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Preparation, Resolution, and Absorption and Circular Dichroism Spectra of $[Co(en)_n\{NH_2CH_2CH_2P(CH_3)_2\}_{3-n}]^{3+}$ and the Related Complexes, and the Absolute Configuration of $(+)_{589}$-*fac*-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ Determined by X-Ray Analysis

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A series of complexes, $[Co(en)_n\{NH_2CH_2CH_2P(CH_3)_2\}_{3-n}]^{3+}$ (en=ethylenediamine, n=0,1,2) and three bis(ethylenediamine)cobalt(III) complexes of the related ligands, $NH_2CH_2CH_2P(C_6H_5)_2$, (*S*)-$NH_2CH(CH_3)CH_2P(C_6H_5)_2$, and *rac*-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)$ were prepared and resolved (or separated) into optical isomers, and their absorption and circular dichroism spectra were recorded. The molecular structure and the absolute configuration of $(+)_{589}$-*fac*-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3\cdot 3H_2O$ were determined by X-ray analysis. The crystals are lemon-yellow, orthorhombic, a=26.501(8), b=9.573(4), c=10.081(5) Å, space group $P2_12_12_1$, z=4. The Co atom is surrounded by 3P and 3N in the facial manner with the average distances of 2.237 and 2.041 Å, respectively. The absolute configuration of the complex ion is Δ. The chelate rings are puckered and chiral to form a pseudo λ gauche conformation.

Most of cobalt(III) complexes of tertiary phosphines so far known are those formed with unsaturated ligands such as dimethylglyoximate or acetylacetonate ions, and no complex with saturated ligands such as ammonia or ethylenediamine seems to be reported.[1] In a previous paper,[2] we have reported that (2-aminoethyl)diphenylphosphine and its related ligands, $NH_2CH(R^1)CH_2PR^2R^3$, give stable bis(acetylacetonato)cobalt(III)-type complexes, forming a five- membered chelate ring. This paper is concerned with preparation, resolution, and absorption and circular dichroism (CD) spectra of a series of complexes, $[Co(en)_n\{NH_2CH_2CH_2P(CH_3)_2\}_{3-n}]^{3+}$ (en=ethylenediamine, n=0, 1, 2), and the related complexes. These diamine–alkylphosphine complexes would be useful for studying ligand field absorption spectra of a cobalt(III)–phosphine complex of which little work has been done, since they have no unsaturated group which often shows strong absorption bands in the region where ligand field absorption bands would arise. The paper also reports the molecular structure and absolute configuration of $(+)_{589}$-*fac*-Δ-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ determined by the X-ray method.

Experimental

Free aminoalkylphosphines were handled under nitrogen atmosphere until they formed air-stable cobalt(III) complexes. Absorption, CD, and ^1H 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.

Preparation of Ligands. (2-Aminoethyl)dimethylphosphine (edmp): To liquid ammonia (100 cm³) containing metallic sodium (1.08 g, 0.047 mol) in a 300 cm³ three-necked, round-bottomed flask equipped with a mechanical stirrer and an ammonia gas inlet was added tetramethyldiphosphine[3] (2.88 g, 0.024 mol) with stirring at −78 °C. After 30 min, 2-chloroethylamine hydrochloride (2.74 g, 0.024 mol) was added with small portions, giving a colorless solution. On evaporation of liquid ammonia, a mixture of a white solid and oily edmp was obtained. The edmp was extracted with chloroform (50 cm³). The chloroform was removed *in vacuo* to give transparent, colorless liquid of edmp (1.1 g). It was used for the preparation of complexes without further purification.

(2-Aminoethyl)diphenylphosphine (edpp),[4] *(S)-(2-aminopropyl)-diphenylphosphine (pdpp)*,[2] and racemic[5] and optically active[6] *(2-aminoethyl)butylphenylphosphine (ebpp)* were prepared according to the procedures reported.

Preparation of Complexes. [Co(edmp)₃]³⁺, [Co(en)-(edmp)₂]³⁺, and [Co(en)₂(edmp)]³⁺: These complexes and the known $[Co(en)_3]^{3+}$ complex were yielded by the reaction of *cis*-$[CoCl_2(en)_2]Cl$ with edmp in *N,N*-dimethylformamide (DMF). To a DMF solution (50 cm³) of *cis*-$[CoCl_2(en)_2]Cl$ (285 mg, 1 mmol) was added edmp (105 mg, 3 mmol) with stirring. The resulting blue-green solution was allowed to stir overnight at room temperature to give a yellow precipitate, which was filtered and dissolved in water. The solution was poured onto a column (ϕ 2.7×80 cm) of SP-Sephadex C-25, and the product adsorbed was eluted with an aqueous 0.4 mol/dm³ NaBr solution. A good separation into four yellow bands was observed. The last orange yellow eluate contained $[Co(en)_3]^{3+}$. Each of the other three eluates was diluted ten times with water and poured again onto a small column of SP-Sephadex C-25. The complex adsorbed was eluted with an aqueous 1 mol/dm³ NaBr solution, and the eluate was concentrated in a vacuum desiccator over P_4O_{10} to give yellow crystals, which were filtered, washed with a small amount of water, and air-dried. The first, second, and third eluates gave racemates of $[Co(edmp)_3]Br_3\cdot 3H_2O$, $[Co(en)(edmp)_2]Br_3\cdot H_2O$, and $[Co(en)_2(edmp)]Br_3\cdot H_2O$, respectively. Although the first two complexes can have geometrical isomers, only one isomer was yielded for each of them, no indication for the presence of other isomers being observed on column chromatography. The total yield of the four complexes including $[Co(en)_3]^{3+}$ was *ca.* 70%, and the formation ratio was *ca.* 8:2:1:7 for $[Co(edmp)_3]^{3+}$: $[Co(en)(edmp)_2]^{3+}$: $[Co(en)_2(edmp)]^{3+}$: $[C(en)_3]^{3+}$.

