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Preparation and Characterization of [Co(acetylacetonato)(diamine or 2,2′-bipyridyl)(aminoalkylphosphine)]$^{2+}$. Crystal Structure of (+)$^{CD}_{531}$-*Λ*-*fac*(*N*)-(Acetylacetonato){(1*R*,2*R*)-1,2-cyclohexanediamine}{(2-aminoethyl)diphenylphosphine}cobalt(III) Perchlorate, $[Co(C_5H_7O_2)(C_6H_{14}N_2)(C_{14}H_{16}NP)](ClO_4)_2$

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Nine new cobalt(III) complexes of the types, [Co(acac)(L)(edpp)]$^{2+}$ (L=ethylenediamine(en), (1*R*,2*R*)-1,2-cyclohexanediamine(*RR*-chxn), 2,2′-bipyridyl(bpy)), [Co(acac)(L′)(empp)]$^{2+}$ (L′=en, bpy), and structurally related [Co(acac)(bpy)(en)]$^{2+}$ were prepared and resolved into optical isomers, where acac, edpp, and empp denote an acetylacetonate ion, (2-aminoethyl)diphenylphosphine, and (2-aminoethyl)methylphenylphosphine, respectively. The molecular structure of (+)$^{CD}_{531}$-[Co(acac)(*RR*-chxn)(edpp)](ClO$_4$)$_2$ was determined by single-crystal X-ray analysis. Crystal data; monoclinic, P2$_1$, a=19.562(3)Å, b=16.882(1)Å, c=9.696(1)Å, β=91.22(1)°, V=3201.3(6)Å^3, Z=4. Three nitrogen donor atoms in the complex ion are arranged in the facial mannar (*fac*(*N*)) and the absolute configuration of the complex ion is *Λ*. The structures of other complexes were assigned by comparing the ^{1}H NMR and circular dichroism spectra with those of the *fac*(*N*)-*Λ*-[Co(acac)(*RR*-chxn)(edpp)]$^{2+}$ complex. The complexes containing a 1,2-diamine yielded selectively the *fac*(*N*) isomer, whereas those containing bpy the *mer*(*N*) isomer.

In our recent studies on cobalt(III)–tertiary phosphine complexes, we have often observed stereoselective formation of a particular geometrical isomer.[1–7] This seems to arise from the steric effect of bulky substituents on a phosphorus donor atom and/or the strong trans effect of a phosphine ligand. In this paper, we have extended the study to cobalt(III) phosphine complexes of the type, [Co(acac)(L)(L′)]$^{2+}$ (L=en, *RR*-chxn, bpy; L′=edpp, empp), where one of the two acac ligands in [Co(acac)$_2$(L′)]$^+$ [6,8] is replaced by the typical chelate ligand with nitrogen donor atoms L. The abbreviations used here are as follows; acac=acetylacetonate ion, en=ethylenediamine, *RR*-chxn=(1*R*,2*R*)-1,2-cyclohexanediamine, bpy=2,2′-bipyridyl, edpp=(2-aminoethyl)diphenylphosphine, empp=(2-aminoethyl)methylphenylphosphine.

Experimental

Phosphine ligands, edpp[9] and empp,[8]* were prepared according to the reported methods and handled under a nitrogen atmosphere until they formed cobalt(III) complexes. Absorption, circular dichroism (CD), and ^{1}H NMR spectra were recorded on a Hitachi 323 spectrophotometer, a Jasco J-40CS spectropolarimeter, and a Jeol JNM-PMX 60 spectrometer, respectively.

Preparation of the Complexes. fac(N)*-[Co(acac)(en)(edpp)]Br$_2$·2H$_2$O*: To a methanol solution (160 cm^3) of [Co(acac)(en)$_2$]Br$_2$[11] (2.5 g, 5.7 mmol) were added edpp (1.17 g, 5.1 mmol) in methanol (10 cm^3) and active charcoal (*ca.* 0.2 g). The solution was stirred at room temperature overnight and then filtered. The filtrate was diluted with water (2 dm^3, pH *ca.* 4 with HCl) and mixed with diethyl ether (500 cm^3) to extract free edpp into the ethereal layer. The aqueous layer was applied on a column (2.5×120 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, three red bands containing [Co(acac)(en)$_2$]$^{2+}$, [Co(acac)(en)(edpp)]$^{2+}$, and [Co(acac)(edpp)$_2$]$^{2+}$ developed in this order. The second eluate containing [Co(acac)(en)(edpp)]$^{2+}$ was collected and concentrated to *ca.* 200 cm^3 under reduced pressure at 45 °C and mixed with an aqueous solution (30 cm^3) of NaB(C$_6$H$_5$)$_4$ (1 g) to give a red precipitate. The precipitate was filtered, washed with water, and then dissolved in a mixture of methanol (500 cm^3) and water (500 cm^3). The solution was applied on a column (2.5×10 cm) of Dowex 1×8 (Br$^-$ form). The eluate was evaporated to dryness under reduced pressure, and the residue was crystallized from water. Yield: 420 mg (13%). Found: C, 39.07; H, 5.55; N, 6.85%. Calcd for $C_{21}H_{35}N_3O_4PBr_2Co$: C, 39.21; H, 5.48; N, 6.53%. The complex is soluble in water and methanol.

fac(N)*-Λ-[Co(acac)(*RR*-chxn)(edpp)](ClO$_4$)$_2$ and* fac(N)*-Δ-[Co(acac)(*RR*-chxn)(edpp)](PF$_6$)$_2$·1.5H$_2$O*: A mixture of [Co(acac)$_3$][12] (5.0 g, 14 mmol), *RR*-chxn (3.2 g, 28 mmol), and active charcoal (*ca.* 0.2 g) in methanol (350 cm^3) was stirred at 25 °C overnight, and filtered. The filtrate was diluted with water (2 dm^3) and applied on a column (5×10 cm) of SP-Sephadex C-25. After red-violet [Co(acac)$_2$(*RR*-chxn)]$^+$ had been eluted from the column with 0.05 mol dm^{-3} NaCl, red [Co(acac)(*RR*-chxn)$_2$]$^{2+}$ was eluted with 0.2 mol dm^{-3} NaCl. The eluate was concentrated to *ca.* 150 cm^3 under reduced pressure at 45 °C. On addition of NaClO$_4$ (5 g) in water (50 cm^3) the concentrate gave a precipitate of a mixture of *Δ*- and *Λ*-[Co(acac)(*RR*-chxn)$_2$](ClO$_4$)$_2$, which was filtered, washed with a small amount of water, and air-dried. Yield: 5.4 g. A mixture of [Co(acac)(*RR*-chxn)$_2$](ClO$_4$)$_2$ (0.90 g, 1.5 mmol), edpp (0.35 g, 1.5 mmol), and active charcoal (*ca.* 0.1 g) in methanol (100 cm^3) was stirred overnight at room temperature. The resulting solution was filtered and subjected to column chromatography in the same way as for the en complex. By elution with 0.2 mol dm^{-3} NaCl, the starting complex, and the *Λ*-(FI) and *Δ*-(FII) isomers of the

