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Preparation, Resolution, and Spectroscopic Properties of Bis[(2-aminoethyl)diphenylphosphine]- and (Ethylenediamine)[1,2-bis(diphenylphosphino)ethane]-Cobalt(III) Complexes of Acetylacetonate, Malonate, Oxalate, and Carbonate Ions

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New complexes of the [Co(O–O)(edpp)$_2$]- and [Co(O–O)(en)(dppe)]- type were prepared from *trans*(Cl, Cl)-[CoCl$_2$(edpp)$_2$]ClO$_4$ and *trans*-[CoCl$_2$(en)(dppe)]ClO$_4$·H$_2$O, respectively, where O–O is an acetylacetonate, malonate, oxalate, or carbonate ion, and en, edpp, and dppe denote ethylenediamine, (2-aminoethyl)diphenylphosphine, and 1,2-bis(diphenylphosphino)ethane, respectively. All the complexes of the former type gave two geometrical isomers of trans(P, P) and trans(P, N) configurations, which were assigned on the basis of the ^{1}H and ^{13}C NMR, and electronic absorption spectra. No trans(N, N) isomers were formed. The yields of the trans(P, N) isomers were always larger than those of the corresponding trans(P, P) isomers. With the decreasing ring members of the O–O chelates, the yield of the trans(P, P) isomer decreases, the trans(P, P)-carbonato complex being formed in trace amounts. The first absorption bands of the trans(P, P) isomers have very strong intensity as compared with those of the corresponding trans(P, N) and the dppe complexes. All the complexes except for [Co(O–O)(en)(dppe)]$^+$ (O–O=malonate and oxalate ions) were resolved by the chemical or SP-Sephadex C-25 column chromatographic method, and the circular dichroism spectra were recorded and compared with those of related complexes.

In previous papers, we have prepared bis(acetylacetonato)-[1)] and bis(ethylenediamine)cobalt(III)[2)] complexes of (2-aminoethyl)diphenylphosphine (edpp). Since the edpp chelate ligand has two bulky phenyl substituents on the phosphorus atom, inter- or intraligand interactions should be great in octahedral complexes. Stereochemical studies on bulky phosphine metal complexes would be significant in connection with stereoselectivity of transition metal phosphine complex catalysts in asymmetric syntheses. However, few octahedral complexes with bulky phosphine chelate ligands, in particular, those of cobalt(III) are known.[3)] Cobalt(III) complexes with chelate phenylphosphine ligands so far known seem to be limited to those with 1,2-bis(diphenylphosphino)ethylene and *trans*-[Co(CN)$_2$(dppe)$_2$]$^+$ (dppe=1,2-bis(diphenylphosphino)ethane).[4)] This paper reports the preparation, resolution, and spectroscopic properties of two geometrical isomers, trans(P,P) and trans(P,N), of the [Co(O–O)(edpp)$_2$]-type complexes (O–O=acetylacetonate, malonate, oxalate, or carbonate ion). The corresponding [Co(O–O)(en)(dppe)]-type complexes (en=ethylenediamine) were also prepared, and their properties were compared with those of the edpp complexes.

Experimental

(2-Aminoethyl)diphenylphosphine was prepared according to the literature method[5)] and handled under nitrogen atmosphere until it formed cobalt(III) complexes. 1,2-Bis(diphenylphosphino)ethane was purchased from Strem Chemicals Inc. and used without further purification. Absorption, circular dichroism (CD), and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, a JASCO J-40 spectropolarimeter, and Jeol JNM-PMX 60 and JNM-FX 100 spectrometers, respectively.

trans*(Cl, Cl)-[CoCl$_2$(edpp)$_2$]ClO$_4$.* To a methanol solution (100 cm^3) of Co(ClO$_4$)$_2$·6H$_2$O (5.10 g, 13.9 mmol) was added edpp (6.36 g, 27.7 mmol) with stirring. A brown solid (probably [Co(edpp)$_2$] (ClO$_4$)$_2$) was obtained by evaporating the solution under reduced pressure. It was dissolved in dichloromethane, and chlorine gas was bubbled into the solution for 15 min to oxidize the Co(II) ions, giving a green solution. The excess chlorine was removed by bubbling nitrogen, and then the green solution was evaporated to dryness. The green residue was recrystallized by dissolving in hot methanol and by adding excess NaClO$_4$. Yield: *ca.* 50%. The complex is insoluble in water, but soluble in most polar organic solvents.

The perchlorate can be converted to chloride by using Dowex 1×8 (Cl$^-$ form) in methanol. The methanol solution give green crystals by evaporating in a desiccator over P$_2$O$_5$. The chloride, *trans*(Cl,Cl)-[CoCl$_2$(edpp)$_2$]Cl·2H$_2$O is also insoluble in water, but more soluble in organic solvents than the perchlorate is.

trans*-[CoCl$_2$(en)(dppe)]ClO$_4$·H$_2$O.* To a solution of dppe (2.00 g, 5.02 mmol) in a mixture of ethanol (20 cm^3) and benzene (40 cm^3) were added ethylenediamine (0.34 g, 5.66 mmol) and Co(ClO$_4$)$_2$·6H$_2$O (1.90 g, 5.19 mmol) with stirring. The resulting orange brown solution was evaporated to dryness under reduced pressure, and the residue was dissolved in dichloromethane. Chlorine gas was bubbled into the solution for 15 min and then nitrogen gas for 20 min to remove excess chlorine. The green solution obtained was filtered, and the filtrate was evaporated to dryness to give a green product. It was dissolved in methanol by heating at 70 °C for *ca.* 30 min, and the solution was filtered. The filtrate was mixed with excess NaClO$_4$ and allowed to stand at room temperature to yield green crystals. Yield: *ca.* 40%. The complex is insoluble in water, but soluble in most polar organic solvents.

trans*(P, P)-[Co(acac)(edpp)$_2$]Br$_2$·2CH$_2$Cl$_2$ and* trans*(P,N)-[Co(acac)(edpp)$_2$]Br$_2$·3H$_2$O.* An ethanol solution (200 cm^3) containing *trans*(Cl,Cl)-[CoCl$_2$(edpp)$_2$]ClO$_4$ (0.50 g, 0.73 mmol) and lithium acetylacetonate (0.08 g, 0.75 mmol) was stirred at room temperature for 1 h. The resulting red brown solution was diluted with water (1 dm^3) and passed through a column (*ϕ* 3 cm×50 cm) of SP-Sephadex C-25. The product adsorbed was first eluted with a 0.05 mol/dm^3 NaCl solution to remove a dark red by-product, [Co(acac)$_2$-

