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Preparation and Circular Dichroism Spectra of *trans*-Dichlorocobalt(III) Complexes with (2-Aminoethyl)diphenylphosphine and Related Ligands. Crystal Structures of *trans*(Cl,Cl), *cis*(P,P)-$[CoCl_2\{NH_2CH_2CH_2P(C_6H_5)_2\}_2]\cdot 1/2[CoCl_4]$ and -$[CoCl_2\{NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}_2]ClO_4$

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Green *trans*-dichlorocobalt(III) complexes with a variety of achiral and chiral (2-aminoalkyl)phosphines have been prepared and characterized. The crystal structures of $[CoCl_2\{$(2-aminoethyl)diphenylphosphine$\}_2]1/2$-$[CoCl_4]$ and $[CoCl_2\{(R)$-(2-aminoethyl)butylphenylphosphine$\}_2]ClO_4$ have been determined by X-ray analyses. Both complex cations have a distorted octahedral coordination with two Cl atoms in the *trans* positions and two P (and N) atoms in the *cis* positions. The Co–N distances (2.02—2.05 Å) are 0.05—0.07 Å longer than the usual Co(III)–N distance, and the P–Co–P angles are widened (99.4 and 103.1°) on account of bulky substituents on the phosphorus atoms. The circular dichroism spectra of $[CoCl_2\{$(2-aminoethyl)diphenylphosphine$\}_2]ClO_4$ (space group $P3_221$) in Nujol mull and the complexes with chiral (aminoalkyl)phosphines in methanol solutions have been recorded and compared with those of related complexes.

In a previous paper,[1] we have reported the preparation, and some spectroscopic and chemical properties of the $[CoCl_2\{NH_2CH_2CH_2P(C_6H_5)_2\}_2]X$ (X=Cl^- or ClO_4^-) complex. The complex has a green color characteristic of the *trans*(Cl,Cl) configuration. However, no clear evidence was obtained for assigning the geometrical configuration of the phosphorus (or nitrogen) donor atoms, *trans*(P,P) or *cis*(P,P). This paper deals with crystal structures of two green complexes, $[CoCl_2\{NH_2CH_2CH_2P(C_6H_5)_2\}_2]1/2[CoCl_4]$ and $[CoCl_2\{(R)\text{-}NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}_2]ClO_4$, determined by X-ray structure analyses. The latter complex is chiral and shows circular dichroism (CD). The perchlorate salt of the former complex, the structure of which could not be solved because of the twin crystal, crystallizes in the chiral space group $P3_221$ and also exhibits CD in the solid state. This paper includes CD spectra of those and several complexes of the same *trans*-dichloro-type formed with related optically active (aminoalkyl)phosphine ligands.

The ligands used in this study and the abbreviations are as follows; (2-aminoethyl)diphenylphosphine, $NH_2CH_2CH_2P(C_6H_5)_2$=edpp; (2-aminoethyl)dimethylphosphine, $NH_2CH_2CH_2P(CH_3)_2$ = edmp; (*S*)-(2-aminopropyl)diphenylphosphine, (*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$ = *S*-pdpp; (*R*)-(2-aminoethyl) butylphenylphosphine, (*R*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ = *R*-ebpp; (*S*)-2-(diphenylphosphinomethyl)pyrrolidine, (*S*)-$CH_2CH_2CH_2NHCHCH_2P(C_6H_5)_2$=*S*-prdpp; (*S*(C),*R*(P))- and (*S*(C),*S*(P))-2-(butylphenylphosphinomethyl)pyrrolidine, (*S*(C), *R*(P))- and (*S*(C), *S*(P))-$CH_2CH_2CH_2NHCHCH_2P(C_4H_9)(C_6H_5)$ = *S*(C),*R*(P)- and *S*(C),*S*(P)-prbpp. The notation of the absolute configurations, *R* and *S*, for the chiral phosphorus atom of a free ligand is reversed upon coordination to the cobalt(III) ion.[2] In this paper, however, we use the same notation for a coordinating ligand as that when it is free.

Experimental

Preparations. Free (aminoalkyl)phosphines were prepared according to methods reported and handled under nitrogen atmosphere until they formed air-stable cobalt(III) complexes; edpp,[3] edmp,[4] *S*-pdpp,[5] *R*-ebpp,[6] *S*-prdpp,[7] and *S*(*C*), *R*(P)- and *S*(C), *S*(P)-prbpp.[8]

$[CoCl_2(edpp)_2]ClO_4$ and $[CoCl_2(edpp)_2]1/2[CoCl_4]$. The perchlorate was prepared by the method reported in a previous paper.[1]

The perchlorate (100 mg) was dissolved in methanol (40 cm^3), and 5 cm^3 of concd hydrochloric acid was added. On standing at room temperature the solution gave green needles of $[CoCl_2(edpp)_2]Cl\cdot HCl\cdot H_2O$ (38 mg). Found: C, 49.86; H, 5.20; N, 4.12%. Calcd for $C_{28}H_{35}N_2OP_2Cl_4Co$: C, 49.58; H, 5.20; N, 4.13%.

The crystals were dissolved again in methanol and $CoCl_2\cdot 6H_2O$ (8 mg) was added. The solution was evaporated slowly by standing at room temperature to give dark green plates of $[CoCl_2(edpp)_2]1/2[CoCl_4]$ which were subjected to X-ray analysis. Found: C, 48.02; H, 4.84; N, 4.09%. Calcd for $C_{28}H_{32}N_2P_2Cl_4Co_{1.5}$: C, 48.82; H, 4.68; N, 4.07%.

