November, 1983] *Bull. Chem. Soc. Jpn.*, ***56***, *3441—3445 (1983)* 3441

A Complete Series of [Co(acac)$_x$(en)$_y$(dmpe)$_z$] Complexes

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(Received June 1, 1983)

A complete series of [Co(acac)$_x$(en)$_y$(dmpe)$_z$] complexes was obtained by preparing four new complexes, [Co(acac)(dmpe)$_2$]$^{2+}$, [Co(en)$_2$(dmpe)]$^{3+}$, [Co(en)(dmpe)$_2$]$^{3+}$, and [Co(acac)(en)(dmpe)]$^{2+}$, where acac, en, and dmpe denote an acetylacetonate ion, ethylenediamine, and 1,2-bis(dimethylphosphino)ethane, respectively. Except for [Co(acac)(dmpe)$_2$]$^{2+}$, the three new complexes were resolved into optical isomers by SP-Sephadex column chromatography. Absorption and circular dichroism spectra of all the complexes were recorded and compared with one another.

In a previous paper,[1] we reported ten [Co(en)$_x$(tn)$_y$(tmd)$_z$]$^{3+}$ (x,y,z=0,1,2, or 3; $x+y+z=3$) complexes as the first example of a complete series of the [Co(AA)$_x$(BB)$_y$(CC)$_z$]-type complexes, where en ($NH_2CH_2CH_2NH_2$), tn ($NH_2CH_2CH_2CH_2NH_2$), and tmd ($NH_2CH_2CH_2CH_2CH_2NH_2$) form a five-, six-, and seven-membered chelate ring, respectively upon coordination. This paper reports the second example of a complete series-complexes belonging to the same type. The complexes are those of the type, [Co(acac)$_x$(en)$_y$(dmpe)$_z$], where acac (acetylacetonate ion), en, and dmpe (1,2-bis(dimethylphosphino)ethane) are typical chelate ligands with O,O, N,N, and P,P donor atoms, respectively. Of the ten complexes belonging to this series, known complexes are the series of [Co(acac)$_{3-n}$(en)$_n$]$^{n+}$ (n=0,1,2,3), [Co(acac)$_2$(dmpe)]$^+$,[2] and [Co(dmpe)$_3$]$^{3+}$,[3] and there remain four unknown complexes, [Co(acac)(dmpe)$_2$]$^{2+}$, [Co(en)$_2$(dmpe)]$^{3+}$, [Co(en)(dmpe)$_2$]$^{3+}$, and [Co(acac)(en)(dmpe)]$^{2+}$, all of which contain the dmpe ligand. Preparative work on such series-complexes comprised of ligands with remarkably different donor properties will be useful for elucidating such properties as stability or electronic spectra of metal complexes.

Experimental

1,2-Bis(dimethylphosphino)ethane, $(CH_3)_2PCH_2CH_2P(CH_3)_2$ was prepared by the literature method,[4] and handled under nitrogen atmosphere until it formed cobalt(III) complexes. Oxygen-free solvents were obtained by bubbling nitrogen for 20 min immediately before use. Absorption and circular dichroism (CD) spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively.

Preparation of Complexes. *[Co(en)$_2$(dmpe)]Br$_3$·H$_2$O*: To a solution of [Co(en)$_3$](ClO$_4$)$_3$[5] (473 mg, 1.4 mmol) in oxygen-free dimethyl sulfoxide (100 cm^3) were added dmpe (210 mg, 1.4 mmol) and active charcoal (100 mg). The mixture was stirred for a day at room temperature and filtered. The filtrate was diluted with water (1 dm^3) and poured on a column (ϕ3.5 cm × 150 cm) of SP-Sephadex C-25. The product adsorbed was eluted with 0.2 mol dm^{-3} NaCl, giving three bands in the order of [Co(en)(dmpe)$_2$]$^{3+}$ (very small amount), [Co(en)$_2$(dmpe)]$^{3+}$, and [Co(en)$_3$]$^{3+}$. The effluent of the second band was diluted five times with water and poured again on a small column (ϕ3.5 cm × 10 cm) of SP-Sephadex C-25. The complex adsorbed was eluted with 1 mol dm^{-3} NaBr, and the effluent was concentrated in a vacuum desiccator over P_4O_{10} to yield yellow crystals, which were filtered, washed with cold methanol–diethyl ether (1:5), and air-dried. Yield: 92 mg (16%). Found: C, 20.46; H, 5.84; N, 9.25%. Calcd for $C_{10}H_{34}N_4CoBr_3OP_2$=[Co(en)$_2$(dmpe)]Br$_3$·H$_2$O: C, 20.46; H, 5.84; N, 9.54%. The complex is soluble in water, methanol, and dimethyl sulfoxide, but insoluble in diethyl ether.