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$(edpp)]^+$,[1] and then with a 0.4 mol/dm^3 NaCl solution. The orange-red eluate of $[Co(acac)(edpp)_2]^{2+}$ was obtained, diluted twenty times with water, and poured again onto a column (ϕ 3 cm × 150 cm) of SP-Sephadex C-25. By elution with a 0.3 mol/dm^3 KBr solution, two orange-red bands (I and II) appeared. The eluate of the first band (I) was concentrated to a small volume under reduced pressure, and the complex was extracted with CH_2Cl_2. On addition of diethyl ether the extract gave red crystals of *trans*(P, P)$[Co(acac)(edpp)_2]Br_2 \cdot 2CH_2Cl_2$ (I). Yield: *ca.* 10%. The presence of CH_2Cl_2 was confirmed by the ^{1}H NMR spectrum.

The second orange-red eluate was concentrated to a small volume under reduced pressure and allowed to stand to yield red crystals of *trans*(P, N)-$[Co(acac)(edpp)_2]Br_2 \cdot 3H_2O$ (II). Yield: *ca.* 40%.

trans*(P,P)-*$[Co(O\text{–}O)(edpp)_2]^+$ *(O–O=Oxalate (ox) and Malonate (mal) Ions), and* trans*(P,N)-*$[Co(O\text{–}O)(edpp)_2]^+$ *(O–O=*CO_3^{2-}*, ox, and mal Ions).* These complexes were prepared by methods similar to those for the corresponding acetylacetonato complexes. A methanol solution (200 cm^3) containing *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$ (0.50 g, 0.73 mmol), a slight excess of the ammonium salt of O–O (*e.g.*, $(NH_4)_2CO_3$), and a small amount of active charcoal was stirred at 50 °C for 1 h, and then filtered. The red filtrate was diluted with water (1 dm^3) and poured onto a column (ϕ 3 cm × 5 cm) of SP-Sephadex C-25. The SP-Sephadex adsorbed the product was placed on the top of the adsorbent layer of an SP-Sephadex column (ϕ 3 cm × 120 cm). By elution with a 0.05 mol/dm^3 NaCl or KBr solution, two bands, the first orange and the second red, were eluted. The choice of an eluent was made for better crystallization of the complex. In the case of the carbonato complex, the first orange band was too small in the amount to isolate the complex. Each eluate of the separated bands was concentrated under reduced pressure to a small volume. The concentrate gave crystals of the isomer on addition of NaCl or KBr and standing at a refrigerator. The complexes obtained from the first orange and the second red bands are trans(P, P) and trans(P, N) isomers, respectively. The total yields were *ca.* 30—50% for all the complexes. No formation of the trans(N, N) isomer was observed in all the complexes including the acac complex. The formation ratios, trans(P, N): trans(P, P), for the acac, mal, ox, and CO_3^{2-} complexes were 0.25 : 1, 0.08 : 1, 0.03 : 1, and 0 : 1, respectively.

$[Co(acac)(en)(dppe)]Br_2 \cdot 2H_2O$. A methanol solution (250 cm^3) containing *trans*-$[CoCl_2(en)(dppe)]ClO_4 \cdot H_2O$ (0.50 g, 0.71 mmol) and lithium acetylacetonate (0.08 g, 0.75 mmol) was stirred for 24 h at room temperature. The resulting red brown solution was diluted with water (2 dm^3) and poured onto a column (ϕ 3 cm × 50 cm) of SP-Sephadex C-25. The adsorbed red brown product was eluted with a 0.1 mol/dm^3 NaBr solution, giving first the brown-red band of $[Co(acac)_2(dppe)]^+$ [1] and then the red orange band of $[Co(acac)(en)(dppe)]^{2+}$. The eluate of the latter was concentrated to a small volume, and the complex was extracted with $CHCl_3$. The extract was evaporated to dryness, and the residue was dissolved in a small amount of methanol. On addition of diethyl ether the solution gave crystals of $[Co(acac)(en)(dppe)]Br_2 \cdot 2H_2O$. Yield: *ca.* 8%.

$[Co(O\text{–}O)(en)(dppe)]^+$ (O–O=CO_3^{2-}, ox, and mal Ions). These complexes were prepared by methods similar to those for the corresponding bis(edpp) complexes, using *trans*-$[CoCl_2(en)(dppe)]ClO_4 \cdot H_2O$ (0.50 g) instead of *trans*(Cl, Cl)-$[CoCl_2(edpp)_2]ClO_4$. Each of the resulting orange-red solutions was diluted with a water–methanol mixture (1 : 1, 1 dm^3), and the solution was poured onto a column (ϕ 3 cm × 50 cm) of SP-Sephadex C-25. After washing the column thoroughly with water and methanol, the product adsorbed was eluted with a 0.05 mol/dm^3 NaCl or KBr solution. One orange band was eluted. The oxalato complex was isolated as chloride by concentrating the eluate to a small volume and then by storeing in a refrigerator. In a similar manner the malonato complex was obtained as bromide. In the case of the carbonato complex, the eluate obtained with a NaCl solution was concentrated to a small volume, and the concentrate was mixed with $NaClO_4 \cdot H_2O$ to give perchlorate of the complex. The yields of all the complexes were *ca.* 40%.

Optical Resolution. trans*(P, P)- and* trans*(P, N)-*$[Co(acac)(edpp)_2]^{2+}$. The racemic trans(P, P) isomer charged on the top of a column (ϕ 3 cm × 120 cm) of SP-Sephadex C-25 was eluted with an aqueous 0.1 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) solution, giving two bands of the enantiomers. Each eluate of the bands was concentrated to a small volume under reduced pressure. On addition of excess KBr the concentrate gave white precipitate of potassium $(+)_{589}$-tartratoantimonate(III), which was filtered off. The filtrate was mixed with CH_2Cl_2 to extract the complex. The red extract was evaporated to dryness under reduced pressure, and the residue was dissolved in water. The solution was poured again onto a small column of SP-Sephadex C-25, and the complex adsorbed was eluted with an aqueous 0.1 mol/dm^3 KBr solution. The eluate was concentrated to a small volume under reduced pressure, and the concentrate was stored in a refrigerator to yield dark red crystals of optically active bromide of the trans(P, P) isomer. The $(+)_{589}$-isomer was obtained from the first band.

