(7)	0.0510(3)	0.5232(4)	0.086(2)
O14	0.2976(5)	0.1791(3)	0.5109(3)	0.049(1)
Cl2	0.4093(1)	−0.2430(1)	0.5738(1)	0.026(1)
O21	0.4749(3)	−0.2641(3)	0.5128(2)	0.037(1)
O22	0.4181(5)	−0.1595(4)	0.5856(4)	0.080(2)
O23	0.3029(3)	−0.2609(3)	0.5586(2)	0.035(1)
O24	0.4445(5)	−0.2815(5)	0.6381(3)	0.078(2)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

phosphorus atoms. So far, no *cis*α isomers of cobalt(III) with PNNP-type ligands have been obtained, and for $[CoX_2(H_2NCH_2CH_2PPh_2)_2]^{n+}$ (X_2 = acac, oxalate, malonate, carbonate) the yield of the *trans*(P,P) isomer is always lower than that of the *cis*(P,P) isomer.[11] The Δ-*cis*β isomer is probably disfavoured because of steric hindrance between the phenyl groups. This was illustrated previously[2] with *SS*-pp-PNNP, where Δ-*cis*β complexes could not be obtained. For [Co(acac)(*SS*-mm-PNNP)]$^{2+}$, in which the substituents on the phosphorus

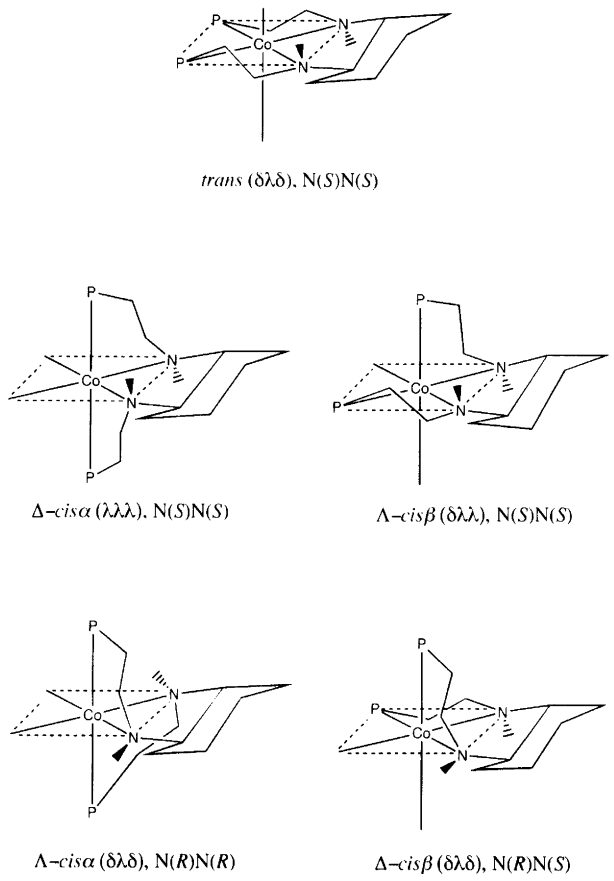


Fig. 2. Isomers topologically expected for a mononuclear octahedral ch-PNNP complex.

atoms are methyl groups, the Δ-*cis*β isomer (δλδ) as well as the Λ-*cis*β isomer (δλλ) were isolated. However, the Δ-isomer was obtained in a yield much lower than that of the Λ-isomer,[2] even though the C–CH_3 bonds are equatorially directed in the Δ-isomer and axially directed in the λ P···N chelate ring of the Λ-isomer.

The Λ-*cis*β is therefore the most probable *cis*(X,X)-$[CoX_2(ch\text{-}PNNP)]^{n+}$ isomer. With X_2 = acac this isomer preference was confirmed in [Co(acac)(*SS*-mm-PNNP)]$^{2+}$ from X-ray structure analysis[2] and in [Co(acac)(*SS*-pp-PNNP)]$^{2+}$ by comparison of the CD spectra of these two complexes.[2] The present [Co(acac)(ch-PNNP)]$^{2+}$ complex is no exception as demonstrated by the structure found by X-ray diffraction (see below).