$[CoCl_2(edmp)_2]Cl\cdot H_2O$ and $[CoCl_2(edmp)_2]ClO_4\cdot 1/2\ NaClO_4$. The chloride was prepared by two methods. *Method 1*: To a methanol solution (50 cm^3) of $CoCl_2\cdot 6H_2O$ (238 mg, 1 mmol) was added edmp (210 mg, 2 mmol) under nitrogen atmosphere, and then the mixture was stirred in the air for 6 h. The resulting brown solution was diluted with water and poured onto an SP-Sephadex column. The product adsorbed was eluted with a 0.01 mol/dm^3 NaCl solution, and the eluate was evaporated to dryness under reduced pressure. The residue was extracted with ethanol. The extract was allowed to evaporate slowly at room temperature, giving blue-green crystals of $[CoCl_2(edmp)_2]Cl\cdot H_2O$. Yield: *ca.* 10%.

Method 2: An *N,N*-dimethylformamide solution (50 cm^3) of *cis*-$[CoCl_2(en)_2]Cl$ (en: ethylenediamine) (285 mg, 1 mmol) was mixed with a methanol solution (10 cm^3) of edmp (105 mg, 1 mmol), and the mixture was stirred for 6 h. The resulting solution was diluted and chromatographed by the same method as the above to give the complex. Yield: *ca.* 7%. Found: C, 24.12; H, 6.54; N, 6.95%. Calcd for $C_8H_{26}N_2OP_2Cl_3Co$: C, 24.42; H, 6.66; N, 7.12%. No dichloro complex was

TABLE 1. CRYSTAL DATA AND EXPERIMENTAL DETAILS

	Compound	
	$[CoCl_2(R\text{-ebpp})_2]$-$ClO_4$	$[CoCl_2(edpp)_2]$-1/2$[CoCl_4]$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12$	C2/c
a/Å	18.30(1)	29.52(2)
b/Å	17.83(1)	14.517(5)
c/Å	9.496(7)	16.928(6)
β/°		119.29(4)
Z	4	8
D_m/g cm^{-3}	1.38	1.45
D_c/g cm^{-3}	1.39	1.45
μ(Mo $K\alpha$)/cm^{-1}	9.7	12.9
Crystal size/mm^3	0.20×0 23×0.35	$0.18\times0.28\times0.50$
Scan type	ω	ω
Scan speed/° s^{-1}	0.033	0.025
Scan range/°	$1.0+0.2\tan\theta$	$1.0+0.2\tan\theta$
Background count/s^{-1}	15	20
$2\theta_{max}$/°	55	50
No. of unique data ($F_0^2>2\sigma(F_0^2)$)	3271	3493
Minimized function	$\sum w(F_o-\lvert F_c\rvert)^2$	$\sum w(F_o-\lvert F_c\rvert)^2$
Weight	$1/\sigma^2\ (F_o)$	$1/\sigma^2\ (F_o)$
$R_1=\sum\Delta F/F_o$	0.069	0.062
$R_2=[\sum w\Delta F^2/\sum wF_0^2]^{1/2}$	0 090	0.078
Convergence maximum shift (Δ/σ)	0.5	0.12
Peak hight in the final difference synthesis/e Å^{-3}	1.0	0.14

obtained when treated with 2 mmol of edmp, yellow $[Co(en)_{3-n}(edmp)_n]^{3+}$ complexes being formed.

The perchlorate was obtained by adding $NaClO_4$ to a solution of the chloride in the minimum amount of ethanol, and recrystallized from ethanol and diethyl ether. Found: C, 19.62; H, 4.92; N, 5.67%. Calcd for $C_8H_{24}N_2O_6P_2Cl_{3.5}$-$CoNa_{0.5}$: C, 19.20; H, 4.83; N, 5.59%.

$[CoCl_2(S\text{-}pdpp)_2]ClO_4$, $[CoCl_2($R$\text{-}ebpp)_2[ClO_4]$, $CoCl_2($S$\text{-}prdpp)_2]$-$ClO_4\cdot H_2O$, $[CoCl_2($S(C), R$(P)\text{-}prbpp)_2]ClO_4\cdot 1/2\ H_2O$, and $[CoCl_2($S(C), S$(P)\text{-}prbpp)_2]ClO_4\cdot H_2O$. These complexes were prepared by a method similar to that for the edpp complex. The *R*-ebpp, and *S*(C), *R*(P)- and *S*(C), *S*(P)-prbpp ligands were obtained from their palladium(II) complexes by the method reported.[6] Found for $[CoCl_2(S\text{-pdpp})_2]$-$ClO_4$: C, 50.07; H, 5.63; N, 3.44%. Calcd for $C_{30}H_{36}N_2$-$O_4P_2Cl_3Co$: C, 50.33; H, 5.07; N, 3.91%. Found for $[CoCl_2$-$(R\text{-ebpp})_2]ClO_4$: C, 44.39; H, 6.20; N, 4.32%. Calcd for $C_{24}H_{40}N_2O_4P_2Cl_3Co$: C, 44.50; H, 6.22; N, 4.32%. Found for $[CoCl_2(S\text{-prdpp})_2]ClO_4\cdot H_2O$: C, 51.75; H, 5.56; N, 3.31% Calcd for $C_{34}H_{42}N_2O_5P_2Cl_3Co$: C, 51.96; H, 5.39; N, 3.56%. Found for $[CoCl_2(S(C), R(P)\text{-prbpp})_2]ClO_4\cdot 1/2$-$H_2O$: C, 48.45; H, 6.31; N, 4.30%. Calcd for $C_{30}H_{49}N_2O_{4.5}$-P_2Cl_3Co: C, 48.89; H, 6.70; N, 3.80%. Found for $[CoCl_2$-$(S(C), S(P)\text{-prbpp})_2]ClO_4\cdot H_2O$: C, 47.68; H, 6.32; N, 4.44%. Calcd for $C_{30}H_{50}N_2O_5P_2Cl_3Co$: C, 48.30; H, 6.76; N, 3.76%.

Spectral Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively.

X-Ray Analyses. X-Ray analyses of $[CoCl_2(edpp)_2]1/2$-$[CoCl_4]$ and $[CoCl_2(R\text{-ebpp})_2]ClO_4$ were performed. Space groups and approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. Crystal data and experimental details are given in Table 1.