The trans(P, N) isomer was resolved by the same column chromatographic method as that for the trans(P, P) isomer. The eluate of the complex resolved was poured on a small column of SP-Sephadex, and the complex was eluted with 0.1 mol/dm^3 NaCl. On addition of an aqueous $NaClO_4$ solution the eluate gave pink, crystalline precipitate of the active perchlorate. The $(+)_{589}$-isomer was eluted faster than its antipode.

trans*(P, P)-*$[Co(O\text{–}O)(edpp)_2]^+$ *(O–O=ox and mal) and* trans*(P, N)-*$[Co(O\text{–}O)(edpp)_2]^+$ *(O–O=*CO_3^{2+}*, ox, and mal).* These complexes were resolved by a similar column chromatographic method with an aqueous 0.03 mol/dm^3 NaCl solution. The band-separation of enantiomers was incomplete in all cases, and no better separation was resulted by using an eluent of sodium $(+)_{589}$-tartratoantimonate(III). However, the first several fractions showed an almost constant $\Delta\varepsilon/\varepsilon$ value. These fractions were collected and used for the measurement of CD spectra without isolating the active complex.

$[CoCO_3(en)(dppe)]^+$. The racemic $[CoCO_3(en)(dppe)]ClO_4 \cdot 1/2(NaClO_4) \cdot 1.5H_2O$ complex (100 mg) was converted into chloride by stirring with an anion exchanger, Dowex 1×8 in the chloride form in a mixture of methanol (50 cm^3) and water (50 cm^3) at 40 °C for 1 h. The exchanger was filtered off, and the filtrate was mixed with 90 mg of Ag(*d*-bcs)$\cdot H_2O$ (*d*-bcs denotes $(+)_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromo-9-camphorsulfonate ion).[6] The mixture was stirred at 40 °C for 20 min, and then white precipitate of AgCl was filtered off. The filtrate was slowly evaporated in a desiccator over silica gel to yield orange crystals of $(+)_{589}$-$[CoCO_3(en)(dppe)]$(*d*-bcs)$\cdot H_2O$ which were filtered and washed with water. The crystals which are hardly soluble in water were dissolved in methanol. The solution was diluted with about the same volume of water and poured onto a small column of SP-Sephadex C-25. The complex adsorbed was eluted with 0.25 mol/dm^3 NaCl. To the eluate was added an aqueous $NaClO_4$ solution to give orange crystals of $(+)_{589}$-$[CoCO_3(en)(dppe)]ClO_4 \cdot 3.5(NaClO_4) \cdot H_2O$ which were filtered and washed with water.

$[Co(acac)(en)(dppe)]^{2+}$. This complex was resolved by SP-Sephadex column chromatography with an eluent of 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III). Although no good separation of the bands of enantiomers was observed, the first several fractions showed an almost constant $\Delta\varepsilon/\varepsilon$ value. These fractions were collected, diluted with water, and poured onto a small column of SP-Sephadex C-25. The complex adsorbed was eluted with 0.5 mol/dm^3 NaCl, and the eluate was used for the measurement of CD spectra. This complex was not resolved by a chemical method with *d*-bcs similar to that for the corresponding carbonato complex.

Attempts to resolve $[Co(O-O)(en)(dppe)]^+$ (O–O=ox and mal) were unsuccessful.

Analytical data of all the new complexes are given in Table 1.

Results and Discussion

trans*(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$ and* trans-*$[CoCl_2(en)(dppe)]ClO_4 \cdot H_2O$.* A *trans*-dichlorobis(diamine)-cobalt(III) complex is known to be a good starting material for preparing various bis(diamine)cobalt(III) complexes. The $[CoCl_2(edpp)_2]ClO_4$ and $[CoCl_2(en)(dppe)]ClO_4 \cdot H_2O$ complexes prepared in this study have the green color characteristic of a trans(Cl,Cl) configuration, and these chloride ions are easily replaced by the O–O chelate ligand such as an acetylacetonate or oxalate ion. Both dichloro complexes were prepared in fairly good yield from the corresponding cobalt(II) complexes, $Co(edpp)_2(ClO_4)_2$ and $Co(en)(dppe)(ClO_4)_2$ which had been prepared in methanol, by oxidizing with chlorine in dichloromethane. In the oxidation the presence of methanol lowered remarkably the yield of the cobalt(III) complexes, although the reason for this remains unknown. Attempts to prepare these Co(II)-phosphine complexes in dichloromethane were unsuccessful, because $Co(ClO_4)_2 \cdot 6H_2O$ is insoluble in this solvent. The $[CoCl_2(edpp)_2]ClO_4$ complex can also be prepared by oxidizing $Co(edpp)_2(ClO_4)_2$ with air in methanol and by treating with hydrochloric acid, but the yield was very poor.

In Fig. 1 are compared absorption spectra of the two dichlorophosphine complexes with that of *trans*-$[CoCl_2(en)_2]^+$. The phosphine complexes exhibit a medium