The racemates were resolved by SP-Sephadex column chromatography. Each racemate charged on the top of a column (ϕ 2.7×80 cm) of SP-Sephadex C-25 was eluted with an aqueous 0.2 mol/dm³ sodium $(+)_{589}$-tartratoantimonate(III) solution. A good separation between enantiomers was observed. In the case of $[Co(edmp)_3]^{3+}$ lemon-yellow crystals of optically active $[Co(edmp)_3]Br_3\cdot 3H_2O$ were obtained by the same method as that for the racemate,

TABLE 1. ANALYTICAL DATA OF THE NEW COMPLEXES

Complex	C (%) Found(Calcd)	H (%) Found(Calcd)	N (%) Found(Calcd)
$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3\cdot 3H_2O$	21.08(21.57)	6.28(6.35)	6.28(6.29)
Λ-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3\cdot 3H_2O$	21.24(21.57)	6.24(6.35)	6.22(6.29)
$[Co(en)\{NH_2CH_2CH_2P(CH_3)_2\}_2]Br_3\cdot H_2O$	20.14(20.46)	5.77(5.83)	9.29(9.54)
$[Co(en)_2\{NH_2CH_2CH_2P(CH_3)_2\}]Br_3\cdot 2H_2O$	17.55(17.73)	5.53(5.58)	12.80(12.92)
$[Co(en)_2\{NH_2CH_2CH_2P(C_6H_5)_2\}]Br_3\cdot 2H_2O$	31.37(31.60)	5.20(5.30)	10.15(10.24)
Λ-$[Co(en)_2\{(S)$-$NH_2CH(CH_3)CH_2P(C_5H_5)_2\}]Br_3\cdot 2H_2O$	32.50(32.69)	5.36(5.48)	9.77(10.03)
Λ-$[Co(en)_2\{(R)$-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}]Br_3\cdot 4NaBr$	18.59(18.48)	3.67(3.49)	6.77(6.74)
$[Co(en)_2\{rac$-$NH_2CH_2CH_2P(C_4H_9)(C_6H_5)\}]Br_3\cdot 2H_2O$(Band II)	29.03(28.94)	5.55(6.07)	10.40(10.54)

en: $NH_2CH_2CH_2NH_2$.

The enantiomer obtained from the faster moving band showed negative rotation at 589 nm (Λ-isomer). In the cases of $[Co(en)(edmp)_2]^{3+}$ and $[Co(en)_2(edmp)]^{3+}$, however, the enantiomers were not isolated because of small amounts, and the CD spectra were obtained by the following method. Each eluate of the enantiomers was diluted with water and poured onto a small column of SP-Sephadex C-25. After washing the column with 0.05 mol/dm^3 hydrochloric acid, the enantiomer was eluted with 1 mol/dm^3 hydrochloric acid. The eluate was evaporated to dryness under reduced pressure, and the residue was dissolved in water. On addition of $K_3[Co(CN)_6]$, a yellow precipitate was obtained. It was filtered, washed with water, and then mixed with Dowex 1×8 anion exchange resin in the bromide form and a small amount of water. The mixture was stirred for a few hours and filtered. The filtrate which contains the complex bromide was used for CD measurement, and its concentration was determined from ε values of the racemate. In all the resolutions, the Λ isomers were always eluted faster than their antipodes.

[Co(en)$_2$(edpp)]$^{3+}$. A DMF solution (50 cm^3) containing *cis*-$[CoCl_2(en)_2]Cl$ (363 mg) and edpp (292 mg) was stirred overnight at room temperature. The resulting brown solution was poured into 1 dm^3 of water to give a precipitate, which was filtered off. The filtrate was poured onto a column (ϕ 2.7×80 cm) of SP-Sephadex C-25, and the product adsorbed was eluted with an aqueous 0.2 mol/dm^3 Na_2SO_4 solution. Many bands were observed. The first and second orange yellow eluates contained $[Co(en)_3]^{3+}$ and $[Co(en)_2(edpp)]^{3+}$, respectively. The second eluate was evaporated to dryness under reduced pressure, and the complex was extracted with methanol. The extract was diluted with water and poured onto a column (ϕ 2.7×80 cm) of SP-Sephadex C-25. By elution with an aqueous 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) solution, two bands corresponding to a pair of enantiomers were obtained. Each eluate was diluted with water, poured again onto a small column of SP-Sephadex C-25, and the enantiomer adsorbed was eluted with an aqueous 1 mol/dm^3 NaBr solution. On concentration *in vacuo*, the eluate gave orange yellow crystals of optically active $[Co(en)_2(edpp)]Br_3\cdot 2H_2O$, which were collected and washed with a small amount of water. Yield: 30 mg for each enantiomer.

[Co(en)$_2$(S-pdpp)]$^{+}$. This complex was prepared by a method similar to that for the edpp complex using *S*-pdpp (242 mg) and *cis*-$[CoCl_2(en)_2]Cl$ (285 mg). A pair of diastereomers were separated by similar column chromatography using an aqueous 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) solution as an eluent. Yellow crystals of Λ-$[Co(en)_2(S$-pdpp)$]Br_3\cdot 2H_2O$ (55 mg) were isolated by a method similar to that for the edpp complex, but another diastereomer was not isolated because of a very small amount.

[Co(en)$_2$(rac-ebpp)]$^{3+}$. Four isomers of this complex were obtained by a method similar to that for the edpp complex, using *rac*-ebpp (252 mg) and *cis*-$[CoCl_2(en)_2]Cl$ (343 mg). By elution with an aqueous 0.2 mol/dm^3 Na_2SO_4 solution, the orange yellow band of $[Co(en)_3]^{3+}$ and two yellow bands, I and II were eluted in succession. Bands I and II correspond to a pair of racemates, $\Lambda(R)$ and $\Lambda(S)$, and $\Lambda(S)$ and $\Lambda(R)$ isomers, respectively. The former racemate was resolved by the same column chromatographic method as that for the edpp complex. Yellow crystals of Λ-$[Co(en)_2(R$-ebpp$)]Br_3\cdot 4NaBr$ (8 mg) were obtained from the faster moving eluate. However, the yield of the latter racemate was poor, and thus the complex was isolated as the racemate, $[Co(en)_2(rac$-ebpp$)]Br_3\cdot 2H_2O$ (3.9 mg). The CD spectrum was determined by a method similar to that for the en-edmp complexes without isolating the active complex, the $\Lambda(S)$ isomer being eluted faster.