Intensity data were collected at room temperature on a Philips PW1100 automated diffractometer by the use of graphite-monochromated Mo $K\alpha$ radiation. The intensities of three standard reflections of each compound showed no appreciable decay throughout the data collections. An absorption collection was applied for the ebpp complex, but not for the edpp complex. The maximum and minimum transmission factors are 1.34 and 1.30, respectively. Relative structure factors were calculated by use the program written

TABLE 2. FRACTIONAL COORDINATES AND TEMPERATURE FACTORS FOR *trans*-$[CoCl_2(edpp)_2]1/2[CoCl_4]$
Standard deviations of the least significant figures are given in parentheses.

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Co(2)	0.11496(4)	0.2336(1)	0.0896(1)	3.16(4)	N(2)	0.0915(3)	0.2241(6)	−0.0440(4)	4.5(3)
Cl(1)	0.0416(1)	0.3099(2)	0.0547(1)	4.5(1)	C(3)	0.1152(4)	0.3861(7)	−0.0392(5)	4.9(4)
Cl(2)	0.1848(1)	0.1503(2)	0.1160(2)	4.1(1)	C(4)	0.1152(4)	0.2913(8)	−0.0795(6)	5.4(4)
N(1)	0.0748(3)	0.1149(5)	0.0714(6)	5.5(4)	P(2)	0.1517(1)	0.3679(2)	0.0843(1)	3.0(1)
C(1)	0.1226(4)	0.0980(6)	0.2375(7)	5.5(5)	C(17)	0.1432(3)	0.4745(5)	0.1342(5)	3.1(3)
C(2)	0.0707(4)	0.0823(7)	0.1526(8)	6.4(5)	C(18)	0.0941(3)	0.5185(6)	0.0898(6)	4.4(4)
P(1)	0.1374(1)	0.2212(1)	0.2370(1)	3.3(1)	C(19)	0.0876(3)	0.5982(6)	0.1318(7)	5.0(4)
C(5)	0.0994(3)	0.2820(6)	0.2797(5)	3.3(3)	C(20)	0.1268(4)	0.6316(7)	0.2121(7)	5.0(4)
C(6)	0.0935(3)	0.3779(6)	0.2684(5)	3.5(3)	C(21)	0.1750(3)	0.5864(7)	0.2544(6)	4.7(4)
C(7)	0.0683(3)	0.4279(6)	0.3070(6)	4.1(3)	C(22)	0.1829(3)	0.5073(6)	0.2145(6)	3.7(3)
C(8)	0.0489(3)	0.3791(7)	0.3565(6)	4.9(3)	C(23)	0.2197(3)	0.3709(6)	0.1133(5)	3.3(3)
C(9)	0.0541(3)	0.2833(7)	0.3661(6)	4.3(3)	C(24)	0.2346(4)	0.4066(7)	0.0514(7)	5.3(4)
C(10)	0.0790(3)	0.2349(6)	0.3270(5)	3.8(3)	C(25)	0.2893(4)	0.4108(7)	0.0805(8)	5.7(5)
C(11)	0.2040(3)	0.2395(6)	0.3261(5)	4.0(3)	C(26)	0.3258(3)	0.3832(6)	0.1654(7)	5.0(4)
C(12)	0.2429(4)	0.1715(8)	0.3454(7)	6.2(5)	C(27)	0.3105(3)	0.3483(6)	0.2253(7)	5.1(4)
C(13)	0.2931(4)	0.1891(9)	0.4085(6)	7.2(5)	C(28)	0.2572(3)	0.3403(6)	0.2000(6)	4.1(3)
C(14)	0.3075(4)	0.272(1)	0.4519(7)	7.5(5)	Co(1)	0.50000(0)	0.4093(1)	0.25000(0)	4.1(1)
C(15)	0.2713(4)	0.3402(9)	0.4365(7)	6.8(5)	Cl(3)	0.4368(1)	0.4909(2)	0.1341(2)	5.0(1)
C(16)	0.2179(3)	0.3231(7)	0.3710(6)	4.6(3)	Cl(4)	0.4646(1)	0.3195(2)	0.3162(2)	8.0(1)

TABLE 3. FRACTIONAL COORDINATES AND TEMPERATURE FACTORS FOR *trans*-$[CoCl_2(R\text{-ebpp})_2]ClO_4$
Standard deviations of the least significant figures are given in parentheses.