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*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.[10] In this paper, we use the same notation for a coordinationg phosphine ligand as that when it is free.

desired complex were eluted separately in this order. The eluate containing FI was diluted ten times with water, applied again on a column (1×10 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 1 mol dm^{-3} $NaClO_4$. The eluate was saturated with $NaClO_4$, and the complex was extracted with chloroform. The chloroform was separated and evaporated to dryness. The residue was crystallized from a mixture of methanol and water (1:1). Yield (FI, Λ-isomer): 94 mg (9%). Found: C, 42.55; H, 5.21; N, 5.62%. Calcd for $C_{25}H_{37}N_3O_{10}PCl_2Co$: C, 42.87; H, 5.32; N, 6.00%.

The formation of the other isomer (FII(Δ)) was poor (*ca.* 1/3 of the Λ-isomer), so that the procedure was repeated several times. The combined eluate containing FII was concentrated to a small volume and mixed with excess $NaPF_6$ to yield a red precipitate, which was recrystallized from a mixture of methanol and water (1:1). Found: C, 36.49; H, 4.52; N, 5.32%. Calcd for $C_{25}H_{40}N_3O_{3.5}P_3F_{12}Co$: C, 36.69; H, 4.93; N, 5.13%. Both complexes FI and FII are soluble in water and methanol.

fac(N)-$\Delta(R),\Lambda(S)$-[Co(acac)(en)(empp)]$Br_2\cdot 2H_2O$ and fac(N)-$\Delta(S),\Lambda(R)$-[Co(acac)(en)(empp)]$Br_2\cdot 1.5H_2O$: These complexes were prepared from $[Co(acac)(en)_2]Br_2$ (0.48 g, 1.05 mmol) and rac-empp (0.18 g, 1.07 mmol) by a method analogous to that for $[Co(acac)(en)(edpp)]^{2+}$. By elution with 0.1 mol dm^{-3} Na_2SO_4, the starting complex, and the $\Delta(R),\Lambda(S)$-(FI) and $\Delta(S),\Lambda(R)$-(FII) isomers of the desired complex were eluted separately in this order. Each eluate containing the empp complex was evaporated to dryness under reduced pressure, and the complex was extracted with ethanol. The extract was applied on a column (1×5 cm) of Dowex 1×8 (Br^- form), and the effluent was evaporated to dryness. The residue was dissolved again in methanol (5 cm^3) and then mixed with diethyl ether (3 cm^3). The solution was stored in a refrigerator, yielding crystals of the complex. Yield: FI (*fac(N)-$\Delta(R),\Lambda(S)$ isomer*), 24 mg (4%); FII (*fac(N)-$\Delta(S),\Lambda(R)$ isomer*), 35 mg (6%). Found for FI: C, 33.26; H, 5.30; N, 7.22%. Calcd for $C_{16}H_{33}N_3O_4PBr_2Co$: C, 33.07; H, 5.72; N, 7.23%. Found for FII: C, 33.88; H, 5.40; N, 7.30%. Cacld for $C_{16}H_{32}N_3O_{3.5}PBr_2Co$: C, 33.59; H, 5.64; N, 7.34%. The complexes are soluble in water and methanol.

mer(N)-[Co(acac)(bpy)(edpp)]$(PF_6)_2$: An *N,N*-dimethylformamide solution (100 cm^3) containing $[Co(acac)(bpy)_2](ClO_4)_2$[13] (440 mg, 0.66 mmol) and edpp (153 mg, 0.67 mmol) was stirred at room temperature overnight. The resulting solution was diluted with 5% aqueous acetic acid (3 dm^3), and the free edpp ligand was extracted with diethyl ether (500 cm^3). The aqueous layer was applied on a column (2.5×50 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, three reddish brown bands containing $[Co(acac)(bpy)_2]^{2+}$, $[Co(acac)(bpy)(edpp)]^{2+}$, and $[Co(acac)(edpp)_2]^{2+}$ were eluted successively. The eluate of the second band was collected and evaporated to *ca.* 50 cm^3 under reduced pressure. On addition of $NaPF_6$ the concentrate gave a reddish brown precipitate, which was filtered and recrystallized from acetone (5 cm^3) by adding water (3 cm^3). Yield: 80 mg (15%). Found: C, 41.96; H, 3.69; N, 5.19%. Calcd for $C_{29}H_{31}N_3O_2P_3F_{12}Co$: C, 41.79; H, 3.75; N, 5.19%. The complex is soluble in methanol and acetone, but hardly in water.

mer(N)-$\Delta(R),\Lambda(S)$-[Co(acac)(bpy)(empp)]$(PF_6)_2$ and mer(N)-$\Delta(S),\Lambda(R)$-[Co(acac)(bpy)(empp)]$(PF_6)_2\cdot 1.5H_2O$: These complexes were prepared by a method similar to that for $[Co(acac)(bpy)(edpp)]^{2+}$ using $[Co(acac)(bpy)_2](ClO_4)_2$ (612 mg, 0.91 mmol) and empp (153 mg, 0.92 mmol). By SP-Sephadex C-25 column chromatography, the eluate containing a mixture of $\Delta(R),\Lambda(S)$- and $\Delta(S),\Lambda(R)$-isomers of *mer(N)*-$[Co(acac)(bpy)(empp)]^{2+}$ was obtained from the second band, the small first and large third bands containing $[Co(acac)(bpy)_2]^{2+}$ and $[Co(acac)(empp)_2]^{2+}$, respectively. The second eluate was diluted with water (1 dm^3) and applied again on a column (2×15 cm) of SE-Toyopearl.[14] The adsorbed band was separated into two (FI and FII in the elution order) by elution with 0.3 mol dm^{-3} NaBr. Each eluate was concentrated to *ca.* 50 cm^3 under reduced pressure, and then mixed with NH_4PF_6 (20 mg) to yield an orange precipitate, which was recrystallized from methanol and water (1:1). Yield: FI(*mer(N)-$\Delta(R)$, $\Lambda(S)$* isomer) 40 mg (6%). FII (*mer(N)-$\Delta(S)$, $\Lambda(R)$* isomer) 20 mg (3%). Found for FI: 37.28; H, 3.71; N, 5.43%. Calcd for $C_{24}H_{29}N_3O_2P_3F_{12}Co$: C, 37.37; H, 3.79; N, 5.45%. Found for FII: C, 35.91; H, 3.64; N, 5.32%. Calcd for $C_{24}H_{32}N_3O_{3.5}P_3F_{12}Co$: C, 36.11; H, 4.04; N, 5.26%. These complexes are soluble in water and common organic solvents such as alcohols, acetone, and chloroform.