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

Structure Determination of $(+)_{589}$-[Co(edmp)$_3$]Br$_3\cdot 3H_2O$. Crystal data: orthorhombic, $a=26.501(8)$, $b=9.573(4)$, $c=10.081(5)$ Å, $U=2557.5(15)$, $D_m=1.73$, $D_c=1.73$ g cm^{-3}, $Z=4$, μ(Mo $K\alpha$)=58.3 cm^{-1}, λ(Mo $K\alpha$)=0.7107 Å, space group $P2_12_12_1$. The Laue symmetry, space group extinctions, and approximate unit-cell dimensions were obtained from Weissenberg photographs. The unit-cell dimensions were refined by the least squares analysis of 38θ values automatically centered on a Phillips PW 1100 diffractometer by the use of Mo $K\alpha$ radiation. The intensity data ($2\theta=52°$) were collected on the diffractometer using Graphite-monochromated Mo $K\alpha$ radiation. The specimen size was 0.17×0.18×0.28 mm^3. The ω-2θ scan mode was employed. The scan range was $(0.7+0.2\tan\theta)°$, and the scan speed, 0.025 °/s. The background was counted for half of the scan time as each end of the scan range. During the data collection, the intensities of 3 standard reflections were monitored every 4 h in order to check the orientation and stability of the crystal. No appreciable decay was observed. A total of 1924 reflections with $I>3\sigma(I)$ were observed and used in the subsequent structure determination and refinement. The observed intensities were corrected for Lorents-polarization and absorption effect, and the relative structure factors were derived.

The crystal structure was solved by the heavy-atom method. The parameters of all the non-hydrogen atoms were refined by the block-diagonal least-squares method, using anisotropic temperature factors for the Br, Co, and P atoms. The final agreement indices, R and $Rw=|W\Delta F^2/WF_o^2|^{1/2}$, were 6.57 and 6.55%, respectively. The function minimized was $\sum W(F_o-|F_c|)^2$, with $W=1/\sigma^2(F_o)$ being used. No attempt was made to locate H atoms. All the parameter shifts in the final cycle refinement were less than 0.5σ. The

Table 2. Positional and thermal parameters with their e.s.d. values in parenthesis

Atom	x	y	z	U/Å^2
Br(1)	0.4930(1)	0.1659(2)	0.5087(2)	a)
Br(2)	0.1268(1)	0.3619(2)	0.0156(2)	a)
Br(3)	0.2295(1)	0.2180(2)	0.5115(2)	a)
Co	0.3633(1)	0.1584(2)	0.0181(2)	a)
P(1)	0.3567(1)	0.1673(4)	0.0008(4)	a)
P(2)	0.4474(1)	0.1377(4)	0.0307(4)	a)
P(3)	0.3664(2)	0.3069(4)	−0.1537(4)	a)
N(1)	0.2859(4)	0.1505(12)	0.0261(11)	0.029(3)
N(2)	0.3643(5)	0.0004(13)	0.1517(13)	0.028(3)
N(3)	0.3551(4)	0.0057(13)	−0.1216(11)	0.024(3)
C(1)	0.2869(6)	0.3548(19)	0.1756(15)	0.039(4)
C(2)	0.2652(6)	0.2147(17)	0.1529(16)	0.039(4)
C(3)	0.3838(6)	0.5011(17)	0.1437(15)	0.033(4)
C(4)	0.3738(6)	0.2827(17)	0.3369(15)	0.038(4)
C(5)	0.4565(6)	−0.0069(17)	0.1498(15)	0.031(4)
C(6)	0.4077(6)	−0.0951(15)	0.1415(13)	0.023(4)
C(7)	0.4872(6)	0.2772(18)	0.0918(17)	0.040(4)
C(8)	0.4813(6)	0.0739(18)	−0.1133(17)	0.040(5)
C(9)	0.3600(5)	0.1891(15)	−0.2991(13)	0.028(4)
C(10)	0.3330(6)	0.0531(16)	−0.2516(14)	0.030(4)
C(11)	0.4217(6)	0.4126(18)	−0.1911(16)	0.037(4)
C(12)	0.3132(6)	0.4350(18)	−0.1732(16)	0.040(5)
O(1)	0.0780(5)	0.2121(16)	0.2793(14)	0.076(5)
O(2)	0.2188(5)	0.2204(15)	0.8283(14)	0.077(4)
O(3)	0.1110(4)	0.0246(12)	0.9469(11)	0.048(3)

a) Anisotropic temperature factors ($\times 10^4$/Å^2) expressed in the form $\exp[-2^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	435(9)	435(9)	398(9)	64(85)	−67(9)	21(12)
Br(2)	757(12)	437(10)	416(10)	13(10)	113(12)	−19(11)
Br(3)	529(10)	487(10)	357(9)	−154(9)	5(10)	−3(16)
Co	231(9)	212(9)	165(8)	−5(9)	17(10)	−5(10)
P(1)	281(24)	288(24)	197(18)	15(21)	34(19)	1(19)
P(2)	295(21)	237(20)	221(20)	19(18)	5(18)	−19(20)
P(3)	291(23)	256(23)	183(18)	31(20)	14(20)	37(18)

final difference Fourier map was rather flat and showed no peak of structural significance. The atomic scattering factors were taken from Ref. 7. The real and imaginary parts of the anomalous dispersion correction were applied for the Br, Co, and P atoms. The atomic coordinates and the temperature factors are listed in Table 2. A complete list of observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 8146).

The absolute configuration of the complex cation was determined by the anomalous dispersion technique. Table 3 gives the calculated structure amplitudes of several Bijvoet pairs and the observed inequality relationships which were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation. The observed relationships indicate that the absolute configuration of the complex ion is $\Lambda(\lambda\lambda\lambda)$.