TABLE 1. ANALYTICAL DATA OF THE NEW COMPLEXES

Complex		C(%) Found(Calcd)	H(%) Found(Calcd)	N(%) Found(Calcd)
trans(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$	**1**	49.42(48.89)	4.72(4.69)	3.57(4.07)
trans(Cl,Cl)-$[CoCl_2(edpp)_2]Cl \cdot 2H_2O$	**2**	50.89(50.97)	5.11(5.50)	3.84(4.25)
trans-$[CoCl_2(en)(dppe)]ClO_4 \cdot H_2O$	**3**	47.64(47.65)	4.69(4.85)	3.85(3.97)
trans(P,P)-$[Co(acac)(edpp)_2]Br_2 \cdot 2CH_2Cl_2$	**4**	43.82(44.43)	4.65(4.58)	3.06(2.96)
trans(P,N)-$[Co(acac)(edpp)_2]Br_2 \cdot 3H_2O$	**5**	47.96(47.73)	5.00(5.46)	3.18(3.37)
$(+)_{589}$-*trans*(P,P)-$[Co(acac)(edpp)_2]Br_2 \cdot 2.5KBr \cdot 3H_2O$	**6**	35.10(35.14)	3.54(4.02)	2.28(2.48)
$(+)_{589}$-*trans*(P,N)-$[Co(acac)(edpp)_2](ClO_4)_2$	**7**	46.38(46.55)	4.80(5.09)	3.04(3.29)
trans(P,N)-$[Co(CO_3)(edpp)_2]Cl \cdot 3.5H_2O$	**8**	51.76(51.53)	5.81(5.82)	3.82(4.14)
trans(P,P)-$[Co(ox)(edpp)_2]Br \cdot 3H_2O$	**9**	48.61(48.78)	4.78(5.17)	3.72(3.78)
trans(P,N)-$[Co(ox)(edpp)_2]Cl \cdot NaCl$	**10**	51.49(51.52)	4.76(4.61)	3.59(4.00)
trans(P,P)-$[Co(mal)(edpp)_2]Cl \cdot 0.5NaCl \cdot H_2O$	**11**	51.75(51.69)	5.31(5.31)	3.61(3.88)
trans(P,N)-$[Co(mal)(edpp)_2]Br \cdot 0.5KBr \cdot 4H_2O$	**12**	44.60(44.80)	5.62(5.69)	3.37(3.37)
$[Co(acac)(en)(dppe)]Br_2 \cdot 2H_2O$	**13**	48.48(48.79)	5.10(5.33)	3.69(3.45)
$[Co(CO_3)(en)(dppe)]ClO_4 \cdot 0.5NaClO_4 \cdot 1.5H_2O$	**14**	45.47(45.52)	4.16(4.61)	3.22(3.66)
$(+)_{589}$-$[Co(CO_3)(en)(dppe)]$(*d*-$C_{10}H_{14}OBrSO_3$)$\cdot 1.5H_2O$	**15**	51.53(51.21)	5.07(5.34)	2.31(3.06)
$(+)_{589}$-$[Co(CO_3)(en)(dppe)]ClO_4 \cdot 3.5NaClO_4 \cdot H_2O$	**16**	31.92(32.01)	3.26(3.15)	2.49(2.57)
$[Co(ox)(en)(dppe)]Cl \cdot 2H_2O$	**17**	53.00(53.22)	5.45(5.35)	4.03(4.13)
$[Co(mal)(en)(dppe)]Br \cdot 0.5KBr \cdot H_2O$	**18**	48.25(47.93)	4.94(4.67)	3.61(3.61)

TABLE 2. ABSORPTION(AB) AND CD SPECTRAL DATA IN THE VISIBLE TO NEAR ULTRAVIOLET REGION

Complex	AB $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
1,2	15.9 (2.03), 21.5(2.1)^{sh}, 27.5(3.7)^{sh}	
3	16.45(2.13), 22.5(2.6)^{sh}, 27.5(3.5)^{sh}	
6	19.3 (3.52), 24.6(3.91)	18.1(+6.93), 19.9(−1.23), 27.7(−25.3), 23.8(+3.80)
7	19.9 (2.81), 24 (2.9)^{sh}	18.9(+7.53), 22.3(+1.82), 25 (−4)^{sh}, 28.3(−44.1)
8	19.8 (2.55), 25 (2.5)^{sh}	18.7(+3.89), 21.2(−1.85), 24.8(+0.70), 27.3(+0.41)
9	20.4 (3.08), 28.3(4.40)	18.2(+2.14), 20.8(−2.72), 28.2(+6.72)
10	20.0 (2.54), 25 (2.5)^{sh}	18.8(+2.14), 21.6(−0.47), 25.1(+0.58)
11	20.4 (3.12), 27.8(4.49)	18.0(+2.72), 20.4(−4.18), 26.5(+5.65)
12	19.9 (2.56), 25 (2.7)^{sh}	18.7(+3.03), 21.7(−0.44), 25.0(+1.03),28.3(+1.35)
13	20.7 (2.96), 28.5(3.8)^{sh}	17.9(+0.21), 19.7(−2.21), 22.3(+4.89)
14	21.1 (2.90)	18.4(+0.94), 20.2(−1.73), 22.3(+1.81)
17	21.3 (2.91), 26 (2.7)^{sh}	
18	21.0 (2.91), 26 (2.7)^{sh}	

Solvent: CH_3OH except **13**(H_2O). sh: Shoulder.

TABLE 3. ^1H AND ^{13}C NMR SPECTRAL DATA (δ from TMS)

Complex	^1H NMR[a)] acac		^{13}C NMR[b)] acac			edpp					
	CH_3	CH	CH_3	CH	CO	P-CH_2	N-CH_2	P-C_1	o-P	m-P	p-P
2						33.28t	41.64s	130.39t	135.51t	129.57t	132.54s
4	1.71	5.37	27.34s	98.50s	190.69s	24.71t	45.02s	125.00t 128.71t	132.66t 133.34t	129.63t 131.39t	131.98s 133.64s
5	1.83 2.27	5.17	27.77s 27.56d	100.30s	190.30s 190.66s	25.56d 34.55dd	41.59s 42.24s	122.18dd c	c	c	c
8						26.21d 31.17d	41.90s 42.85s	c	c	c	c
10						23.27d 35.04d	40.60s 41.58s	c	c	c	c
11						24.32t	45.83t	125.10t 128.17t	134.03t 134.42t	130.76t 131.73t	132.95s 134.37s

a) Solvent: $CDCl_3$. b) Solvent: $CDCl_3$ for **4**, **5**, **10**. CD_3OD for **2**, **8**, **11**. c) Not assigned. s: Singlet, d: doublet, dd: doublet of doublets, t: triplet.

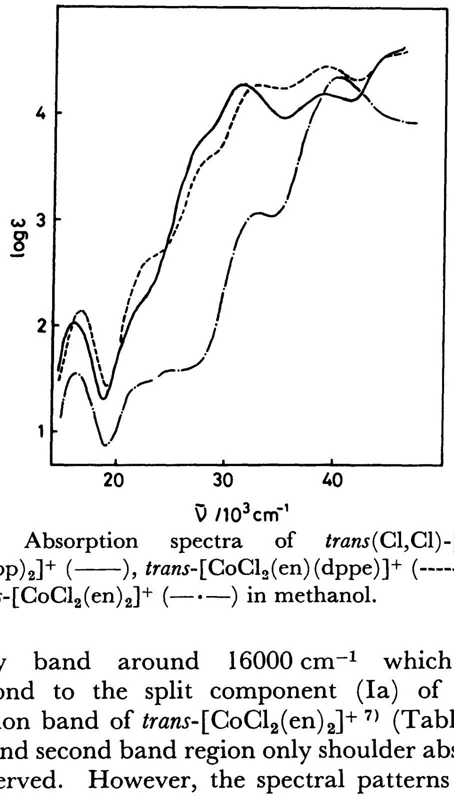


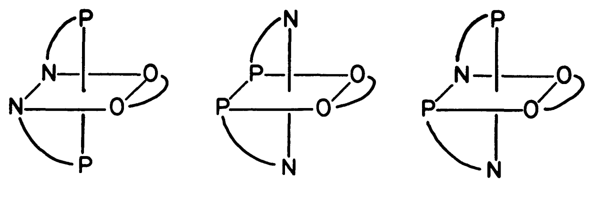
Fig. 1. Absorption spectra of *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]^+$ (——), *trans*-$[CoCl_2(en)(dppe)]^+$ (------), and *trans*-$[CoCl_2(en)_2]^+$ (—·—) in methanol.