[Co(acac)(bpy)(en)]$(PF_6)_2$: An aqueous solution containing $[Co(CO_3)_3]^{3-}$ was prepared from $KHCO_3$ (10 g, 100 mmol) and $CoCl_2\cdot 6H_2O$ (3.5 g, 15 mmol) according to a literature method.[15] The solution was diluted with water (400 cm^3) and then mixed with a solution of bpy (1.8 g, 12 mmol) in methanol (50 cm^3). The solution was stirred at room temperature for 2 h, and then en$\cdot H_2CO_3$[15] (1.7 g, 14 mmol) was added with stirring. After 30 min the solution was stirred at 50 °C for 30 min. The resulting red solution was diluted 100 times with water and applied on a column (5×15 cm) of SP-Sephadex C-25. By elution with 0.03 mol dm^{-3} NaCl, red fractions containing complexes with the +1 charge were collected and concentrated to *ca.* 100 cm^3 under reduced pressure. On addition of $NaBF_4$ (13 g) the concentrate yielded a light brown precipitate of $[Co(CO_3)(bpy)_2]BF_4$, which was filtered off. The filtrate was mixed with additional $NaBF_4$ (5 g), and the mixture was kept at 0 °C for a while, yielding a red precipitate of $[Co(CO_3)(bpy)(en)]BF_4$ (5.8 g). The precipitate was filtered and washed with a small amount of cold water. To an aqueous solution (50 cm^3) of $[Co(CO_3)(bpy)(en)]BF_4$ (0.8 g, 1.9 mmol) were added acetylacetone (0.5 cm^3) and acetic acid (0.3 cm^3). The mixture was stirred at 50 °C for 3 h and then filtered. The filtrate was diluted with water (1 dm^3) and applied on a column (2×50 cm) of SP-Sephadex C-25. The desired red complex was eluted from the column with 0.2 mol dm^{-3} NaCl. The eluate was concentrated to *ca.* 50 cm^3 under reduced pressure. The concentrate was mixed with NH_4PF_6 (50 mg) to yield a red precipitate, which was recrystallized from methanol and water (3:1). Yield: 165 mg (13%). Found: C, 30.70; H, 3.30; N, 8.47%. Calcd for $C_{19}H_{23}N_4O_2P_2F_{12}Co$: C, 30.74; H, 3.49; N, 8.43%. The complex is soluble in methanol, but hardly in water.

Optical Resolution of the Complexes. Optical resolution of the complexes was carried out by an SP-Sephadex C-25 column-chromatographic method using a column (2.5×120 cm) and 0.2 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$ as an eluent.[16] For $[Co(acac)(bpy)(en)]^{2+}$ and isomers FI and FII of $[Co(acac)(bpy)(empp)]^{2+}$, the resolution was complete, while it was incomplete for $[Co(acac)(en)(edpp)]^{2+}$, $[Co(acac)(bpy)(edpp)]^{2+}$, and isomer FII of $[Co(acac)(en)(empp)]^{2+}$. However, the first several fractions of the band containing each of these three complexes showed a constant $\Delta\varepsilon/\varepsilon$ value, and were subjected to CD measurements. No resolution was achieved for isomer FI of [Co(acac)(en)(empp)]$^{2+}$.

The eluate containing the resolved complex was diluted 20 times with water and applied on a column (0.7×5 cm) of SP-Sephadex C-25. After the column had been washed with water, the adsorbed complex was eluted with 1 mol dm^{-3} NaCl, and the effluent was used for CD measurements. The complex concentration in the effluent was determined by measuring the optical density of the first absorption band.

X-Ray Analysis. X-Ray analysis of $(+)^{\mathrm{CD}}_{531}$-[Co(acac)(*RR*-chxn)(edpp)](ClO$_4$)$_2$ (FI) was performed. Crystal Data: monoclinic, $P2_1$, a=19.562(3) Å, b=16.882(1) Å, c=9.696(1) Å, β=91.22(1)°, V=3201.3(6) Å^3, Z=4, D_m=1.45 g cm^{-3}, D_c=1.45 g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha)$=0.832 mm^{-1}. A specimen with dimensions 0.50×0.45×0.45 mm^3 was used for the X-ray work. Diffraction data were collected on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Within the range $2\theta<60°$, 5053 independent reflections with $|F_o|\geq 3\sigma(|F_o|)$ were obtained. In order to determine the absolute configuration, intensity data for Bijvoet pair reflections were also collected up to $2\theta=35°$. The intensity data were corrected for Lorentz-polarization effects, and for absorption.

The calculations of the structure analysis were performed on a HITAC M-180 computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III.[17] The structure was solved by the direct method (MULTAN). The positions of all the hydrogen atoms were identified in subsequent difference-Fourier maps. The structure was refined by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. The weighting scheme, $w=[\sigma^2_{\mathrm{count}}+(0.015|F_o|)^2]^{-1}$, was employed. At the final stage, refinements were carried out on two enantiomeric models, *Λ(R,R)* and *Δ(S,S)*, using 6577 intensities including the Bijvoet pair reflections. The R and R_w values were reduced to 0.052 and 0.065, respectively, for the *Λ(R,R)* configuration, whereas the values were 0.060 and 0.074 for the *Δ(S,S)* model, respectively. Thus application of the R-factor ratio test[18] showed that the *Δ(S,S)* model can be rejected at the 99.5% confidence level. This result is consistent with the fact that *RR*-chxn was used for the preparation of the complex.

Table 1 lists the atomic parameters for non-hydrogen atoms. Complete lists of observed and calculated structure factors, hydrogen atomic parameters, and thermal parameters for non-hydrogen atoms are preserved by the Chemical Society of Japan (Document No. 8539).