Results and Discussion

Preparation and Properties of the Complexes. The reaction of edmp with *cis*-$[CoCl_2(en)_2]^+$ in the mole ratio of 3:1 in DMF under nitrogen atmosphere gives a series of complexes, $[Co(edmp)_3]^{3+}$, $[Co(en)(edmp)_2]^{3+}$, $[Co(en)_2(edmp)]^{3+}$, and $[Co(en)_3]^{3+}$ in the ratio of 8:2:1:7. The formation ratio of these tris-type complexes varies on changing the mole ratio of the starting materials. The reaction with a large excess of edmp affords almost only $[Co(edmp)_3]^{3+}$. However, the product obtained with an equivalent mole of the ligand involves the blue *trans*-$[CoCl_2(edmp)_2]^+$ complex, which can be isolated.[8] This suggests that the en ligands in *cis*-$[CoCl_2(en)_2]^+$ are easily replaced by edmp without dissociating the chloride ions. The fact that on addition of edmp the DMF solution of *cis*-$[CoCl_2(en)_2]^+$ changes almost instantly from violet to blue-green also implies the rapid formation of *trans*-$[CoCl_2(edmp)_2]^+$ (Experimental). The dichloro complex thus formed will be transformed to the tris en-edmp complexes by substitution reactions with free en or edmp ligands. On the other hand, the other phenyl- and diphenyl-(aminoalkyl)-phosphines form only $[Co(en)_2$(aminoalkylphos-

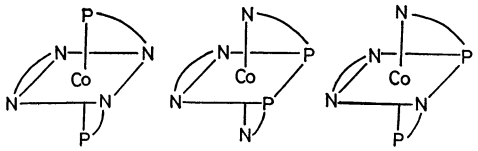

Fig. 1. Three geometrical isomers of $[Co(en)(N\text{-}P)_2]^{3+}$.

phine)]$^{3+}$ by similar reactions with *cis*-$[CoCl_2(en)_2]^+$. Aminoalkylphosphines with a bulky and electron withdrawing phenyl group on the phosphorus atom seem to have weaker affinity than edmp toward the cobalt(III) ion. All the aminoalkylphosphine complexes thus obtained are stable in both the solid state and aqueous solutions.

The $[Co(edmp)_3]^{3+}$ and $[Co(en)(edmp)_2]^{3+}$ complexes have two (*mer* and *fac*) and three (*trans*(P,P), *trans*(N,N), and *trans*(P,N)) possible geometrical isomers, respectively, for the arrangement of P and N atoms of edmp (Fig. 1). However, each complex gives only one isomer by the reactions under the conditions given. The *S*-pdpp complex which has a chiral carbon atom on the chelate ring yields almost one diastereomer stereoselectively, a very small amount of another diastereomer being observed in column chromatography. The *rac*-ebpp ligand has a chiral phosphorus donor atom and its bis-en complex gives a pair of racemates, $\Lambda(R)$ and $\Lambda(S)$, and $\Lambda(S)$ and $\Lambda(R)$, but there is also a fairly difference between the yields of the racemates. All racemates of the aminoalkylphosphine complexes were resolved completely by the SP-Sephadex column chromatographic method using 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) as an eluent. The Λ isomers are always eluted faster than the Δ isomers. The isomers are stable to racemization in aqueous solutions.

The Structure of $(+)_{589}$-$[Co(edmp)_3]Br_3\cdot 3H_2O$.
A perspective view of the $(+)_{589}$-$[Co(edmp)_3]^{3+}$ ion is shown in Fig. 2. Table 4 gives the interatomic distances and bond angles within the complex ion. The complex ion has approximate C_3 symmetry, and the P atoms are arranged in the facial manner. The absolute configuration is determined to be Λ on the basis of the data given in Table 3. The chelate rings are puckered with a pseudo λ gauche form. The C–C bonds are nearly parallel to the C_3 axis of the complex ion. Thus, the complex ion can be designated as the $lel_3(\Lambda(\lambda\lambda\lambda))$ isomer. The average Co–P distance of 2.237 Å is fairly short as compared with those (2.3—2.4 Å) reported for $[CoX(PR_3)(dmg)_2]$-type complexes (R=$-C_6H_5$, $-C_4H_9$; dmg=dimethylglyoximate ion).[9] The Co–N distance averages 2.041 Å, which is significantly longer than that of 1.978 Å in $[Co(en)_3]^{3+}$.[10] The elongation of Co–N distances can be attributed to the strong *trans* effect of the donating P atoms. Each ligand forms a five-membered chelate ring with an average P–Co–N angle of 84.8°, which is nearly the same as the average N–Co–N angle of 85.4° in $[Co(en)_3]^{3+}$.[10] The average distances of P–CH_3 and P–CH_2 are 1.827 and 1.859 Å, respectively. The average angle of P–Co–P (94.3°) is fairly larger than that of N–Co–N (85.8°), and the

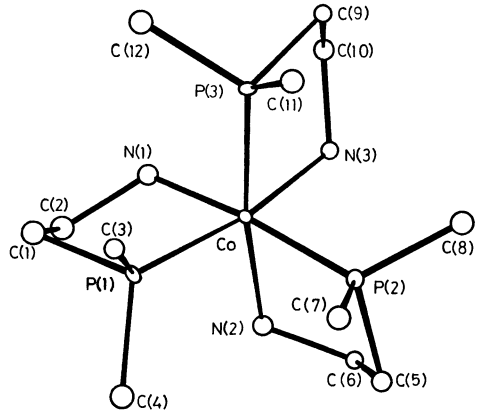

Fig. 2. A perspective view of the $(+)_{589}$-$[Co(edmp)_3]^{3+}$ ion.