intensity band around 16000 cm^{-1} which should correspond to the split component (Ia) of the first absorption band of *trans*-$[CoCl_2(en)_2]^+$ [7)] (Table 2). In the Ib and second band region only shoulder absorptions are observed. However, the spectral patterns of three complexes in Fig. 1 are similar to one another in the d-d transition region. Thus both phosphine complexes can be assigned to have the trans(Cl,Cl) configuration.

The *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]^+$ complex has additional isomerism arising from the arrangement of nitrogen and phosphorus donor atoms, trans(P,P) and cis(P,P). In this study, only one isomer was obtained and no formation of the other was observed on column chromatography of Sephadex LH-20. The structure of the isomer obtained was recently determined to be the cis(P,P) configuration by X-ray analysis.[8)] The preferential formation of the cis(P,P) isomer, in which steric interactions between the two diphenylphosphino groups should be larger than those in the trans(P,P) isomer, might result from a strong trans effect of the phosphine donor group. The absorption spectrum of *trans*(Cl,Cl),*cis*(P,P)-$[CoCl_2(edpp)_2]^+$ quite resembles that of $[CoCl_2(en)(dppe)]^+$ in which the three kinds of donor atoms are in the same geometrical arrangement. In the ^{13}C NMR spectrum, the edpp complex shows clear triplet signals for all the carbons except for the N-CH_2 and *p*-C of the phenyl group. Appearance of the triplet signals is attributable to the presence of coupling between the two phosphorus atoms in the cis positions (Table 3). Such virtual coupling has been observed for octahedral phosphine complexes of both trans(P,P) and cis(P,P) configurations, although it is observed for almost only a trans(P,P) complex in a four-coordinate, planar type.[1,3)]

$[Co(O\text{-}O)(edpp)_2]^{n+}$ and $[Co(O\text{-}O)(en)(dppe)]^{n+}$ Complexes. The acac and other O-O chelate complexes of edpp were prepared from *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$ and lithium acetylacetonate in ethanol in the absence of active charcoal, and ammonium salts of the O-O anions in methanol in the presence of active charcoal, respectively. The corresponding dppe complexes were prepared by similar methods from *trans*-$[CoCl_2(en)(dppe)]ClO_4\cdot H_2O$. For the mal, ox, and CO_3^{2-} complexes, the use of the ammonium salts was necessary. No reactions took place with the sodium or potassium salts. All the complexes thus obtained are stable to air in the solid state, and soluble in water, alcohols, CH_2Cl_2, and $CHCl_3$. The complexes in solution, however, decompose gradually on heating above 60—70 °C to give Co(II) species, the acac complexes being the most stable. The CO_3^{2-} complexes regenerate the original *trans*-dichloro complexes by heating with hydrochloric acid.

Attempts to prepare $[Co(acac)(en)(dppe)]^{2+}$ by other methods were all unsuccessful. For example, reactions between $[Co(acac)_2(dppe)]^+$ [1)] and en, and $[Co(acac)_2(en)]^+$ and dppe gave $[Co(acac)_2(en)]^+$ and $[Co(acac)(en)_2]^{2+}$, and $[Co(acac)_2(dppe)]^+$, respectively as main products, no desired complex being formed. In general, there is no convenient method for preparing cobalt(III) complexes consisting of three different chelate ligands. A good method for preparing such complexes is to derive from a *trans*-dichloro complex with two different chelate ligands, although preparative methods for which



Λ-trans(P,P) Λ-trans(N,N) Λ(S)-trans(P,N)

Fig. 2. Geometrical isomers of the [Co(O–O)(edpp)$_2$]-type complex.

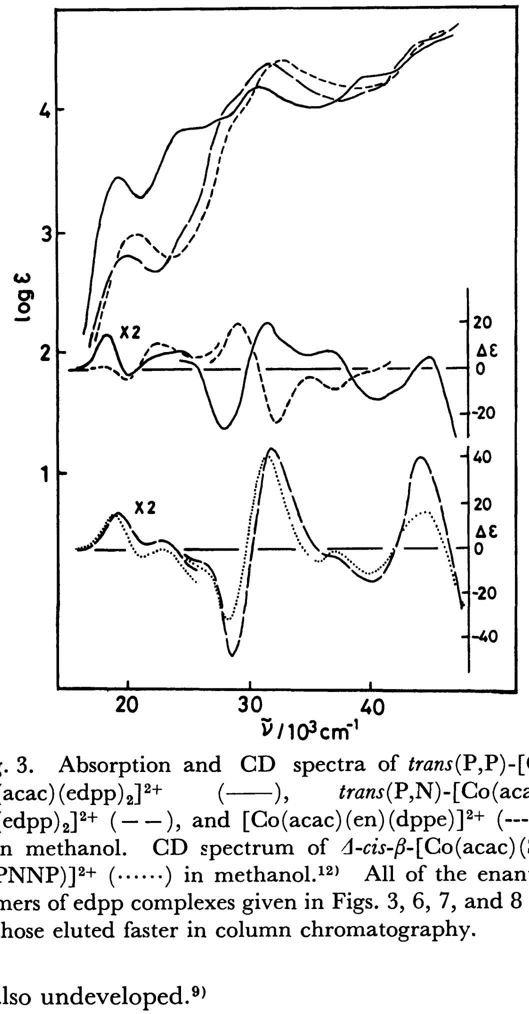


Fig. 3. Absorption and CD spectra of *trans*(P,P)-[Co(acac)(edpp)$_2$]$^{2+}$ (——), *trans*(P,N)-[Co(acac)(edpp)$_2$]$^{2+}$ (— —), and [Co(acac)(en)(dppe)]$^{2+}$ (-----) in methanol. CD spectrum of Δ-*cis*-β-[Co(acac)(SS-PNNP)]$^{2+}$ (······) in methanol.[12] All of the enantiomers of edpp complexes given in Figs. 3, 6, 7, and 8 are those eluted faster in column chromatography.