Dichloro and bis(isothiocyanato) complexes. The green $[CoCl_2(ch\text{-}PNNP)]^+$ complex was prepared by oxidizing the cobalt(II) complex, [Co(ch-PNNP)]$^{2+}$, with chlorine in dichloromethane. This method has been applied for the preparation of other cobalt(III) dichloro complexes with phosphine ligands, e.g. *trans*-$[CoCl_2(en)(Ph_2PCH_2CH_2PPh_2)]^+$,[10] *trans*-$[CoCl_2(H_2NCH_2CH_2PPh_2)_2]^+$,[11] and *trans*-$[CoCl_2(pp\text{-}PNNP)]^+$.

The liquid SIMS spectrum of $[CoCl_2(ch\text{-}PNNP)](ClO_4)$ shows relatively weak peaks from the mother cation (m/e = 667) and two major daughters (m/e = 632 and m/e = 596). The ^{13}C NMR spectrum shows that the complex has a symmetrical structure (i.e. *trans* or *cis*α). The absorption spectrum is similar to those of related *trans*-dichloro(aminoalkylphosphine)cobalt(III) complexes, e.g.[1,2] *trans*-$[CoCl_2(pp\text{-}PNNP)]^+$ and *trans*-$[CoCl_2(SS\text{-}pp\text{-}PNNP)]^+$, and the CD spectrum shows a pattern quite similar to the latter complex (Fig. 3). These observations give strong evidence that this $[CoCl_2(ch\text{-}PNNP)]^+$ complex is the *trans*-isomer with δλδ conformation.

The reaction of *trans*-$[CoCl_2(ch\text{-}PNNP)]^+$ with NCS^- gave only one product: *trans*-$[Co(NCS)_2(ch\text{-}PNNP)]^+$. In contrast, the similar reaction with the $(edpp)_2$ analogue (edpp = $H_2NCH_2CH_2PPh_2$) gives the *trans*(NCS,NCS) as well as the *cis*(NCS,NCS) isomer.[12] The *trans* assignment of the ch-PNNP complex is based on the observations that ^{13}C NMR shows a symmetrical structure, and the absorption spectrum is quite similar to that of *trans*(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]^+$, the structure of which has been determined by X-ray diffraction.[12]

The acac complex. $[Co(acac)(ch\text{-}PNNP)](ClO_4)_2$ was prepared by a reaction between *trans*-$[CoCl_2(ch\text{-}PNNP)]^+$ and Li(acac) in methanol. Only one isomer was obtained. ^1H NMR showed two sharp methyl signals at 1.574 and 2.149 ppm, respectively, suggesting that the