TABLE 3. OBSERVED AND CALCULATED INTENSITIES BETWEEN SOME *hkl* AND $\bar{h}kl$ REFLECTIONS

hkl	$\lvert F_c(hkl)\rvert$	$\lvert F_c(\bar{h}kl)\rvert$	Observed
221	85	73	>
321	71	50	>
421	121	127	<
521	222	193	>
131	59	35	>
511	159	171	<
322	124	96	>
323	129	141	<
423	99	110	<

average Co–P–CH_3(//) angle of 122.7° is also larger than the other Co–P–CH_3($\perp$) and Co–P–CH_2 angles as shown in Table 4, where the CH_3(//) and CH_3($\perp$) denote those parallel and perpendicular to the C_3 axis of the complex ion, respectively. Thus the overcrowding due to the facial three CH_3(//) groups is relieved, although the non-bonded C···C distances (3.51—3.62 Å) among these CH_3(//) groups are still shorter than the sum of the van der Waals radius of a methyl group (4 Å). The non-bonded C···C distances between the CH_3($\perp$) and the P–CH_2 are also shorter than 4 Å. Such a crowded structure seems to afford the conformation of the chelate ring differing from the typical gauche form. The dihedral angles of the N–C–C–P moieties are 53.3°, 48.7°, and 44.3°.

The packing mode of the complex ions, bromide ions, and water molecules is illustrated in Fig. 3. Some short interatomic distances outside the complex ions are listed in Table 5. One out of three bromide ions lies approximately on the C_3 axis of the complex ion to form weak N–H···Br hydrogen bonds (3.38—3.56 Å) with three N–H atoms parallel to the C_3 axis in the three facial NH_2 groups. The other N–H groups are also linked by N–H···O or N–H···Br hydrogen bonds.

Absorption and CD Spectra. Absorption spectra of a series of the $[Co(en)_n(edmp)_{3-n}]^{3+}$ complexes are shown in Fig. 4, and the data given in Table 6. With an increase in the number of ligating phosphorus

Table 4. Bond distances (l/Å) and angles (ϕ/°)

Co-P(1)	2.231(5)	P(1)-C(1)	1.869(18)	P(3)-C(9)	1.858(16)	N(3)-C(10)	1.505(20)
Co-P(2)	2.239(4)	P(1)-C(3)	1.810(17)	P(3)-C(11)	1.824(18)		
Co-P(3)	2.242(5)	P(1)-C(4)	1.825(17)	P(3)-C(12)	1.877(17)	C(1)-C(2)	1.479(24)
Co-N(1)	2.055(12)	P(2)-C(5)	1.849(16)			C(5)-C(6)	1.548(22)
Co-N(2)	2.024(13)	P(2)-C(7)	1.809(18)	N(1)-C(2)	1.521(20)	C(9)-C(10)	1.560(22)
Co-N(3)	2.043(12)	P(2)-C(8)	1.816(18)	N(2)-C(6)	1.472(19)		

P(1)-Co-P(2)	96.0(2)	Co-P(1)-C(1)	101.7(6)	C(9)-P(3)-C(12)	104.4(7)
P(1)-Co-P(3)	93.3(2)	Co-P(1)-C(3)	123.2(6)		
P(1)-Co-N(1)	85.5(4)	Co-P(1)-C(4)	115.7(6)	Co-N(1)-C(2)	112.3(9)
P(1)-Co-N(2)	95.8(4)	C(1)-P(1)-C(3)	106.3(8)	Co-N(2)-C(6)	115.4(9)
P(1)-Co-N(3)	169.3(4)	C(1)-P(1)-C(4)	103.6(8)	Co-N(3)-C(10)	115.2(9)
		C(3)-P(1)-C(4)	104.4(8)		
P(2)-Co-P(3)	93.7(2)			N(1)-C(2)-C(1)	110.7(13)
P(2)-Co-N(1)	171.0(4)	Co-P(2)-C(5)	103.5(5)	N(2)-C(6)-C(5)	108.0(12)
P(2)-Co-N(2)	83.4(4)	Co-P(2)-C(7)	122.3(6)	N(3)-C(10)-C(9)	109.8(12)
P(2)-Co-N(3)	94.7(4)	Co-P(2)-C(8)	118.5(6)		
		C(5)-P(2)-C(7)	104.8(8)	P(1)-C(1)-C(2)	105.1(12)
P(3)-Co-N(1)	95.1(4)	C(5)-P(2)-C(8)	101.7(8)	P(2)-C(5)-C(6)	105.3(10)
P(3)-Co-N(2)	170.6(4)	C(7)-P(2)-C(8)	103.4(8)	P(3)-C(9)-C(10)	107.8(10)
P(3)-Co-N(3)	85.7(4)				
		Co-P(3)-C(9)	102.8(5)		
N(1)-Co-N(2)	87.5(5)	Co-P(3)-C(11)	122.7(6)		
N(1)-Co-N(3)	83.9(5)	Co-P(3)-C(12)	118.0(6)		
N(2)-Co-N(3)	85.7(5)	C(9)-P(3)-C(11)	104.3(7)		

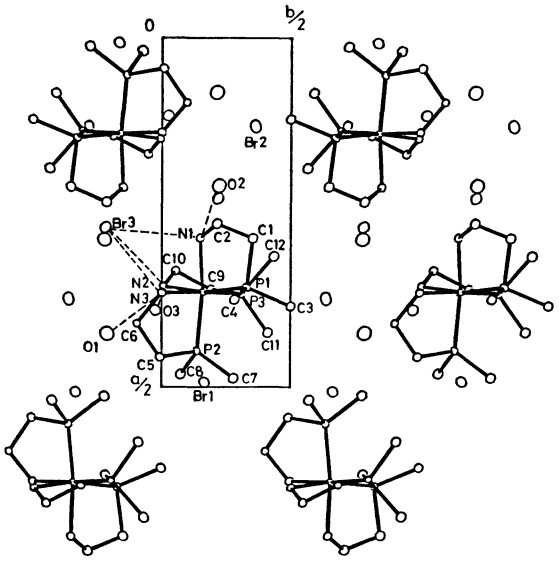

Fig. 3. Projection of the crystal structure along the c axis. Possible hydrogen bonds are indicated by broken lines.