are also undeveloped.[9]

The [Co(O–O)(edpp)$_2$]-type complex has three possible geometrical isomers, trans(P,P), trans(P,N), and trans(N,N) (Fig. 2). Except for the CO_3^{2-} complex, all the O–O complexes yielded two isomers. Only one isomer was obtained for the CO_3^{2-} complex, a trace of the other being formed. Isomers of I and II of [Co(acac)(edpp)$_2$]$^{2+}$ are red and orange-red in color, respectively, and show one and two kinds of the methyl signals for the acac part, respectively in the ^{1}H NMR spectra (Table 3). Thus I and II can be assigned to either trans(P,P)(C_2) or trans(N,N)(C_2), and trans-(P,N)(C_1) isomers, respectively from symmetry argument. Isomer I as well as isomer II gives the methine proton signal at a higher field than that of the [Co(acac)(en)$_2$]$^{2+}$ complex.[10] The methine proton signal should shift to the high field when the complex has the trans-(P,P) configuration, since it is shielded by the phenyl group of the phosphine ligand disposed over the acac ring.[1] Thus isomer I can be assigned to the trans(P,P) isomer. The magnitude of the high field shift is fairly small as compared with those of bis(acac) complexes of a phenyl-substituted tertiary phosphine. However, the absorption spectrum confirms the trans(P,P) configuration for isomer I. Figure 3 shows absorption spectra of trans(P,P)(I) and trans(P,N)(II) isomers of [Co(acac)(edpp)$_2$]$^{2+}$. The former gives the very strong first absorption band and shows the remarkable red shift in the charge transfer bands as compared with the corresponding bands of the latter. Similar spectral differences have been observed between the trans(P,P) and cis(P,P) isomers of [Co(acac)$_2$(PMe$_2$Ph)$_2$]$^+$.[11] The absorption spectrum of the trans(P,N) isomer (II) resembles that of [Co(acac)(en)(dppe)]$^{2+}$ in which the donor atoms are arranged in the same manner, although the whole spectrum of the dppe complex shifts to the high energy side.

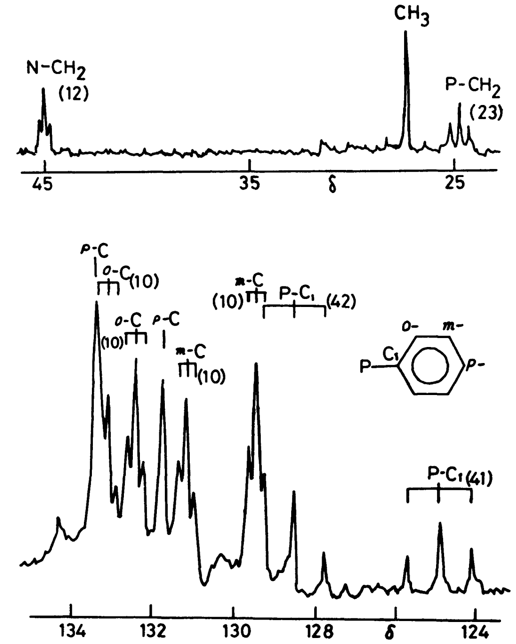


Fig. 4. ^{13}C NMR spectrum of *trans*(P,P)-[Co(acac)(edpp)$_2$]$^{2+}$. The number in parentheses is a coupling constant in Hz.

The ^{13}C NMR spectrum of the *trans*(P,P)-[Co(acac)(edpp)$_2$]$^{2+}$ isomer is shown in Fig. 4. Each carbon of the acac and of two methylenes of the edpp ligand is observed as one kind of signal. On the other hand, the signals of the phenyl carbons show two kinds of the phenyl group. The two phenyl groups on each phosphorus atom should be diastereotopic in a complex of chiral symmetry. The spectral assignment was made according to the previous work on bis(acac)cobalt(III) complexes of edpp and related ligands.[1] The chemical shifts and coupling constants are all similar among these complexes except one *m*-carbon of isomer I. Its chemical shift (131.4 ppm) is somewhat apart from those of other complexes (*ca.* 129 ppm). The P–CH$_2$ and all carbons of the phenyl groups except for the *p*-carbons show triplet signals owing to the couplings with the two

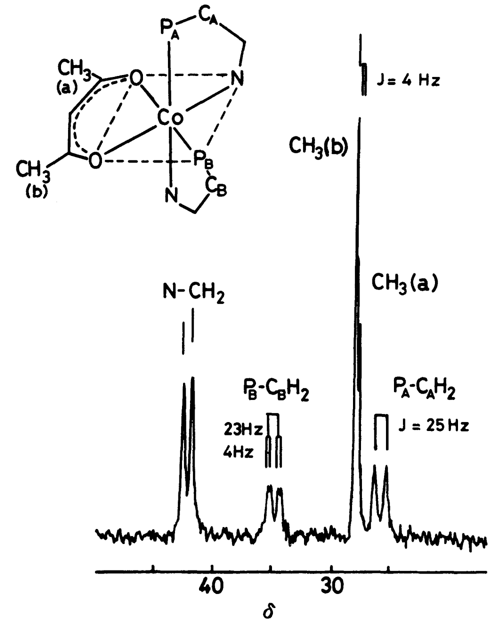


Fig. 5. ^{13}C NMR spectrum of *trans*(P,N)-[Co(acac)-(edpp)$_2$]$^{2+}$.