Atom	x	y	z	B_{eq}/Å^2
Co	0.1524(1)	0.0768(1)	−0.0185(1)	3.19(2)
Cl(3)	0.4037(1)	0.3656(1)	−0.3517(3)	5.1(1)
O(1)	0.3398(1)	0.4025(1)	−0.3368(3)	19.4(1)
O(2)	0.4011(4)	0.2851(4)	−0.3413(9)	11.0(2)
O(3)	0.4492(6)	0.3944(6)	−0.248(1)	10.5(3)
O(4)	0.4346(4)	0.3833(4)	−0.4802(8)	16.7(2)
Cl(1)	0.0377(6)	0.1063(7)	−0.082(1)	4.0(3)
Cl(2)	0.2620(1)	0.0398(1)	0.0560(2)	4.6(1)
N(1)	0.1342(6)	−0.0309(5)	−0.085(1)	4.6(3)
C(1)	0.1471(4)	0.0179(5)	−0.3263(9)	5.0(2)
C(2)	0.1622(5)	−0.0496(7)	−0.228(1)	6.2(3)
N(2)	0.1113(1)	0.0462(1)	0.1724(2)	4.5(1)
C(3)	0.1185(5)	0.1809(6)	0.239(1)	5.2(3)
C(4)	0.1308(5)	0.0959(5)	0.2886(9)	6.0(2)
P(1)	0.1902(5)	0.0989(5)	−0.238(1)	3.4(2)
C(5)	0.1602(1)	0.1806(1)	−0.3318(3)	3.8(1)
C(6)	0.0878(5)	0.1903(6)	−0.379(2)	4.0(9)
C(7)	0.0648(6)	0.2535(5)	−0.439(1)	5.2(4)
C(8)	0.1142(5)	0.3183(5)	−0.462(1)	6.9(4)
C(9)	0.187(1)	0.3105(7)	−0.413(1)	6.0(6)
C(10)	0.2112(5)	0.2422(5)	−0.3563(9)	4.6(2)
P(2)	0.1663(5)	0.1913(6)	0.072(1)	3.5(3)
C(11)	0.2581(6)	0.2219(7)	0.116(1)	3.8(4)
C(12)	0.3033(6)	0.2479(6)	0.006(1)	4.4(3)
C(13)	0.3752(5)	0.2688(6)	0.039(1)	4.6(3)
C(14)	0.4012(5)	0.2637(5)	0.171(1)	6.2(2)
C(15)	0.3573(5)	0.2395(5)	0.284(1)	5.7(3)
C(16)	0.2838(5)	0.2199(6)	0.253(1)	5.6(3)
C(17)	0.2887(6)	0.0936(6)	−0.267(1)	6.2(3)
C(18)	0.1223(6)	0.2697(6)	−0.011(1)	4.5(3)
C(19)	0.3096(6)	0.0795(6)	−0.426(1)	6.2(2)
C(20)	0.3888(8)	0.0608(9)	−0.440(2)	9.5(4)
C(21)	0.409(1)	0.042(1)	−0.602(2)	13.7(6)
C(22)	0.1233(7)	0.3441(8)	0.078(2)	7.9(3)
C(23)	0.0785(9)	0.4048(9)	0.017(2)	10.3(4)
C(24)	0.018(2)	0.396(2)	0.056(3)	24(1)

by Hornstra and Stubbe.[9]

The structures were solved by the conventional Patterson and Fourier techniques. The parameters were refined by the block-diagonal least-squares method. The six carbon atoms of the two butyl groups were isotropically refined because they were disordered. The atomic scattering factors of the Co, Cl, P, O, N, and C atoms were taken from the reference.[10] The real part of the anomalous dispersion corrections were applied for the Co, Cl, and P atoms. The absolute configuration of the ebpp complex could not be determined, since the Weissenberg photographs taken with Cu *Ka* radiation showed no appreciable difference in intensities of any Bijvoet pairs.

The atomic coordinates are listed in Tables 2 and 3.

The F_o-F_c tables and anisotropic thermal parameters are preserved by the Chemical Society of Japan (Document No. 8314). The computation were carried out by the FACOM 230-60 computer at Osaka City University and the ACOS 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The programs used included local versions of the UNICS[11] and ORTEP II.[12]

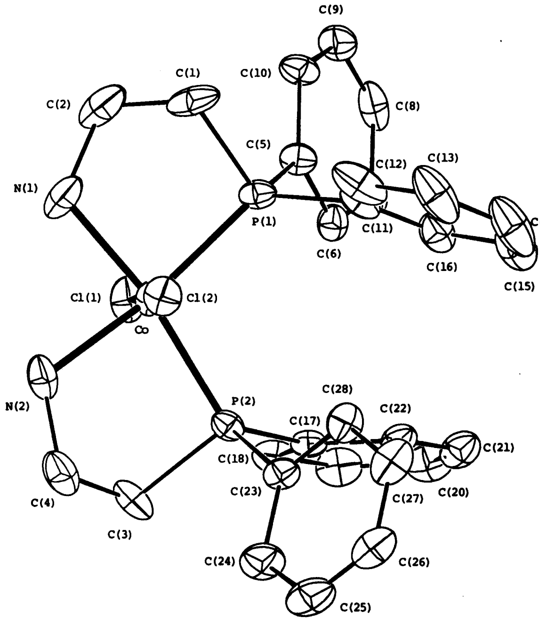


Fig. 1. The *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2(edpp)_2]^+$ ion viewed along the Cl–Co–Cl axis. The thermal ellipsoids are drawn at the 30% probability level.

Results and Discussion

Crystal Structures of $[CoCl_2(edpp)_2]1/2[CoCl_4]$ *(A) and* $[CoCl_2(R\text{-}ebpp)_2]ClO_4$ *(B).* Figures 1 and 2 show the X-ray structures of the complex cations in **A** and **B**, respectively. Both cations have a distorted octahedral coordination with two Cl atoms in the *trans* positions and two P (and N) atoms in the *cis* positions. The complex cation in **A** has an approximate two-fold axis running through the Co atom and the mid point of the P···P edge. Thus both edpp chelate rings form the same δδ or λλ chiral conformation, although the crystal has the achiral space group C2/c, comprising of an equal amount of the δδ and λλ conformers. The corresponding perchlorate salt crystallizes in the chiral space group $P3_221$ (or $P3_121$), and all the chelate rings in a crystal should have the same chirality (*vide infra*). Complex **B** contains the optically active ebpp ligand. The absolute configuration of the ligand could not be determined by the X-ray method (Experimental), but has been assigned conclusively to *R* from CD studies of the Pd(II)–dichloro complex of this ligand and the corresponding *S*(C),*S*(P)- and *S*(C),*R*(P)-prbpp complexes.[6] The absolute configuration of the *S*(C),*S*(P)-prbpp complex was determined by the X-ray method.[8] The two *R*-ebpp chelate rings take enantiomeric conformations to each other, δ and λ and the two phenyl (or butyl) groups are disposed in the opposite directions to each other from the plane formed with the two chelate rings. The selected bond distances and angles are given in Tables 4 and 5.