atoms, the first absorption bands are shifted to higher wavenumbers and increase the intensity. The wavenumber difference in the first absorption bands between $[Co(edmp)_3]^{3+}$ and $[Co(en)_3]^{3+}$ amounts to 2300 cm^{-1}, and edmp stands at a fairly higher position than en in the spectrochemical series. The band of $[Co(edmp)_3]^{3+}$ is symmetrical and shows no splitting, which agrees with a pattern expected from Yamatera's rule[11] for a complex with C_3 symmetry (*fac* isomer). The *fac* structure was confirmed by X-ray analysis (*vide ante*). The $[Co(en)_2(edmp)]^{3+}$ complex gives the first absorption band at 22400 cm^{-1}. This value is just an average of those of *fac*-$[Co(edmp)_3]^{3+}$ and $[Co(en)_3]^{3+}$, and also agrees with that expected for one of two components split in the first absorption band.[11] Another component which should be at the same wavenumber as that of the first absorption band of $[Co(en)_3]^{3+}$ would be hidden by this strong component. The first absorption band of $[Co(en)(edmp)_2]^{3+}$ shows the maximum at 23700 cm^{-1} and a shoulder at 21000 cm^{-1}. These values quite agree with those calculated for the *trans*(P,P) isomer according to Yamatera's rule. Thus the complex can be assigned to the *trans*(P,P) isomer. However, the absorption spectrum of this complex is very similar over the whole region to that of $[Co(en)_2(P\text{–}P)]^{3+}$ (P–P=1,2-bis(dimethylphosphino)ethane), which forms necessarily *cis*(P,P) configuration.[12] In general, ligands which exhibit the strong *trans* effect such as a phosphine tend to occupy the *cis* positions to each other in metal complexes.[13] In fact, the $[Co(edmp)_3]^{3+}$ complex yielded only the *fac* isomer, despite its structure seems to be more crowded than

Table 5. Relevant interatomic distances (l/Å)

Br(3)-N(1)	3.555(12)	C(3)-C(7)	3.518(23)
Br(3)-N(2)	3.542(13)	C(7)-C(11)	3.580(24)
Br(3)-N(3)	3.377(12)	C(11)-C(3)	3.621(23)
O(1)-N(3)	2.912(19)	C(1)-C(12)	3.665(25)
O(2)-N(2)	3.420(19)	C(4)-C(5)	4.007(25)
O(3)-N(2)	3.058(17)	C(8)-C(9)	3.877(23)
O(2)-N(1)	2.877(19)		

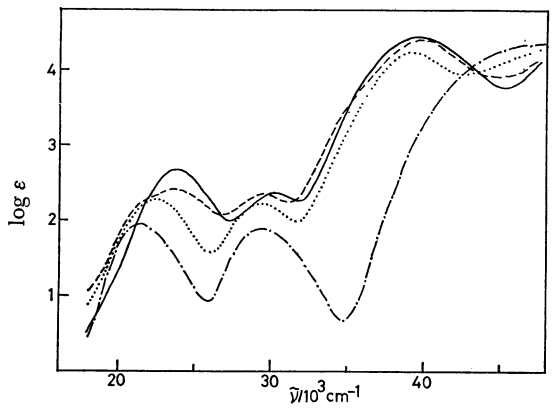

Fig. 4. Absorption spectra of $[Co(edmp)_3]^{3+}$ (——), $[Co(en)(edmp)_2]^{3+}$ (----), $[Co(en)_2(edmp)]^{3+}$ (·····), and $[Co(en)_3]^{3+}$ (—·—·—).

TABLE 6. ABSORPTION(AB) AND CD SPECTRAL DATA

Complex	$\tilde{\nu}^{AB}/10^3$ cm^{-1}(log ε)	$\tilde{\nu}^{CD}/10^3$ cm^{-1}($\Delta\varepsilon$)
Λ-$[Co(edmp)_3]^{3+}$	23.70(2.68)	22.32(+1.45)
		24.84(−1.57)
	30.18(2.36)	30.03(+0.49)
	39.76(4.42)	37.88(−20.6)
		40.98(+4.74)
		45.00(−9.33)
Λ-$[Co(en)(edmp)_2]^{3+}$	21.4 (2.2)(sh)	20.90(+2.07)
	23.72(2.41)	23.98(−0.89)
	29.43(2.34)	29.41(+0.62)
	39.84(4.38)	37.74(−9.9)
		40.50(+5.4)
		44.84(−14.9)
Λ-$[Co(en)_2(edmp)]^{3+}$	22.46(2.28)	20.47(+1.26)
		23.39(−0.16)
	29.28(2.23)	27.40(+0.36)
	39.22(3.92)	39 (−3.3)(sh)
		46.73(−17.8)
Λ-$[Co(en)_2(edpp)]^{3+}$	21.51(2.53)	19.88(+1.67)
		22.47(−0.91)
	32.63(4.17)	33.67(+10.4)
	44.44(4.39)	38 (+5)(sh)
		41.32(−0.7)
Λ-$[Co(en)_2(S\text{-pdpp})]^{3+}$	21.51(2.54)	19.92(+1.80)
		22.30(−1.28)
	32.79(4.15)	34.36(+2.98)
	40.98(4.00)	38 (+4.5)(sh)
	44.50(4.43)	42.37(−3.4)
Λ-$[Co(en)_2(S\text{-ebpp})]^{3+}$	21.90(2.51)	20.16(+1.77)
		22.86(−0.58)
		27.97(+0.51)
	33.56(4.18)	33.22(−8.9)
	41 (4)(sh)	40.82(+0.9)
		43.96(−10.1)
		47.17(−3.7)
Λ-$[Co(en)_2(R\text{-ebpp})]^{3+}$	21.93(2.45)	20.08(+0.96)
		22.62(−1.42)
		28 (+0.6 ((sh)
	33.73(4.05)	34.01(+12.6)
	41 (3.9)(sh)	45.66(−29)

sh: Shoulder.