Results and Discussion

In general, it is difficult to prepare octahedral complexes comprising of three different kinds of bidentate ligands in good yield.[16,19] The [Co(acac)(en)(edpp)]$^{2+}$ complex was obtained in a 13% yield by reaction of [Co(acac)(en)$_2$]$^{2+}$ with edpp in methanol in the presence of active charcoal. The complex was also obtained by a similar reaction between [Co(acac)$_2$(en)]$^+$ and edpp in a yield of less than 10%. However, no desired complex was formed by reaction of

TABLE 1. ATOMIC PARAMETERS OF *Λ-fac(N)*-[Co(acac)(*RR*-chxn)(edpp)](ClO$_4$)$_2$. POSITIONAL PARAMETERS ARE MULTIPLIED BY 10^5 AND THERMAL PARAMETERS ARE GIVEN BY THE EQUIVALENT TEMPERATURE FACTORS (Å^2)

Atom	x	y	z	B_{eq}
Co(1)	11337(4)	0(6)	53278(8)	3.6
P(1)	18895(10)	−7307(11)	65140(18)	4.1
N(1)	4679(28)	6878(31)	42367(50)	4.1
N(2)	3809(27)	−1224(31)	66428(47)	3.9
N(3)	15258(30)	9215(33)	63600(51)	4.6
O(1)	7463(22)	−8876(25)	44141(39)	4.0
O(2)	18174(23)	1970(25)	40163(43)	4.5
C(1)	−2267(35)	5150(38)	47683(65)	4.0
C(2)	−1715(36)	4792(36)	62779(65)	4.1
C(3)	−8275(43)	3021(44)	70134(74)	5.5
C(4)	−13612(40)	9202(50)	65306(98)	6.6
C(5)	−14359(45)	9172(54)	49246(104)	7.3
C(6)	−7633(40)	11132(41)	42677(79)	5.3
C(7)	8891(38)	−10660(39)	31467(63)	4.4
C(8)	13923(41)	−7050(43)	23726(64)	5.0
C(9)	18376(37)	−1428(41)	28210(65)	4.6
C(10)	4213(51)	−16868(59)	25111(78)	7.4
C(11)	24227(45)	1174(59)	19384(77)	6.8
C(12)	22606(46)	7966(49)	68042(89)	6.7
C(13)	23086(41)	238(51)	76205(87)	6.6
C(14)	16066(39)	−14966(39)	77259(67)	4.5
C(15)	10050(37)	−18874(41)	74613(65)	4.6
C(16)	7686(46)	−24618(46)	83954(73)	5.8
C(17)	11857(45)	−26535(43)	95103(65)	5.6
C(18)	17969(41)	−22478(51)	97233(68)	5.9
C(19)	20033(39)	−16791(44)	88455(65)	4.9
C(20)	25060(39)	−12127(47)	54871(72)	5.3
C(21)	31300(47)	−8608(61)	52285(108)	8.1
C(22)	35846(53)	−12781(89)	42317(122)	11.3
C(23)	34009(55)	−19966(77)	37312(94)	9.2
C(24)	27989(57)	−23397(70)	39975(93)	8.9
C(25)	23436(48)	−19351(54)	48720(82)	7.1
Co(2)	61671(5)	−19423(5)	93969(8)	3.6
P(2)	68874(10)	−11961(11)	81994(18)	4.2
N(4)	55249(29)	−26472(30)	104676(48)	4.0
N(5)	53647(27)	−17839(29)	81572(44)	3.7
N(6)	64996(31)	−28459(32)	83036(54)	4.6
O(3)	58277(24)	−10804(26)	103960(39)	4.4
O(4)	69023(23)	−21807(26)	106056(43)	4.6
C(26)	48280(33)	−24716(40)	99896(62)	3.8
C(27)	48532(35)	−24022(38)	84650(61)	4.0
C(28)	41339(36)	−2211(45)	77983(70)	4.9
C(29)	36379(44)	−28281(53)	82793(92)	6.7
C(30)	35980(40)	−28746(53)	97813(84)	6.2
C(31)	43062(40)	−30879(50)	103974(75)	5.7
C(32)	60264(39)	−9093(41)	116501(69)	4.9
C(33)	65883(43)	−12205(45)	123000(67)	5.5
C(34)	70168(37)	−18120(43)	117525(68)	4.9
C(35)	56017(59)	−2727(58)	123328(85)	8.6
C(36)	76599(46)	−20717(57)	124989(95)	7.7
C(37)	72134(44)	−27211(48)	77758(79)	6.0
C(38)	72233(41)	−19135(49)	70362(80)	5.9
C(39)	65568(35)	−3859(39)	71517(65)	4.2
C(40)	59575(36)	21(43)	74663(64)	4.7
C(41)	57253(42)	6084(46)	66515(69)	5.2
C(42)	60911(45)	8411(48)	55153(88)	6.4
C(43)	66986(44)	4692(51)	51710(76)	6.1
C(44)	69471(36)	−1627(48)	59953(72)	5.1
C(45)	75846(40)	−7704(50)	91984(81)	5.8
C(46)	82083(45)	−11725(66)	93507(96)	7.7
C(47)	87457(52)	−8184(78)	101676(119)	9.9
C(48)	86146(66)	−1415(97)	108233(115)	11.9

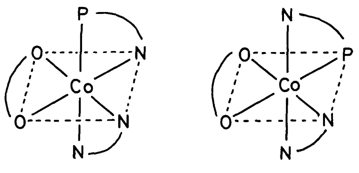
TABLE 1. (Continued)

Atom	*x*	*y*	*z*	B_{eq}
C(49)	80149(69)	2832(68)	106904(107)	10.4
C(50)	74742(57)	−284(60)	98728(87)	8.3
CL(1)	90564(9)	−21127(11)	54618(21)	5.3
CL(2)	59853(9)	−48456(13)	2741(24)	6.3
CL(3)	56553(13)	−26520(18)	46145(20)	7.9
CL(4)	93010(13)	−39501(18)	7(21)	8.1
O(7)	85498(36)	−26661(40)	56674(87)	10.0
O(8)	95948(51)	−25490(49)	49365(129)	14.7
O(9)	88440(47)	−14655(40)	47306(105)	13.1
O(10)	92984(65)	−18032(59)	67305(114)	17.7
O(11)	64845(41)	−42649(47)	4688(90)	11.0
O(12)	62964(53)	−55137(41)	131(118)	13.8
O(13)	54577(52)	−50131(86)	9874(115)	17.4
O(14)	56988(77)	−44388(70)	−7565(154)	21.3
O(15)	57313(38)	−18717(46)	51665(55)	9.6
O(16)	52032(45)	−26082(72)	35010(69)	13.2
O(17)	62494(50)	−28967(54)	40037(106)	13.8
O(18)	53895(47)	−31531(52)	56733(69)	11.5
O(19)	90841(56)	−46236(85)	6047(71)	18.4
O(20)	97053(60)	−41106(74)	−10267(78)	15.7
O(21)	87525(65)	−36405(95)	−5666(179)	22.9
O(22)	96545(72)	−35055(76)	9701(78)	17.1

$[\mathrm{Co(acac)_2(edpp)}]^+$ and en. Other edpp and empp complexes were prepared by methods analogous to that for $[\mathrm{Co(acac)(en)(edpp)}]^{2+}$ from $[\mathrm{Co(acac)(diamine\ or\ bpy)_2}]^{2+}$ and the phosphine ligand. The $[\mathrm{Co(acac)(bpy)_2}]^{2+}$ complex reacted with the phosphine ligand in the absence of active charcoal to give $[\mathrm{Co(acac)(bpy)(phosphine)}]^{2+}$, while the corresponding bis(diamine) complexes did not react under the same conditions.