The average Co–P distance in **B** is slightly shorter

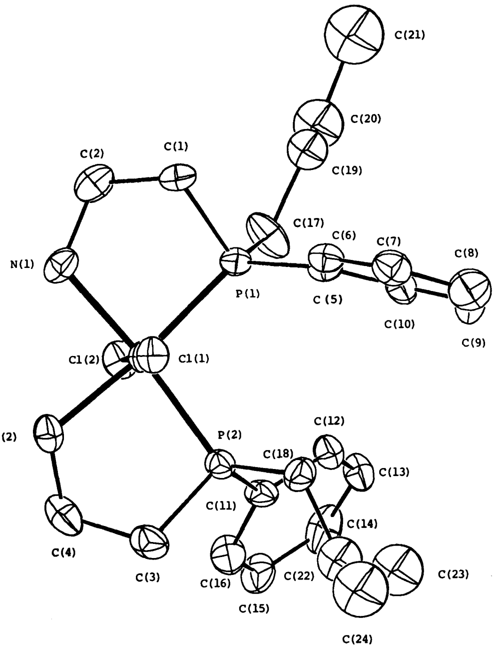


Fig. 2. The *trans*(Cl, Cl), *cis*(P, P)-[CoCl$_2$(*R*-ebpp)$_2$]$^+$ ion viewed along the Cl–Co–Cl axis. The thermal ellipsoids are drawn at the 30% probability level, except for C(24) which is represented by a sphere with arbitrary radius.

than that in **A**, although the difference is not significant in view of the e.s.d.'s. These distances are 0.03—0.10 Å shorter than the Co(III)–P distances found for unidentate phosphine complexes.[13] The Co–N distances range from 2.02 to 2.05 Å which are 0.05—0.07 Å longer than the usual Co(III)–N distance. The lengthening of the Co–N bond has been found in *fac*-[Co(edmp)$_3$]Br$_3\cdot$3H$_2$O (Co–N=2.04 Å).[4] Such elongation of the Co–N distance is ascribable to the trans influence of phosphine ligands.

The chelate P–Co–N angles in both complexes are less than 90° and similar to the N–Co–N angles in Co(III) complexes of en and its derivatives.[14] In the chelate rings, the average P–C distance of 1.84 Å is *ca.* 0.30 Å longer than the N–C distance. The Co–P–C angle is *ca.* 9—10° smaller than the tetrahedral angle, while the Co–N–C angle is *ca.* 6° greater than the tetrahedral one.

For bis- and tris(aminoalkyl)phosphine complexes, the two phosphino groups tend to prefer the *cis* positions as have been found in the present complexes and *fac*-[Co(edmp)$_3$]$^{3+}$.[4] No fraction indicative of the *trans*-(P,P) isomer was obtained in column chromatography. The *cis* disposition of the phosphino groups seems to be unfavorable in view of the inter-ligand overcrowding among bulky substituents on the P atoms. However, such overcrowding appears to be alleviated by i) widenning the P–Co–P angle to 103.1° (**A**) and 99.4° (**B**), and ii) varing the Co–P-substituent angle (116°—122°) so as to keep inter-ligand contact distance normal. Such large deviations from the normal angle would cause strain in the ligand. The *cis* preference of the phosphino groups at the expence of the strain of the

Table 4. Selected bond lengths and angles in *trans*-[CoCl$_2$(edpp)$_2$]1/2[CoCl$_4$][a]

Bond length	l/Å		l/Å
Co(2)–Cl(1)	2.239(3)	P(2)–C(17)	1.838(9)
Co(2)–Cl(2)	2.240(3)	P(2)–C(23)	1.817(9)
Co(2)–P(1)	2.255(3)	N(1)–C(2)	1.52(2)
Co(2)–P(2)	2.254(3)	C(1)–C(2)	1.52(1)
Co(2)–N(1)	2.028(8)	C(1)–P(1)	1.842(9)
Co(2)–N(2)	2.020(7)	N(2)–C(4)	1.49(2)
P(1)–C(5)	1.831(10)	C(3)–C(4)	1.54(2)
P(1)–C(11)	1.819(7)	C(3)–P(2)	1.843(8)
Bond angle	ϕ/°		ϕ/°
Cl(1)–Co(2)–Cl(2)	175.8(1)	C(2)–C(1)–P(1)	105.9(6)
Cl(1)–Co(2)–N(1)	87.9(3)	Co(2)–P(1)–C(1)	98.1(4)
Cl(1)–Co(2)–P(1)	93.1(1)	Co(2)–P(1)–C(5)	119.6(2)
Cl(1)–Co(2)–N(2)	88.9(2)	Co(2)–P(1)–C(11)	121.3(4)
Cl(1)–Co(2)–P(2)	89.1(1)	C(5)–P(1)–C(11)	103.0(4)
Cl(2)–Co(2)–N(1)	89.1(3)	N(2)–Co(2)–P(2)	85.6(2)
Cl(2)–Co(2)–P(1)	89.6(1)	Co(2)–N(2)–C(4)	115.8(5)
Cl(2)–Co(2)–N(2)	87.9(2)	N(2)–C(4)–C(3)	107.8(9)
Cl(2)–Co(2)–P(2)	93.5(1)	C(4)–C(3)–P(2)	104.4(6)
N(1)–Co(2)–N(2)	85.2(4)	Co(2)–P(2)–C(3)	98.2(3)
P(1)–Co(2)–P(2)	103.1(1)	Co(2)–P(2)–C(17)	122.2(3)
N(1)–Co(2)–P(1)	86.2(3)	Co(2)–P(2)–C(23)	120.0(3)
Co(2)–N(1)–C(2)	115.4(6)	C(17)–P(2)–C(23)	103.6(4)
N(1)–C(2)–C(1)	108.6(10)		
		Cl(3)–Co(1)–Cl(4)	110.1(1)
		Cl(3)–Co(1)–Cl(3′)	117.0(1)
		Cl(3)–Co(1)–Cl(4′)	104.7(1)
		Cl(4)–Co(1)–Cl(4′)	110.2(2)

a) Primed atoms are those in the equivalent position $(1-x, y, (1/2)-z)$.