the *mer* isomer. In column chromatographic resolution using SP-Sephadex C-25 and a sodium $(+)_{589}$-tartratoantimonate(III) solution, the Λ-isomers are eluted faster for both $[Co(edmp)_3]^{3+}$ and $[Co(en)(edmp)_2]^{3+}$. For five-membered chelate complexes, it is reported that in complexes with three facial NH_2 groups which can form hydrogen bonds with the $(+)_{589}$-tartratoantimonate(III) ion, a Λ isomer is eluted almost always faster than the antipode.[14] For complexes with no such facial NH_2 groups, for example $[Co(en)_2(C_2O_4)]^{+}$ [14] and $[Co(en)_2(P\text{-}P)]^{3+}$ [12], the elution order is reversed to give a Λ isomer as the faster moving enantiomer. The $[Co(en)(edmp)_2]^{3+}$ complex can have the three facial NH_2 groups in only the *trans*(P,N) isomer. These considerations lead to the conclusion that $[Co(en)(edmp)_2]^{3+}$ is the *trans*-(P,N) isomer. This isomer has C_1 symmetry and the two edmp ligands are not in equivalent environment. Thus NMR spectroscopy would give useful information for assigning the structure. However, the ^1H NMR spectrum was too complicated to assign, and no good ^{13}C NMR spectrum was obtained because of the small amount of the complex. Thus the structure of $[Co(en)(edmp)_2]^{3+}$ remains unknown.

In contrast with the first absorption bands, the second absorption bands of the edmp complexes do not show any remarkable shift when en is replaced by edmp. Thus the energy difference between the first and the second absorption bands in the edmp complexes becomes small as compared with that in $[Co(en)_3]^{3+}$. The energy difference between the first and the second absorption bands is expressed by 16B, where B is the Racah's parameter of interelectronic repulsion.[15] The B value is known to be a measure for representing covalent character of the bond between a ligand and a metal ion, the smaller the value the more the covalent character.[16] The B values for *fac*-$[Co(edmp)_3]^{3+}$ and $[Co(en)_3]^{3+}$ are 406 and 506 cm^{-1}, respectively. The value of 406 cm^{-1} is as small as that of $[Co(CN)_6]^{3-}$ (416 cm^{-1}).[17] The coordinate bond between the edmp ligand and the cobalt(III) ion might involve fairly strong covalent character.

The edmp complexes show a strong absorption band around 40000 cm^{-1}, which can be assigned to the charge transfer band from the phosphine group to the cobalt(III) ion. With an increase in the number of ligating phosphorus atoms, these bands increase the intensity, while the absorptions around 46000 cm^{-1} which can be assigned to the charge transfer band from the amine group to the cobalt(III) ion decrease the intensity.

Absorption spectra of $[Co(en)_2(edpp)]^{3+}$ and $[Co(en)_2(ebpp)]^{3+}$ (lst fraction) are compared with that of $[Co(en)_2(edmp)]^{3+}$ in Fig. 5. By replacing the methyl group in edmp by a phenyl group, both the first and the charge transfer absorption bands are shifted progressively to smaller wavenumbers. The shift of the latter bands are particularly noticeable and the second absorption bands are hidden by these bands. The maximum wavenumber of the first absorption band of the edpp complex is nearly the same as that of $[Co(en)_3]^{3+}$.

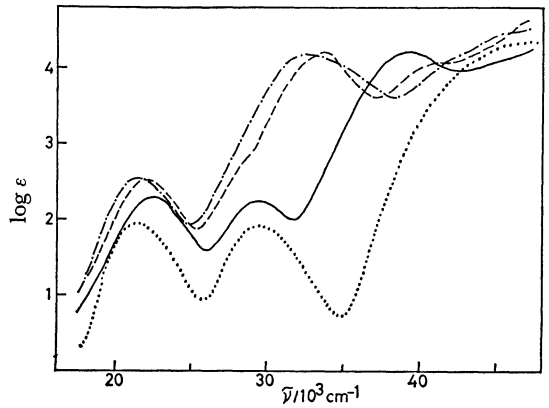

Fig. 5. Absorption spectra of $[Co(en)_2(edmp)]^{3+}$ (——), $[Co(en)_2(ebpp)]^{3+}$ (----), $[Co(en)_2(edpp)]^{3+}$ (—·—), and $[Co(en)_3]^{3+}$ (·····).

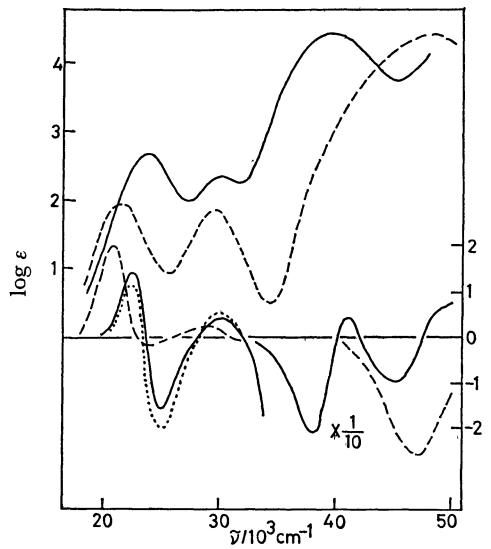

Fig. 6. Absorption and CD spectra of *Λ*-*fac*-$[Co(edmp)_3]^{3+}$ in water (——) and in 0.1 mol/dm^3 PO_4^{3-} (·····), and *Λ*-$[Co(en)_3]^{3+}$ in water (----).

The CD spectrum of $(-)_{589}$-*Λ*-*fac*-$[Co(edmp)_3]^{3+}$ is compared with that of *Λ*-$[Co(en)_3]^{3+}$ in Fig. 6. Both complexes show a similar CD pattern in the first absorption band region, although the negative component of *Λ*-*fac*-$[Co(edmp)_3]^{3+}$ is very strong. On addition of phosphate ions, the positive and the negative components are diminished and enhanced, respectively. The same effect is well known to occur in the CD spectrum of *Λ*-$[Co(en)_3]^{3+}$.[17] In the ultraviolet region, a negative and a positive CD band are observed corresponding to each charge transfer band from the phosphine and the amine groups to the cobalt(III) ion. The appearance of the negative CD band in the small wavenumber side in each charge transfer region is the same as cases of tris-diamine complexes in the *Λ* configuration.[18] Thus the CD spectrum of *fac*-$[Co(edmp)_3]^{3+}$ can be understood on the basis of that of $[Co(en)_3]^{3+}$. Figure 7 shows the CD spectra of $[Co(en)_n(edmp)_{3-n}]^{3+}$, all of which are eluted faster on column chromatography. All the complexes can be assigned to *Λ* configuration