There are two possible geometrical isomers, *fac(N)* and *mer(N)*, for $[\mathrm{Co(acac)(N{-}N)(N{-}P)}]^{2+}$, where N-N and N-P represent diamine or bpy and aminoalkylphosphine chelate ligands, respectively (Fig. 1). Each of the geometrical isomers has a pair of enantiomers, Δ and Λ, when all the chelate ligands are achiral, and can have a pair of diastereomers, $\Delta(R)(\Lambda(S))$ and $\Lambda(R)(\Delta(S))$, when a chiral ligand is contained. Both $[\mathrm{Co(acac)(en)(edpp)}]^{2+}$ and $[\mathrm{Co(acac)(bpy)(edpp)}]^{2+}$ formed only one of the two possible geometrical isomers as evidenced by column chromatography. The same isomer of $[\mathrm{Co(acac)(en)(edpp)}]^{2+}$ was also yielded selectively by the reaction of edpp with $[\mathrm{Co(acac)_2(en)}]^+$ in place of $[\mathrm{Co(acac)(en)_2}]^{2+}$. Each of $[\mathrm{Co(acac)}(RR\text{-chxn})\mathrm{(edpp)}]^{2+}$, $[\mathrm{Co(acac)(en)(empp)}]^{2+}$, and $[\mathrm{Co(acac)(bpy)(empp)}]^{2+}$ yielded two isomers. However, the isomers were a pair of diastereomers with the same geometrical configuration, *fac*(*N*) or *mer*(*N*). (*vide infra*) Thus the $[\mathrm{Co(acac)(N{-}N)(N{-}P)}]^{2+}$-type complex forms selectively only one of two possible geometrical isomers.

In order to assign geometrical structures of the complexes, a crystal of $(+)^{\mathrm{CD}}_{531}$-$[\mathrm{Co(acac)}(RR\text{-chxn})\mathrm{(edpp)}](\mathrm{ClO_4})_2$ (FI) was subjected to X-ray analysis. There are two crystallographically independent but chemically equivalent complex ions (**1** and **2**). Figure 2 shows a stereoview of complex **1** and the numbering scheme of the atoms. The complex ion has three nitrogen donor atoms arranged in a facial manner and is assigned as the *fac(N)* isomer shown in Fig. 1. The absolute configuration of the complex ion is Λ. The selected bond distances and angles for complex **1** are listed in Table 2. The Co(1)–P distance of 2.224(3) Å (Co(2)–P: 2.234(3) Å) is slightly shorter than those found in *trans*(*Cl*, *Cl*),*cis*(*P*,*P*)-$[\mathrm{CoCl_2(edpp)_2}]_2[\mathrm{CoCl_4}]$ (2.255(3) Å)[4], *trans*(*NCS*, *NCS*),*cis*(*P*,*P*)$[\mathrm{Co(NCS)_2(edpp)_2}]\mathrm{Br}\cdot3\mathrm{H_2O}\cdot(\mathrm{CH_3})_2\mathrm{CO}$ (2.270 Å)[20], and *cis*(*NCS*, *NCS*), *trans*-



fac(N) mer(N)

Fig. 1. Geometrical isomers of $[\mathrm{Co(acac)(N{-}N)(N{-}P)}]^{2+}$.

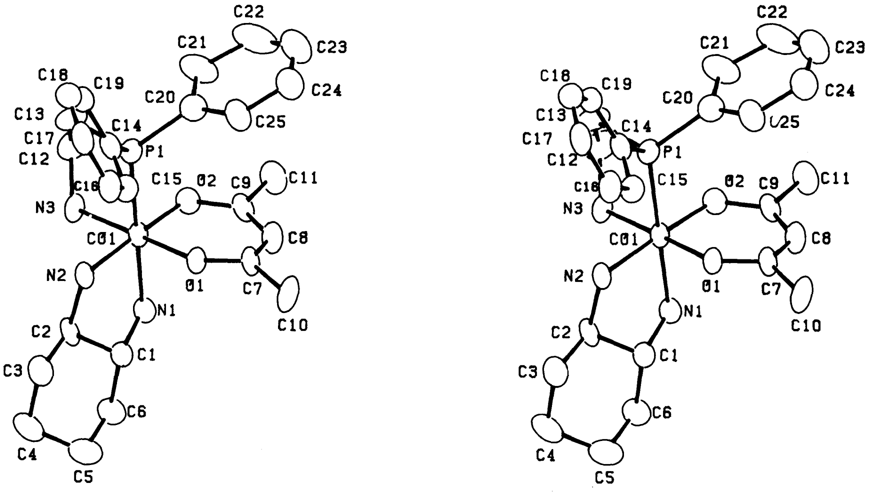


Fig. 2. A stereoview for complex **1**.