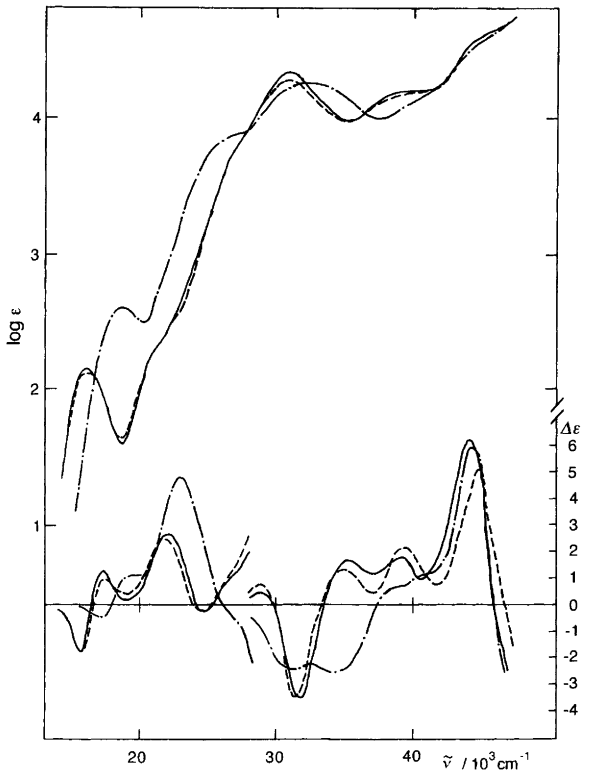


Fig. 3. Absorption and CD spectra of $[CoCl_2(ch\text{-}PNNP)]^+$ (——), $[CoCl_2(SS\text{-}pp\text{-}PNNNP)]^+$ (– – –) and $[Co(NCS)_2(ch\text{-}PNNP)]^+$ (·–·–).

complex has a low symmetry, i.e. the *cis*β isomer. Since the absorption and CD spectrum of the product showed quite similar patterns to those of Λ-*cis*β-[Co(acac)(*SS*-pp-PNNP)]$^{2+}$ (Fig. 4) we expected the product to be Λ-*cis*β-[Co(acac)(ch-PNNP)](ClO$_4$)$_2$. This was confirmed by the X-ray structure analysis given below.

The crystal structure of Λ-cisβ-*[Co(acac)(ch-PNNP)](ClO$_4$)$_2$*. The crystal structure is built from the cationic complex (Fig. 5) and two well ordered perchlorate ions. One of these is linked to the cation through a long hydrogen bond with N1···O24 being 3.23 Å and the angle N1–HN1–O24 169°. Selected bond lengths and angles in the complex are given in Table 3.

The complex has Λ-*cis*β geometry in which three distorted gauche rings have δλλ conformations. The geometry of the P–C–C–N–C–C–N–C–C–P backbone is similar to that of Λ-*cis*β-[Co(acac)(*SS*-mm-PNNP)](ClO$_4$)$_2$·H$_2$O.[2]

Comparison of this complex, having two methyl groups on the phosphorus atoms (PMe$_2$), with the ch-PNNP complex with two phenyl groups (PPh$_2$), shows that the Co–PPh$_2$ bonds (2.287 and 2.244 Å) are longer than the corresponding Co–PMe$_2$ bonds (2.208 and 2.196 Å), and the Ph$_2$P–Co–PPh$_2$ angle (103.6°) is larger than the Me$_2$P–Co–PMe$_2$ angle (96.0°). This is probably due to delocalization of the phosphorus lone pair electrons to the phenyl groups and to the steric demands of these groups, which are almost parallel [the angle between the two least-squares planes of the staggered phenyl groups is only 17.5(3)°]. Accordingly, the *trans* influence of the phosphorus donors on the Co–O and Co–N bond lengths is bigger in the *SS*-mm-PNNP complex showing larger differences between the two Co–O bond lengths and between the two Co–N bond lengths than in the ch-PNNP complex.