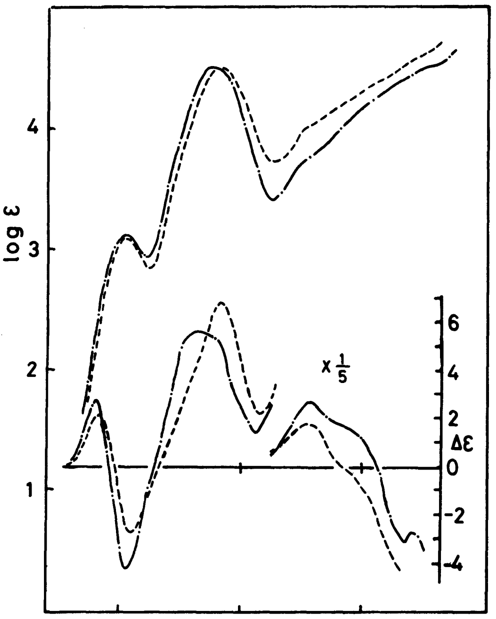


Fig. 6. Absorption and CD spectra of trans(P, P) isomers of [Co(ox)(edpp)$_2$]$^+$ (------) and [Co(mal)-(edpp)$_2$]$^+$ (·—·) in methanol.

phosphorus atoms in the trans positions.

Isomer II shows a complicated ^{13}C NMR spectrum, particularly in the phenyl region, because of C_1 symmetry of the complex. The singlet (27.77 ppm) and the doublet (27.56 ppm, $^4J(P_B,C)=4$ Hz) signals of the methyl groups can be assigned to the CH$_3$(b) and CH$_3$(a), respectively from a comparison of the spectrum of [Co(acac)$_2$(edpp)]$^+$ [1] (Fig. 5). The doublet (25.56 ppm, $^2J(P_A,C_A)=25$ Hz) and the doublet of doublets (34.55 ppm, $^2J(P_B,C_B)=23$ Hz, $^4J(P_A,C_B)=4$ Hz) can be assigned to the C$_A$ and C$_B$, respectively of the P–CH$_2$ groups. The coupling constant between the two phosphorus atoms in the cis positions seems to be practically zero. The two N–CH$_2$ groups show singlet signals with similar chemical shifts (41.59 and 42.24 ppm). The spectrum in the phenyl region is complicated because of the presence of four different phenyl groups, and was not assigned except for one doublet of doublets (122.18 ppm) which can be assigned to the P–C$_1$ bonded to the phosphorus atom.

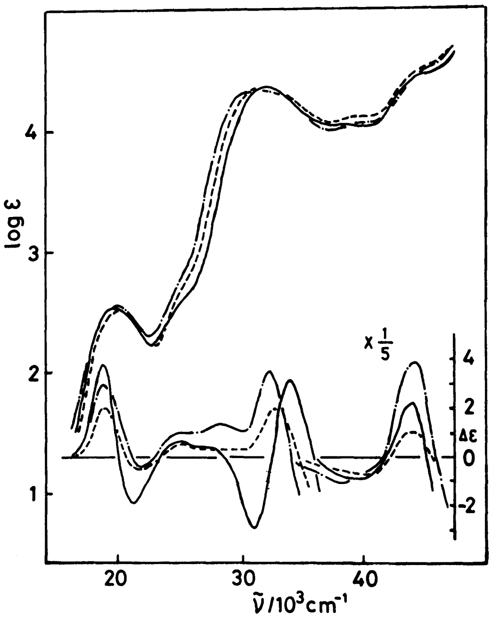


Fig. 7. Absorption and CD spectra of trans(P,N) isomers of [Co(CO$_3$)(edpp)$_2$]$^+$ (——), [Co(ox)(edpp)$_2$]$^+$ (------), and [Co(mal)(edpp)$_2$]$^+$ (·—·) in methanol.

The structures of other [Co(O–O)(edpp)$_2$]$^+$ (O–O= mal, ox, and CO$_3^{2-}$) complexes were also assigned on the basis of the absorption and ^{13}C NMR spectra. Two orange-red isomers of the mal and ox complexes show absorption spectra very similar to each other, and can be assigned to have the same geometrical configuration for the two edpp ligands (Fig. 6). The same conclusions can be given for three red isomers of the mal, ox, and CO$_3^{2-}$ complexes (Fig. 7). The orange-red isomers have strong intensity in the first absorption bands and show a remarkable red shift in the charge transfer bands as compared with the corresponding bands of the red isomers. Such spectral differences between the isomers are the same as those observed for the acac complexes. Thus the orange-red and red isomers can be assigned to trans(P,P) and cis(P,P) (trans(P,N) or trans(N,N)) configurations, respectively. Further, the ^{13}C NMR spectra clearly indicate that the orange-red and red isomers have C_2 and C_1 symmetries, respectively (Table 3). Thus it is concluded that the orange-red and red isomers have trans(P,P) and trans(P,N) configurations, respectively for all the [Co(O–O)(edpp)$_2$]$^+$ complexes.

No trans(N,N) isomers were formed in the [Co(O–O)-(edpp)$_2$]-type complexes. Molecular models indicate that steric hindrance between the two edpp ligands in the [Co(O–O)(edpp)$_2$]-type complex increases in the order of the trans(P,P)<trans(P,N)<trans(N,N) isomers. In particular, the trans(N,N) isomer involves considerable steric hindrance among the phenyl groups. The reason for this isomer being not formed is attributable to such steric hindrance. However, the yields of the more crowded trans(P,N) isomers are always much larger than those of the less crowded trans(P,P) isomers. The less stability of the trans(P,P) isomers should result from the strong trans effect of phosphine donor groups as seen in the *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(edpp)$_2$]$^+$ complex. The formation ratios of the trans(P,P) to trans(P,N) isomers increase with the increasing size of the O–O chelate ligands; trans(P,P): trans(P,N)=0.25 : 1, 0.08 : 1, 0.03 : 1, and 0 : 1 for the acac, mal, ox, and CO$_3^{2-}$ complexes, respectively. When the O–O chelate ligand becomes larger, the more crowded trans(P,N) isomer will become further crowded to decrease the stability, while the less crowded trans-(P,P) isomer will be less affected. Thus the stability difference between the trans(P,N) and trans(P,P) isomers becomes smaller, and the relative yield of the latter increases. The CO$_3^{2-}$ complex with the smallest O–O ligand forms almost only the trans(P,N) isomer.