Table 2. Selected bond distances (l/Å) and angles (ϕ/°) for complex **1**

Co(1)-P(1)	2.224(3)	N(1)-C(1)	1.521(14)
Co(1)-N(1)	1.975(8)	N(2)-C(2)	1.487(14)
Co(1)-N(2)	2.037(8)	N(3)-C(12)	1.532(16)
Co(1)-N(3)	1.998(9)	O(1)-C(7)	1.299(11)
Co(1)-O(1)	1.899(7)	O(2)-C(9)	1.295(12)
Co(1)-O(2)	1.886(7)	C(1)-C(2)	1.492(14)
P(1)-C(13)	1.855(13)	C(7)-C(8)	1.385(16)
P(1)-C(14)	1.848(12)	C(8)-C(9)	1.325(16)
P(1)-C(20)	1.778(13)	C(12)-C(13)	1.569(18)
P(1)-Co(1)-N(1)	95.6(3)	Co(1)-P(1)-C(13)	102.0(4)
P(1)-Co(1)-N(2)	178.7(3)	Co(1)-P(1)-C(14)	120.5(4)
P(1)-Co(1)-N(3)	86.6(3)	Co(1)-P(1)-C(20)	114.0(4)
P(1)-Co(1)-O(1)	93.1(2)	C(13)-P(1)-C(14)	105.4(5)
P(1)-Co(1)-O(2)	88.8(2)	C(13)-P(1)-C(20)	108.9(6)
N(1)-Co(1)-N(2)	85.7(3)	C(14)-P(1)-C(20)	105.3(6)
N(1)-Co(1)-N(3)	92.9(3)	Co(1)-N(1)-C(1)	108.0(6)
N(1)-Co(1)-O(1)	85.5(3)	Co(1)-N(2)-C(2)	106.0(6)
N(1)-Co(1)-O(2)	175.5(3)	Co(1)-N(3)-C(12)	112.7(7)
N(2)-Co(1)-N(3)	93.1(4)	Co(1)-O(1)-C(7)	121.8(7)
N(2)-Co(1)-O(1)	87.3(3)	Co(1)-O(2)-C(9)	124.8(7)
N(2)-Co(1)-O(2)	90.0(3)	N(1)-C(1)-C(2)	106.2(8)
N(3)-Co(1)-O(1)	178.3(3)	N(2)-C(2)-C(1)	107.3(8)
N(3)-Co(1)-O(2)	86.1(3)	N(3)-C(12)-C(13)	107.3(10)
O(1)-Co(1)-O(2)	95.6(3)	O(1)-C(7)-C(8)	124.8(10)
		O(2)-C(9)-C(8)	123.5(10)
		P(1)-C(13)-C(12)	105.0(8)

(*P,P*)-[Co(NCS)$_2$(edpp)$_2$]Br · CH$_3$OH (2.269 Å).[20] The Co(1)-N(2) distance is longer by *ca.* 0.05 Å than the mean of Co(1)-N(1) and Co(1)-N(3) distances, indicating trans influence of the P donor atom. Elongations of Co-N bonds due to trans influence of a phosphine ligand have been observed in the above trans-dianiono complexes, and *fac*-[Co{NH$_2$CH$_2$CH$_2$P(CH$_3$)$_2$}$_3$]$^{3+}$[7] and related complexes.[1,3,21] Bond angles around P deviate fairly largely from the tetrahedral angle. In particular, the widening of Co(1)-P(1)-C(14) (120.5(4) Å) is noticeable. This widening may be caused by the steric interaction between the phenyl group containing C(14) and the hydrogen atom(s) on N(1) of *RR*-chxn. The other phenyl group is disposed over the acac ring. (Fig. 3) The angle between the best planes of chelate Co-acac and phenyl rings is 25.6 (3) °. The maximum deviations from the best planes of Co-acac and phenyl rings are 0.152 Å and 0.04 Å, respectively. The distance from C(20) to the best plane of the Co-acac ring is 3.062(8) Å. As shown later, such a stacking structure of the phenyl and acac rings causes a high-field shift of the methine proton signal of acac in ^{1}H NMR spectra. The chelate ring formed by *RR*-chxn takes a typical λ gauche conformation, whereas that formed by edpp an envelope conformation.

Table 3 lists ^{1}H NMR data of the complexes. The *fac(N)*-Δ-[Co(acac)(*RR*-chxn)(edpp)]$^{2+}$ isomer (FI) whose structure has been determined shows the methine proton signal of acac at a remarkably high field (5.00 ppm). The high-field shift is attributable to the shielding effect of the phenyl ring disposed over the acac ring.[8] The [Co(acac)(en)$_2$]$^{2+}$ and [Co(acac)$_2$(edmp)]$^+$ (edmp=NH$_2$CH$_2$CH$_2$P(CH$_3$)$_2$) complexes give the corresponding signals at 5.78 ppm,[22] and 5.34 and 5.51 ppm,[8] respectively. The other isomer FII of [Co(acac)(*RR*-chxn)(edpp)]$^{2+}$ also exhibits the methine proton signal at a high field (5.16 ppm) and can be assigned to the same *fac(N)* isomer (Δ-isomer). Thus [Co(acac)(*RR*-chxn)(edpp)]$^{2+}$ yields selectively the *fac(N)* geometrical isomer. In the corresponding *mer(N)* isomer, one of the two phenyl groups on P is to be placed above the puckered *RR*-chxn ring. Molecular models show that the *mer(N)* structure brings about a large steric interaction between the phenyl group and the axial hydrogen atoms on nitrogen and carbon atoms of *RR*-chxn. The interaction will render the *mer(N)* isomer unstable.

The methine protons of [Co(acac)(en)(edpp)]$^{2+}$ and isomer FII of [Co(acac)(en)(empp)]$^{2+}$ resonate at a high field, and both complexes are assigned as the *fac(N)* isomer. For *fac(N)*-[Co(acac)(en)(empp)]$^{2+}$, two racemic pairs of diastereomers, $\Delta(R)$,$\Lambda(S)$ and $\Delta(S)$, $\Lambda(R)$, are possible. (Fig. 4) The former and the latter diastereomers have the phenyl and the methyl groups of empp, respectively over the acac ring. Thus isomer FII of [Co(acac)(en)(empp)]$^{2+}$ is assigned to the racemic pair of *fac(N)*-$\Delta(R)$,$\Lambda(S)$ from a high-field shift of the methine proton signal. The other isomer FI of [Co(acac)(en)(empp)]$^{2+}$ shows the methine proton signal at a low field (5.81 ppm), but exhibits the

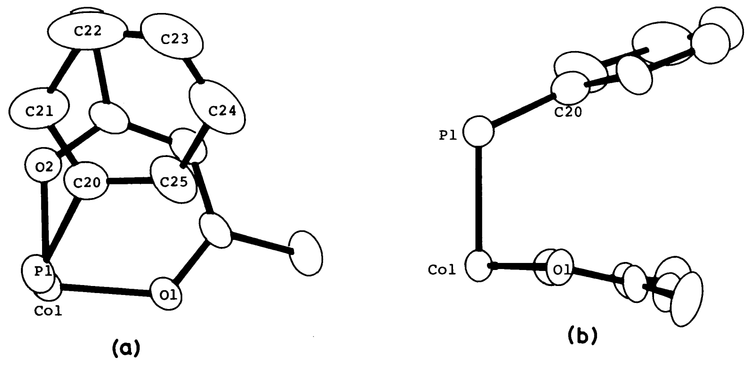
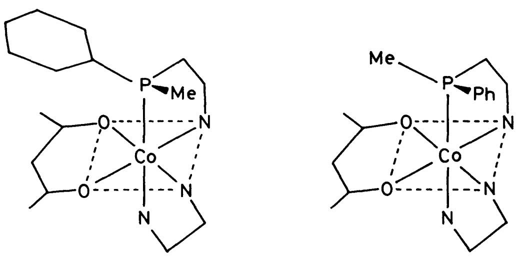


Fig. 3. A stucking structure of the Co-acac and phenyl rings of complex **1**.