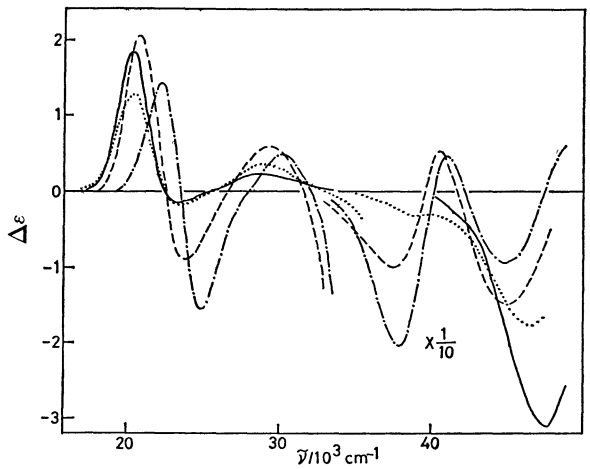

Fig. 7. CD spectra of *Λ*-$[Co(edmp)_3]^{3+}$ (—·—·—), *Λ*-$[Co(en)(edmp)_2]^{3+}$ (----), *Λ*-$[Co(en)_2(edmp)]^{3+}$ (·····), and *Λ*-$[Co(en)_3]^{3+}$ (——).

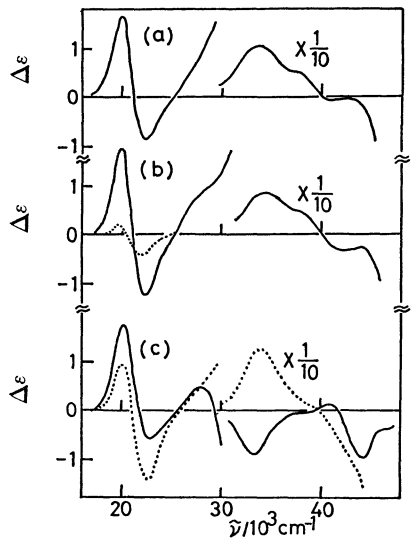

Fig. 8. CD spectra of *Λ*-$[Co(en)_2(N-P)]^{3+}$. N-P: (a) edpp, (b) *S*-pdpp (——) and the vicinal effect curve of *S*-pdpp (·····) (see text), and (c) *R*-ebpp (——) and *S*-ebpp (·····).

from the CD patterns in the first absorption band region. The CD bands corresponding to the charge transfer transitions from the phosphine and the amine groups to the cobalt(III) ion decrease or increase the strength depending on the number of phosphorus or nitrogen donor atoms. In Fig. 8 are shown the CD spectra of $[Co(en)_2(N-P)]^{3+}$ (N-P=edpp, *S*-pdpp, and *S*- and *R*-ebpp). The CD patterns in the first absorption band region are all similar, and these enantiomers can be assigned to *Λ* configuration. However, the CD spectra in the ultraviolet region differ from those of the edmp complexes probably because of the presence of the phenyl group or the chiral phosphorus or carbon atom. The absolute configurations of the phosphorus atoms in the diastereomeric ebpp complexes were assigned by comparing the CD spectra with those of the authentic complexes prepared by use of optically active *S*-ebpp.[6,19]

The *S*-pdpp complex involves a chiral chelate ligand.

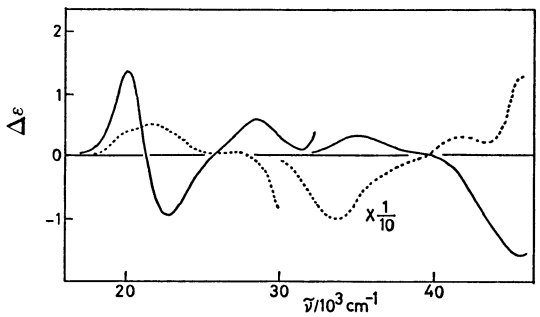

Fig. 9. Configurational(Λ) (——) and vicinal(R) (·····) effect CD curves of $[Co(en)_2(ebpp)]^{3+}$.

When the additivity[20] in CD between the configurational and vicinal effects holds in the CD of this complex, the vicinal effect of S-pdpp can be estimated by subtracting the CD spectrum of Λ-$[Co(en)_2(edpp)]^{3+}$ from that of Λ-$[Co(en)_2(S\text{-pdpp})]^{3+}$. The vicinal CD curve thus obtained quite resemble those of (S)-propylenediamine (S-pn) chelate ligands in some S-pn complexes[20-22] (Fig. 8), indicating the same conformational chirality for both S-pdpp and S-pn chelate rings. Thus the S-pdpp chelate ring is assumed to be stabilized in a δ gauche conformation with the equatorial methyl group as seen in the S-pn chelate ring.[23] The ebpp complex has a chiral donating phosphorus atom, and gives a pair of diastereomers, $\Lambda(R)$ and $\Lambda(S)$. These diastereomers show a similar CD pattern in the first absorption band region, but give a CD band with the different sign from each other around 34000 cm^{-1}, where the charge transfer transition between the phosphine group and the cobalt(III) ion arises. From these CD spectra, the configurational (Λ) and vicinal (R) curves are obtained by the usual method[20] (Fig. 9). The configurational CD curve resembles the CD spectra of the other aminoalkylphosphine complexes. The curve in the ultraviolet region seems to be an average of the CD spectra of the edpp and the emdp complexes. The vicinal CD curve shows a positive and a negative peak in the regions of the first and the charge transfer, from the phosphine group to the cobalt(III) ion, bands, respectively. The vicinal effect of chiral phosphorus atoms donating to the cobalt(III) ion is only known for the $[Co(acac)_2(ebpp)]^+$ (acac=acetylacetonate ion).[2] In order to discuss such optical activity, more data will be needed.

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