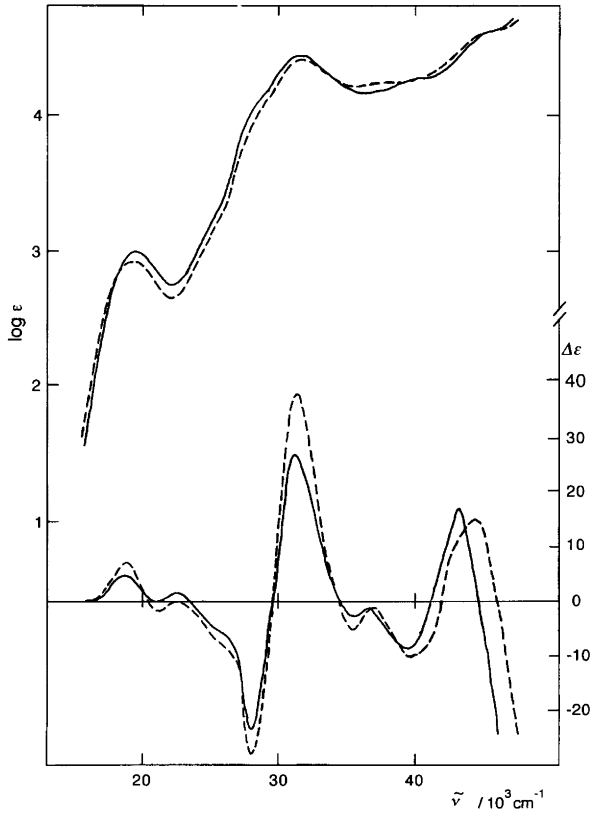


Fig. 4. Absorption and CD spectra of Λ-*cis*β-[Co(acac)(ch-PNNP)]$^{2+}$ (——) and Λ-*cis*β-[Co(acac)(*SS*-pp-PNNP)]$^{2+}$ (– – –).

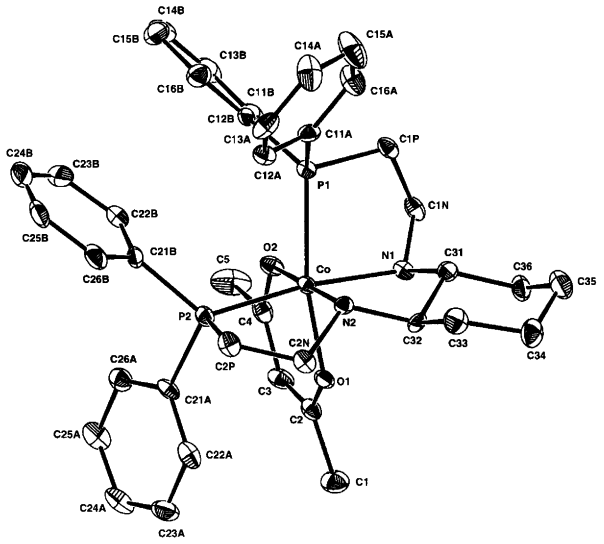


Fig. 5. ORTEP drawing of Λ-*cis*β[Co(acac)(ch-PNNP)]$^{2+}$ complex including the labelling of the atoms. The thermal ellipsoids enclose 50% probability.

Salts of *trans*(X,X),*cis*(P,P)-[CoX$_2$(edpp)$_2$]$^+$ (X being Cl[13] or NCS[12]) resemble the ch-PNNP complex in having P–Co–P angles equal to 103° and Co–P bond lengths in the interval 2.254–2.272 Å. The chelate bite angles, P1–Co–N1, P2–Co–N2 and N1–Co–N2, and the torsion angles in the three chelate rings of the present ch-PNNP complex are rather similar to those of the *SS*-mm-PNNP complex.

Conclusion

ch-PNNP is a convenient ligand for the investigation of phosphine complexes. With cobalt(III) the isolated complexes are robust and not air-sensitive. For octahedral complexes the preferred isomers are *trans* or Λ-*cis*β. In planar four-coordinated complexes ch-PNNP is expected to coordinate in the same manner as in *trans*-octahedral complexes, i.e. with a δλδ conformation of the three successive chelate rings. The complex formation between ch-PNNP and other metals, such as chromium(III), rhodium(III) and palladium(II) are at present being studied.

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Table 3. Selected geometrical parameters.