TABLE 3. ^{1}H NMR AND ABSORPTION SPECTRAL DATA

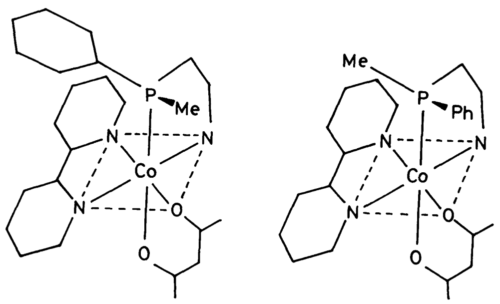
Complex	^{1}H NMR$^{a)}$ (acac)				Absorption$^{b)}$	Assignment
	$-CH_3$		$=CH-$	Solvent		
$[Co(acac)(RR\text{-chxn})(edpp)]^{2+}$(FI)	1.69	2.05	5.00	$CDCl_3$	19.9(2.84)	*fac(N)*-$\Lambda(RR)$
$[Co(acac)(RR\text{-chxn})(edpp)]^{2+}$(FII)	1.67	2.11	5.16	$CDCl_3$	19.9(2.84)	*fac(N)*-$\Delta(RR)$
$[Co(acac)(en)(edpp)]^{2+}$	1.80	2.14	5.14	D_2O	20.0(2.79)	*fac(N)*
$[Co(acac)(en)(empp)]^{2+}$(FI)	2.10	2.13	5.81	CD_3OD	20.8(2.63)	*fac(N)*-$\Delta(R),\Lambda(S)$
$[Co(acac)(en)(empp)]^{2+}$(FII)	1.67	1.84	4.89	CD_3OD	20.6(2.79)	*fac(N)*-$\Delta(S),\Lambda(R)$
$[Co(acac)(en)_2]^{2+}$	2.17		5.78	D_2O	20.0(2.14)	
$[Co(acac)(bpy)(edpp)]^{2+}$	2.12	2.40	5.99	D_2O	20.9(2.88)	*mer(N)*
$[Co(acac)(bpy)(empp)]^{2+}$(FI)	2.16	2.43	6.03	D_2O	21.5(2.62)	*mer(N)*-$\Delta(R),\Lambda(S)$
$[Co(acac)(bpy)(empp)]^{2+}$(FII)	2.06	2.21	6.19	D_2O	21.5(2.64)	*mer(N)*-$\Delta(S),\Lambda(R)$
$[Co(acac)(bpy)(en)]^{2+}$	1.92	2.47	5.83	CD_3OD	19.9(2.23)	

a) δ/ppm from TMS. b) First absorption band peak, $\tilde{\nu}/10^3\,cm^{-1}(\log \varepsilon)$, solvent: CH_3OH for the bpy complexes and H_2O for the other complexes.



Δ(R) Δ(S)

Fig. 4. Diastereomers of *fac(N)*-$[Co(acac)(en)(empp)]^{2+}$.



Δ(R) Δ(S)

Fig. 5. Diastereomers of *mer(N)*-$[Co(acac)(bpy)(empp)]^{2+}$.

P-CH_3 proton signal at a remarkably high field (1.77 ppm) compared with that of the isomer FII (2.17 ppm). The high-field shift will be attributable to the shielding effect of the pseudo aromatic acac ring. Thus isomer FI can be assigned as the racemic pair of *fac(N)*-$\Delta(S),\Lambda(R)$. The assignment is supported by absorption spectra of these two isomers. The first absorption band of isomer FI is at a higher energy and smaller in intensity (20800 cm^{-1}, $\log \varepsilon=2.63$) than that of isomer FII (20600 cm^{-1}, $\log \varepsilon=2.79$), although the spectral patterns are very similar. A similar spectral relation has been observed between the two analogous diastereomers, $\Delta(R),\Lambda(S)$ (19700 cm^{-1}, $\log \varepsilon=2.40$) and $\Delta(S),\Lambda(R)$ (19500 cm^{-1}, $\log \varepsilon=2.62$) of $[Co(acac)_2(empp)]^+$,[8] the first absorption band of the isomer having the phenyl group disposed over the acac ring being more intense and at lower energy than that of the other isomer. Thus $[Co(acac)(en)(empp)]^{2+}$ also forms selectively the *fac(N)* geometrical isomer ($\Delta(R),\Lambda(S)$ (FII), $\Delta(S),\Lambda(R)$ (FI)).

All of the bpy complexes, $[Co(acac)(bpy)(edpp)]^{2+}$ and isomers FI and FII of $[Co(acac)(bpy)(empp)]^{2+}$ exhibits the methine proton signal of acac at a low field (5.99—6.19 ppm). The results suggest that the complexes are the *mer(N)* geometrical isomer. When $[Co(acac)(bpy)(empp)]^{2+}$ has the *mer(N)* structure, two racemic pairs of the diastereomers, $\Delta(R),\Lambda(S)$ and $\Delta(S),\Lambda(R)$ have the phenyl and the methyl groups of empp, respectively over the aromatic bpy ring (Fig. 5). In ^{1}H NMR spectra, isomer FII gives the P-CH_3 proton signal at a remarkably high field (1.20 ppm) compared with that of isomer FI (2.02 ppm). The high-field shift is attributable to the aromatic bpy ring and is more remarkable than that observed for the P-CH_3 protons in *fac(N)*-$[Co(acac)(en)(empp)]^{2+}$ (1.77 and 2.17 ppm), in which the P-CH_3 group is shielded by the pseudo aromatic acac ring. Thus isomer FII of $[Co(acac)(bpy)(empp)]^{2+}$ can be assigned as the racemic pair of *mer(N)*-$\Delta(S),\Lambda(R)$. As described above, neither P-CH_3 nor acac-CH_3 proton signal of isomer FI shows a high-field shift, and thus the isomer is assigned as the racemic pair of *mer(N)*-$\Delta(R),\Lambda(S)$. When the bpy complexes take a *fac(N)* structure, a steric interaction arises between the substituent on P and H on C(3) of bpy. The selective formation of the *mer(N)*-bpy complexes, in contrast to the corresponding *fac(N)*-diamine complexes, will be attributable to this steric interaction in the *fac(N)* structure.