Figure 3 shows CD spectra of trans(P,P) and trans-(P,N) isomers of [Co(acac)(edpp)$_2$]$^{2+}$, and [Co(acac)-(en)(dppe)]$^{2+}$, all of which are eluted faster on column chromatography. Both edpp complexes exhibit a similar spectral pattern and give a main CD band with the positive sign in the first absorption band region, suggesting *Δ* configuration. However, the CD spectrum of [Co(acac)(*SS*-PNNP)]$^{2+}$ (*SS*-PNNP=(*S,S*)-(C$_6$H$_5$)$_2$PCH$_2$CH(CH$_3$)NHCH$_2$CH$_2$NHCH(CH$_3$)CH$_2$P-(C$_6$H$_5$)$_2$), which forms only the *Δ*-*cis*-*β* isomer stereoselectively owing to the equatorial preference of the methyl group,[12] is quite similar to that of the trans-(P,N) isomer. In the *cis*-*β*-PNNP complex, the geometrical arrangement of N, P, and O donor atoms, and the distribution of chelate rings linking these donor atoms are the same as those in the trans(P,N) isomer when the central –NCH$_2$CH$_2$N– chelate ring is ignored. The presence of the central chelate ring would not play an important role in the CD spectrum of the *Δ*-*cis*-*β*-(*SS*-PNNP) complex, and the vicinal effect of the asymmetric nitrogen donor atoms would also be small. Thus the trans(P,N) isomer in Fig. 3 is assigned to Δ configuration. The trans(P,P) isomer which gives a CD pattern similar to that of the trans(P,N) isomer should also have the same Δ configuration. In addition to the chiral distribution of chelate rings, the *Δ*-trans(P,N) isomer as well as the *Δ*-*cis*-*β*-(*SS*-PNNP) complex involves another chirality of (*R*) configuration[13] arising from the arrangement of N, P, and O donor atoms. The *Δ*-trans-(P,P) isomer has no such chirality. However, the similarlity in the CD spectra of both isomers indicates that the optical activity arises mainly from the chiral distribution of chelate rings, the contribution of the chiral arrangement of donor atoms being small.

The CD spectrum of [Co(acac)(en)(dppe)]$^{2+}$ in Fig. 3 gives a pattern differing from those of the *Δ*-trans(P,N) and -trans(P,P) isomers in the first absorption band region, but nearly the opposite pattern in the higher energy region. The dppe complex has also chirality in the arrangement of the donor atoms, giving Δ(*S*) and Λ(*R*) configurations. The *trans*(P,N)-[Co(acac)-(edpp)$_2$]$^{2+}$ complex forms a different pair of enantiomers from those of the dppe complex, Δ(*R*) and Λ(*S*). Fujinami and Shibata[14] reported CD spectra of cobalt-(III) complexes of a similar type, *Δ*(*R*)-*cis*-[Co(CN)$_2$-(ox)(en)]$^-$ and *Δ*(*R*)-*cis,cis,cis*(C,N,O)-[Co(CN)$_2$(am)$_2$]$^-$ (am=glycinate or *β*-alaninate ion), and concluded that the CD pattern of the *cis,cis,cis*(C,N,O)-[CoC$_2$N$_2$O$_2$]-type complex in the first absorption band region depends mainly on the chiral arrangement of the donor atoms. It seems to be difficult to apply this conclusion to the CD spectrum of [Co(acac)(en)(dppe)]$^{2+}$ in Fig. 3, since it differs considerably from that of the *trans*(P,N)-edpp complex in the first absorption band region. However, the whole CD pattern of the dppe complex appears to be opposite to those of both *Δ*-isomers of the edpp complex. Thus we tentatively assign the dppe complex in Fig. 3 to Λ(*R*) configuration.

The trans(P,N) isomers of the mal, ox, and CO$_3^{2-}$ complexes show CD spectra similar to one another over the whole region (Fig. 7). The spectrum of the CO$_3^{2-}$ complex quite resemble that of *Δ*(*R*)-*cis*-*β*-[Co(CO$_3$)(*SS*-PNNP)]$^+$ prepared as an authentic complex for assigning the absolute configuration.[12] Thus all the isomers in Fig. 7 are assigned to Δ(*R*) configuration, although the CD spectra in the first absorption band region are the pattern characteristic of a *Λ*-tris(chelate) complex. The trans(P,P) isomers of the mal and ox complexes show CD spectra similar to each other (Fig. 6), and the pattern resembles that of *Δ*-trans(P,N) isomers. Since both *Δ*-trans(P,N) and -trans(P,P) isomers of the acac complex exhibit a similar CD spectra, these trans(P,P)

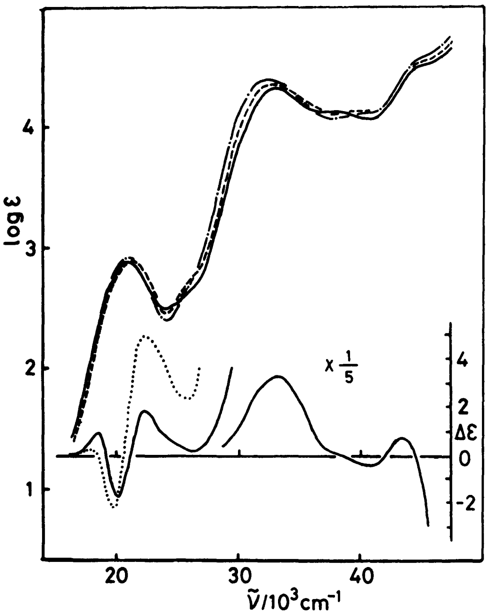


Fig. 8. Absorption spectra of [Co(CO$_3$)(en)(dppe)]$^+$ (——), [Co(ox)(en)(dppe)]$^+$ (------), and [Co(mal)(en)-(dppe)]$^+$ (—•—) in methanol. CD spectra of (+)$_{589}$-[Co(CO$_3$)(en)(dppe)]$^+$ and [Co(acac)(en)(dppe)]$^+$ (······) in methanol.

isomers can be assigned to Δ configuration, although the spectra around 29000 cm^{-1} fairly differ from those of the trans(P,N) isomers. All the trans(P,N) and trans(P,P) isomers given in Figs. 6 and 7 are those eluted faster on column chromatography.

The CD spectrum of $[Co(CO_3)(en)(dppe)]^+$ which was obtained from the less soluble diastereomeric salt with *d*-bcs$^-$ is compared with that of $\Lambda(R)$-$[Co(acac)(en)(dppe)]^{2+}$ in Fig. 8. Both CD spectra are similar in shape in the first absorption band region, although their strength and the spectra in the higher energy region differ remarkably between these complexes. From the similarity in the CD patterns of both isomers in the first absorption band region, we tentatively assign the CO_3^{2-} complex to $\Lambda(R)$ configuration. In order to discuss the optical activity of mixed cobalt(III) complexes containing a phosphine ligand, more CD data will be needed.

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