The complex			
Bond lengths/Å			
Co–O1	1.914(4)	Co–O2	1.890(4)
Co–N1	2.005(5)	Co–N2	1.990(4)
Co–P1	2.287(2)	Co–P2	2.244(3)
Bond angles°			
O1–Co–N1	85.4(2)	O1–Co–N2	84.9(2)
O1–Co–P1	168.4(1)	O1–Co–P2	88.0(1)
O2–Co–N1	94.1(2)	O2–Co–N2	179.5(2)
O2–Co–P1	83.8(1)	O2–Co–P2	93.7(1)
O2–Co–O1	94.8(2)	N2–Co–N1	85.4(2)
N1–Co–P1	83.2(2)	N1–Co–P2	170.2(1)
N2–Co–P1	96.4(1)	N2–Co–P2	86.8(1)
P2–Co–P1	103.62(9)		
C11B–P1–Co	121.3(2)	C21B–P2–Co	122.2(2)
C11A–P1–Co	118.7(2)	C21A–P2–Co	113.7(2)
C1P–P1–Co	100.9(2)	C2P–P2–Co	100.4(2)
C1N–N1–Co	114.0(3)	C2N–N2–Co	111.9(3)
C31–N1–Co	109.1(3)	C32–N2–Co	108.9(3)
C2–O1–Co	124.7(3)	C4–O2–Co	125.2(3)
N1–C31–C36	113.8(4)	N2–C32–C33	114.2(5)
N1–C31–C32	108.0(4)	N2–C32–C31	106.6(4)
Torsion angles/°			
N1–Co–P1–C11A	−104.5(2)	N1–Co–P1–C11B	123.1(2)
N2–Co–P1–C11A	−19.9(2)	N2–Co–P1–C11B	−152.3(2)
The ch-PNNP ligand			
Bond lengths/Å			
P1–C11A	1.813(6)	P1–C11B	1.809(5)
P2–C21A	1.818(5)	P2–C21B	1.807(6)
P1–C1P	1.837(6)	P2–C2P	1.835(6)
N1–C1N	1.481(7)	N2–C2N	1.516(7)
N1–C31	1.502(7)	N2–C32	1.485(6)
C11A–C16A	1.381(8)	C11B–C16B	1.394(8)
C11A–C12A	1.390(8)	C11B–C12B	1.407(8)
C12A–C13A	1.400(8)	C12B–C13B	1.391(8)
C13A–C14A	1.373(9)	C13B–C14B	1.366(9)
C14A–C15A	1.367(10)	C14B–C15B	1.376(9)
C15A–C16A	1.381(9)	C15B–C16B	1.393(8)
C21A–C22A	1.392(8)	C21B–C22B	1.393(8)
C21A–C26A	1.399(8)	C21B–C26B	1.401(8)
C22A–C23A	1.389(8)	C22B–C23B	1.379(9)
C23A–C24A	1.372(9)	C23B–C24B	1.389(11)
C24A–C25A	1.384(9)	C24B–C25B	1.389(11)
C25A–C26A	1.395(9)	C25B–C26B	1.395(9)
C31–C36	1.519(8)	C33–C34	1.546(8)
C31–C32	1.533(8)	C34–C35	1.530(9)
C32–C33	1.520(8)	C35–C36	1.528(9)
C1P–C1N	1.524(8)	C2P–C2N	1.515(8)
Bond angles/°			
C11B–P1–C11A	104.8(2)	C21B–P2–C21A	103.8(3)
C11B–P1–C1P	102.5(2)	C21B–P2–C2P	108.8(3)
C11A–P1–C1P	106.3(3)	C21A–P2–C2P	107.2(3)
C1N–N1–C31	112.2(4)	C2N–N2–C32	111.6(4)
C1N–C1P–P1	110.0(4)	C2N–C2P–P2	109.0(4)
N1–C1N–C1P	108.0(4)	N2–C2N–C2P	109.3(4)
C33–C32–C31	110.1(4)	C36–C35–C34	111.3(5)
C32–C33–C34	111.4(5)	C31–C36–C35	109.3(5)
C35–C34–C33	111.6(5)	C36–C31–C32	110.6(5)
Torsion angles/°			
N1–C1N–C1P–P1	42.1(5)	N2–C2N–C2P–P2	46.8(5)
N1–C31–C32–N2	−50.6(5)		

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