Figure 6 shows absorption and CD spectra of isomers FI and FII of $[Co(acac)(RR\text{-chxn})(edpp)]^{2+}$. While the absorption spectra are similar, the CD spectra are nearly enantiomeric to each other. Since isomer FI has been determined to have the Λ configuration by X-ray analysis, isomer FII is assigned as the Δ isomer. The configurational effect(Λ) curve estimated by $1/2[\Delta\varepsilon(\Lambda)-\Delta\varepsilon(\Delta)]$[23] is very similar to the CD spectrum of $[Co(acac)(en)(edpp)]^{2+}$ which was obtained

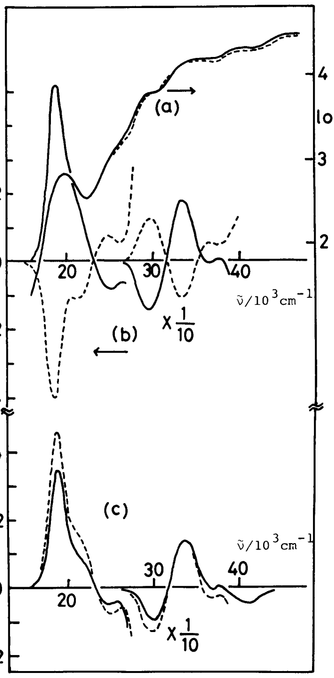


Fig. 6. Absorption (a) and CD (b) spectra of FI (——) and FII (----) isomers of [Co(acac)(*RR*-chxn)(edpp)]$^{2+}$, and the configurational effect (*Λ*) curve estimated by 1/2[Δε(*Λ*)−Δε(*Δ*)] (----) and the CD spectrum of [Co(acac)(en)(edpp)]$^{2+}$ (——) in (c).

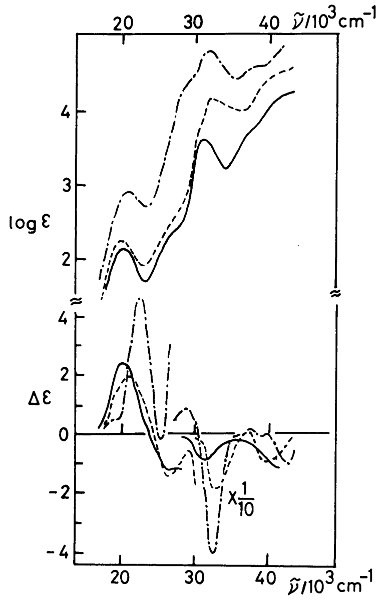


Fig. 7. Absorption and CD spectra of *Λ*-[Co(acac)(en)$_2$]$^{2+}$ (——), [Co(acac)(bpy)(en)]$^{2+}$ (----), and [Co(acac)(bpy)(edpp)]$^{2+}$ (-·-·-·).

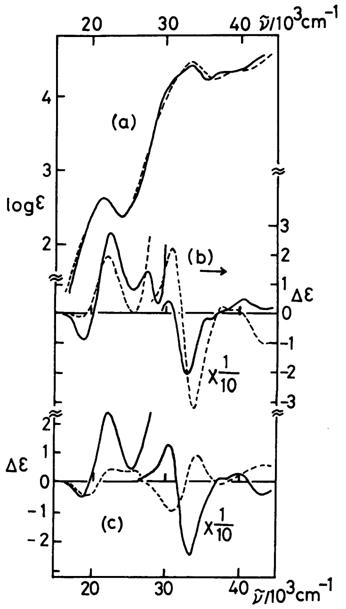


Fig. 8. Absorption (a) and CD (b) spectra of FI (——) and FII (----) isomers of [Co(acac)(bpy)(empp)]$^{2+}$, and the configurational (——) and vicinal (----) effect curves estimated by 1/2[Δε(FI)+Δε(FII)] and 1/2[Δε(FI)−Δε(FII)], respectively, in (c).

from the first fraction in SP-Sephadex C-25 column chromatography (see Experimental) (Fig. 6(c)). Thus the en complex given in Fig. 6(c) is assigned to have the *Λ* configuration. In Fig. 7 are compared the absorption and CD spectra of *Λ*-[Co(acac)(en)$_2$]$^{2+}$[24] with those of [Co(acac)(bpy)(en)]$^{2+}$ and [Co(acac)(bpy)(edpp)]$^{2+}$, both bpy complexes being the faster-moving enantiomer in similar SP-Sephadex C-25 column chromatography. Although the absorption intensity and CD strength of the edpp complex are larger than those of the other complexes over nearly the whole spectral region, the spectral patterns are similar among the three complexes. Thus [Co(acac)(bpy)(en)]$^{2+}$ and [Co(acac)(bpy)(edpp)]$^{2+}$ given in Fig. 7 will have the same absolute configuration as *Λ*-[Co(acac)(en)$_2$]$^{2+}$.

Figure 8 shows absorption and CD spectra of isomers FI and FII of [Co(acac)(bpy)(empp)]$^{2+}$. Both isomers were resolved by SP-Sephadex C-25 column chromatography, and the optically active isomers given in Fig. 8 are those eluted faster in chromatography (see Experimental). Both CD spectral patterns (Fig. 8(b)) are similar, and the isomers will have the same absolute configuration for the arrangement of the chelate rings around Co(III). In Fig. 8(c) are given the configurational and vicinal effect curves estimated by 1/2[Δε(FI)+Δε(FII)] and 1/2[Δε(FI)−Δε(FII)], respectively. The configurational effect curve is similar to the CD spectrum of *Λ*-[Co(acac)(bpy)(edpp)]$^{2+}$ in Fig. 7, indicating the same *Λ* configuration for both optical isomers of FI and FII. Since isomers FI and FII of [Co(acac)(bpy)(empp)]$^{2+}$ have been assigned to racemic pairs, *Δ*(*R*),*Λ*(*S*) and *Δ*(*S*),*Λ*(*R*), respectively, on the basis of the ^{1}H NMR spectra, the optical isomers given in Fig. 8 are assigned to have the *Λ*(*S*)(FI) and *Λ*(*R*)(FII) configurations. Accordingly, the vicinal effect curve should be of the (*S*)-empp ligand. The curve is fairly different from those of an analogous (*S*)-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ (ebpp) ligand estimated from CD spectra of [Co(acac)$_2$(ebpp)]$^{+}$[8] and [Co(en)$_2$(ebpp)]$^{3+}$.[7] In order to relate the absolute configuration of chiral phosphorus donor atoms to CD spectra, more CD data of chiral phosphine complexes will be needed.

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