TABLE 5. SELECTED BOND LENGTHS AND ANGLES IN *trans*-[$CoCl_2$(*R*-ebpp)$_2$]ClO_4

Bond length	l/Å		l/Å
Co–Cl(1)	2.248(2)	C(1)–P(1)	1.845(10)
Co–Cl(2)	2.227(3)	N(2)–C(4)	1.46(1)
Co–P(1)	2.235(3)	C(3)–C(4)	1.60(2)
Co–P(2)	2.229(3)	C(3)–P(2)	1.823(10)
Co–N(1)	2.048(7)	P(1)–C(5)	1.792(9)
Co–N(2)	2.037(8)	P(1)–C(17)	1.825(10)
N(1)–C(2)	1.50(2)	P(2)–C(11)	1.815(9)
C(1)–C(2)	1.55(1)	P(2)–C(18)	1.794(9)
Bond angle	ϕ/°		ϕ/°
Cl(1)–Co–Cl(2)	175.0(1)	C(2)–C(1)–P(1)	105.1(7)
Cl(1)–Co–N(1)	89.1(2)	Co–P(1)–C(1)	98.8(3)
Cl(1)–Co–N(2)	87.5(2)	Co–P(1)–C(5)	120.7(3)
Cl(1)–Co–P(1)	89.8(1)	Co–P(1)–C(17)	115.7(4)
Cl(1)–Co–P(2)	89.8(1)	C(5)–P(1)–C(17)	105.8(5)
Cl(2)–Co–N(1)	88.1(2)	N(2)–Co–P(2)	86.8(2)
Cl(2)–Co–N(2)	88.3(2)	Co–N(2)–C(4)	114.8(6)
Cl(2)–Co–P(1)	94.0(1)	N(2)–C(4)–C(3)	108.6(8)
Cl(2)–Co–P(2)	92.7(1)	C(4)–C(3)–P(2)	106.5(7)
N(1)–Co–N(2)	87.8(3)	Co–P(2)–C(3)	100.8(3)
P(1)–Co–P(2)	99.4(1)	Co–P(2)–C(11)	117.9(3)
N(1)–Co–P(1)	85.9(2)	Co–P(2)–C(18)	119.5(3)
Co–N(1)–C(2)	115.7(6)	C(11)–P(2)–C(18)	106.4(4)
N(1)–C(2)–C(1)	108.3(8)		

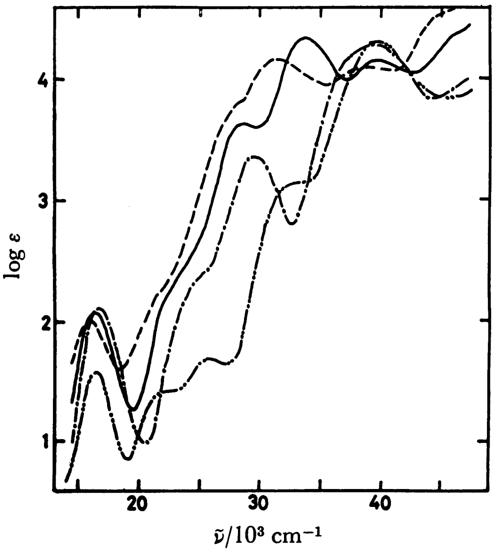


Fig. 3. Absorption spectra of *trans*(Cl, Cl), *cis*(P, P)-[$CoCl_2L_2$]$^+$ in methanol, L: edpp (------), edmp (·-·-), *R*-ebpp (——),-and *trans*-[$CoCl_2$(*S*-pn)$_2$]$^+$ (-··-··) in methanol.

ligand suggests that the *trans*(P,P) configuration is unfavorable because of the mutual trans influence of P atoms.

The complex ions in **A** and **B** have a very similar coordination geometry, but there is a slight difference between the structural parameters. The P–Co–P angle in **B** is 3.7° smaller than that in **A**. All of the inter-ligand distances among substituents on the P atoms in **B** are longer than 4.0 Å, but some of them in **A** are less than 4.0 Å (*ca.* 3.7 Å). These facts indicate that the

TABLE 6. ABSORPTION (AB) AND CD SPECTRAL DATA IN THE d-d TRANSITION REGION

trans(Cl, Cl)-type complex	$\tilde{\nu}_{AB}$/10^3 cm^{-1} (log ε)	$\tilde{\nu}_{CD}$/10^3 cm^{-1} (Δε)
[$CoCl_2$(edpp)$_2$]$^+$	15.9(2.03)	
	21.5(2.1)sh	
[$CoCl_2$(edmp)$_2$]$^+$	16.6(2.14)	
	23.8(2.2)sh	
[$CoCl_2$(*S*-pdpp)$_2$]$^+$	16.1(1.92)	15.5(+1.75)
		17.2(−0.67)
	21.5(2.0)sh	21.9(−3.25)
[$CoCl_2$(*R*-ebpp)$_2$]$^+$	16.3(2.08)	15.9(+1.27)
		18.2(−0.06)
	23.0(2.3)sh	23.4(−2.80)
[$CoCl_2$(*S*-prdpp)$_2$]$^+$	15.5(2.02)	15.0(+1.77)
		16.7(−0.92)
	21.5(2.1)sh	20.5(−1.39)
[$CoCl_2${*S*(C), *R*(P)-prbpp}$_2$]$^+$	15.9(1.85)	15.4(+0.88)
		17.3(−0.36)
		20.7(+0.32)
	22.7(2.5)sh	22.7(−0.18)
[$CoCl_2${*S*(C), *S*(P)-prbpp}$_2$]$^+$	15.9(1.94)	14.6(+0.05)
		16.4(−0.59)
	22.7(2.5)sh	23.8(+0.82)sh
[$CoCl_2$(*S*-pn)$_2$]$^+$	16.3(1.60)	16.5(−0.81)
	22.0(1.43)	21.5(+0.11)
	25.7(1.69)	

Solvent: methanol. sh: shoulder

–P(C_4H_9)(C_6H_5) group is smaller in bukiness than the –P(C_6H_5)$_2$ group. This is in accord with the cone angle for these groups.[15] On the other hand, the –P(C_4H_9)(C_6H_5) group should be more basic than the –P(C_6H_5)$_2$ one, since in phenylphosphines, replacement of a phenyl substituent by an alkyl one generally increases basicity of a phosphine.[16] Thus the smaller and more basic –P(C_4H_9)(C_6H_5) group would form a stronger Co–P bond and hence would exert stronger trans influence on a trans ligand than the case of the –P(C_6H_5)$_2$ group. Indeed, the Co–P bonds in **B** are shorter than those in **A**, while the Co–N bonds in **B** are longer than those in **A**, although the differences are less significant on the statistical ground.

Nonbonded distances in both crystals are normal. The shortest hydrogen bond length is 3.01(1) Å [N-(NH_2)···O(ClO_4)] in the *R*-ebpp complex, and 3.37(1) Å [N(NH_2)···Cl($CoCl_4$)] in the edpp complex.

The geometry of green [$CoCl_2$(edmp)$_2$]$^+$ has not yet been determined. However, this complex ion should also have the *cis*(P,P) configuration in view of the small size and strong basicity of the –P(CH_3)$_2$ group. Other aminoalkyl-diphenyl- and -butylphenyl-phosphine complexes prepared in this study can be assigned to the *cis*(P,P) configuration. In fact, all the complexes show absorption spectral patterns very similar to one another (*vide infra*).

Absorption and CD Spectra. Figure 3 shows absorption spectra of the edpp, *R*-ebpp, and edmp complexes together with that of *trans*-[$CoCl_2$(*S*-pn)$_2$]$^+$ (*S*-pn=(*S*)-1,2-propanediamine), and Table 6 lists the spectral data in the region of 15000 to 25000 cm^{-1} (the d-d transition region). All the (aminoalkyl)phosphine complexes exhibit a medium intensity band at *ca.* 16000 cm^{-1}. This band should correspond to the split component, Ia of the first d-d band of the *S*-pn complex, since the complexes have the *trans*(Cl,Cl), *cis*(P,P) configuration as stated previously, and ligand field strength of these (aminoalkyl)phosphines are similar to or a little stronger than that of *S*-pn.[5] The absorption maxima of these bands are shifted to the high energy side in the order of edpp<*R*-ebpp<edmp complexes. This order is the same as that found for bis(ethylenediamine)complexes of these ligands.[4] The absorption intensities increase in the same order, but it is reverse to that of the bis(ethylenediamine)complexes.

The Ib component and the second d-d bands are observed as shoulders (21000—24000 cm^{-1}) by overlapping of the strong bands (26000—29000 cm^{-1}) which can be assigned to the Co–Cl charge transfer bands.[17] The bands at 31450 and 33600 cm^{-1} of the edpp and *R*-ebpp complexes, respectively, and the shoulder at *ca.* 36500 cm^{-1} of the edmp complex can be assigned to the Co–P charge transfer bands, since the corresponding bis(ethylenediamine) complexes of these phosphine ligands also show similar strong bands at nearly the same wavenumbers. The bands at *ca.* 40000 cm^{-1} can be assigned to another Co–Cl charge transfer band from a comparison with the spectrum of the *S*-pn complex.[17]

As stated previously, the green $[CoCl_2(edpp)_2]ClO_4$ complex crystallizes in the chiral space group. Figure 4a shows the solid CD spectrum of this complex dispersed in Nujol in the d-d transition region. The spectral pattern quite resembles that of *trans*(Cl,Cl)-$[CoCl_2(S\text{-}pdpp)_2]^+$ in methanol (Fig. 4b). The *S*-pdpp complex has two sources of optical activity, the chiral carbon atom and the chiral conformation of the chelate ring. However, the similarity in the two CD spectra indicates that the optical activity of both complexes arises mainly from the chiral conformation of the chelate ring. The *S*-pdpp ligand will be stabilized in the δ conformation with the methyl group disposed equatorially. Thus the chelate rings in the edpp complex given in Fig. 4a should be of the δ conformation. In Fig. 4c is given the CD spectrum of *trans*-$[CoCl_2(S\text{-}pn)_2]^+$ in methanol for comparison. The *S*-pn chelate ring also forms the same δ conformation. However, the spectrum is different to a large extent from those of the *S*-pdpp and edpp complexes.

Figure 5 compares CD spectra of the *S*-pdpp and *S*-prdpp complexes in methanol. Both CD spectra are similar over the whole region, in particular, in the Ia band region. The *S*-prdpp chelate ring should be fixed in the δ conformation, producing a new chiral source on the nitrogen atom (*S*) stereoselectively.[18] Thus it is presumed that the *S*-pdpp chelate ring is conformationally stable in the δ form, and that the vicinal effect of the chiral nitrogen atom in the *S*-prdpp complex is small.

Figure 6 shows CD spectra of a diastereomeric pair of the *S*(C),*S*(P)- and *S*(C),*R*(P)-prbpp complexes. The nitrogen atoms in these isomers are also chiral to form the *S* configuration. The spectra exhibit the main CD bands with different signs in the Ia band region and are almost enantiomeric to each other in the high energy

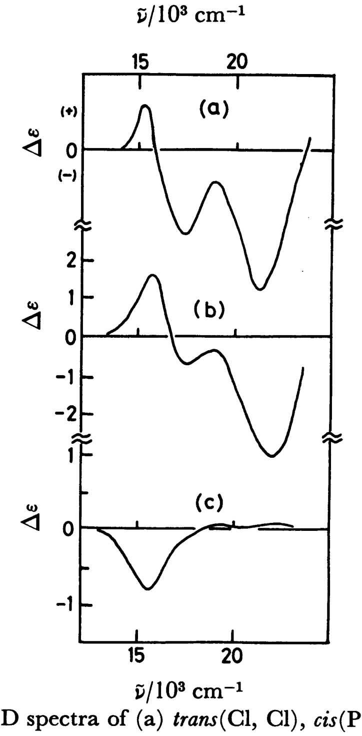


Fig. 4. CD spectra of (a) *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2(edpp)_2]ClO_4$ in Nujol mull, (b) *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2(S\text{-}pdpp)_2]^+$ in methanol, and (c) *trans*-$[CoCl_2(S\text{-}pn)_2]^+$ in methanol.

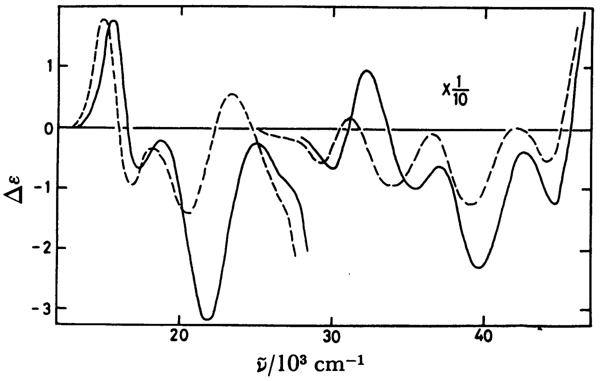


Fig. 5. CD spectra of *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2L_2]^+$ in methanol, L: *S*-pdpp (——), *S*-prdpp (------).

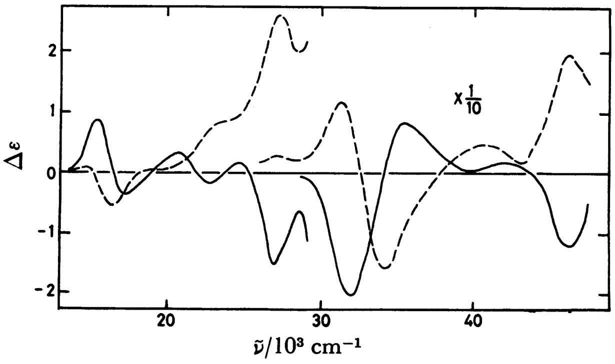


Fig. 6. CD spectra of *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2L_2]^+$ in methanol, L: *S*(C), *R*(P)-prbpp (——), *S*(C), *S*(P)-prbpp (------).

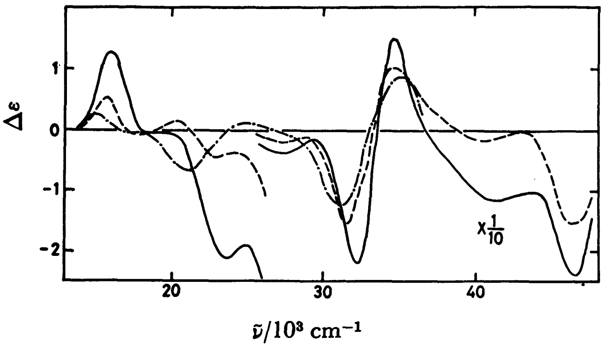
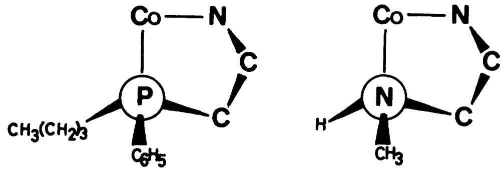


Fig. 7. CD spectra of *trans*(Cl, Cl), *cis*(P, P)-$[CoCl_2(R\text{-}ebpp)_2]^+$ (——) and *trans*(Cl, Cl), *trans*(CH_3, CH_3)-$[CoCl_2\{(R)\text{-}N\text{-}methylethylenediamine\}_2]^+$ (·—·—·)[20] in methanol. The vicinal CD curve (------) for the *R*(P)-ligand obtained from CD curves of a pair of diastereomers, *trans*(Cl, Cl)*cis*(P, P) complexes of *S*(C), *R*(P)- and *S*(C), *S*(P)-prbpp (1/2[Δε{*S*(C), *R*(P)-isomer}-Δε-{*S*(C), *S*(P)-isomer)}).



S-configuration *R*-configuration

Fig. 8. Absolute configuration of donating phosphorus and nitrogen atoms.

region. Thus it is suggested that the vicinal effect of the chiral phosphorus atom is considerably large in these complexes. The vicinal effect of the (*R*)-phosphorus atom can be estimated from the observed CD spectra by calculating 1/2[Δε{*S*(C),*R*(P)-isomer}—Δε{*S*(C),*S*-(P)-isomer}]. The result is compared with the CD spectrum of the *R*-ebpp complex, in which the chiral phosphorus atom is the sole source of optical activity (Fig. 7). Both curves are similar, although there is some difference in strength. In Fig. 7 these curves are compared with the CD spectrum of *trans*(Cl,Cl), *trans*-(CH_3, CH_3)-$[CoCl_2\{(R)\text{-}N\text{-}methylethylenediamine\}_2]^+$ in methanol.[19,20] The CD curve calculated for the vicinal effect of the (*R*)-nitrogen atom in *trans*(Cl,Cl), *trans*(C_2H_5,C_2H_5)-$[CoCl_2\{(2S)\text{-}2\text{-}amino\text{-}4\text{-}azahexane\}_2]^+$ is also very similar to the CD spectrum of the (*R*)-*N*-methylethylenediamine complex.[21] The absolute configuration of the *R*-ebpp ligand is denoted as *S* upon coordination, as stated previously. Thus the (*S*)-phosphorus and (*R*)-nitrogen donor atoms in the *trans*-dichloro-type complex shown in Fig. 8 induce the vicinal effect of the positive sign in the Ia band region.

For the *R*-ebpp complex, the two chelate rings in crystals are diastereomeric to have *R*(δ) and *R*(λ) chiralities, indicating a small energy difference between the two chiral forms of the ring. In solution the chelate ring would exist in the two forms in a similar amount. Hence the CD spectrum of the *R*-ebpp complex would involve a small vicinal effect of the chiral conformation, δ and λ. This is supported by the fact that the spectrum is similar to the vicinal CD curve of the (*R*)-phosphorus atom obtained from a pair of diastereomeric prbpp complexes.

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