[Co(en)(dmpe)$_2$]Br$_3$: To a solution of *trans*-[CoCl$_2$(dmpe)$_2$]ClO$_4$[3] (300 mg, 0.57 mmol) in oxygen-free methanol (100 cm^3) was added excess en (180 mg, 2.9 mmol). The mixture was stirred for a day at room temperature, and diluted with water (1 dm^3). The solution was poured on a column (ϕ3.5 cm × 150 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, the product adsorbed gave four bands in the order of *trans*-[CoCl$_2$(dmpe)$_2$]$^+$, [Co(en)(dmpe)$_2$]$^{3+}$, [Co(en)$_2$(dmpe)]$^{3+}$ (very small amount), and [Co(en)$_3$]$^{3+}$. Orange crystals of the desired complex were obtained from the effluent of the second band by the same method as that for [Co(en)$_2$(dmpe)]$^{3+}$. Yield: 67 mg (18%). Found: C, 25.15; H, 6.23; N, 4.19%. Calcd for $C_{14}H_{40}N_2Br_3CoP_4$=[Co(en)(dmpe)$_2$]Br$_3$: C, 25.52; H, 6.12; N, 4.25%. The complex is soluble in water, methanol, and dimethyl sulfoxide, but insoluble in diethyl ether.

[Co(acac)(dmpe)$_2$](PF$_6$)$_2$: To a solution of *trans*-[CoCl$_2$(dmpe)$_2$]ClO$_4$ (163 mg, 0.31 mmol) in oxygen-free methanol (100 cm^3) was added Li(acac) (32.6 mg, 0.31 mmol). The color of the solution changed immediately from blue-green to orange. After 30 min the solution was diluted with water (1 dm^3) and poured on a column (ϕ3.5 cm × 150 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, only orange-yellow effluent was obtained. The effluent was evaporated to dryness under reduced pressure, and the residue was extracted with methanol. On addition of excess NaPF$_6$ (100 mg) in water (5 cm^3) the extract gave orange crystals, which were filtered, washed with cold water, and air-dried. Yield: 168 mg (73%). Found: C, 26.97; H, 5.01%. Calcd for $C_{17}H_{39}CoF_{12}O_2P_6$=[Co(acac)(dmpe)$_2$](PF$_6$)$_2$: C, 27.29; H, 5.25%. The complex is soluble in methanol, ethanol, and acetonitrile, but hardly soluble in water.

[Co(acac)(en)(dmpe)](PF$_6$)$_2$·H$_2$O: To an oxygen-free methanol solution (100 cm^3) of [Co(acac)$_2$(en)]PF$_6$ (660 mg, 1.53 mmol) which had been prepared from [Co(acac)$_2$(en)]ClO$_4$[6] and NaPF$_6$ was added dmpe (230 mg, 1.53 mmol). The mixture was kept at 50 °C for 5 h, and then mixed with water (400 cm^3) and diethyl ether (100 cm^3) to extract unreacted dmpe into diethyl ether. The aqueous layer was diluted with water (1 dm^3) and poured on a column (ϕ3.5 cm × 150 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} Na$_2$SO$_4$, [Co(acac)$_2$(dmpe)]$^+$ (red), [Co(acac)(en)(dmpe)]$^{2+}$ (orange-red), and [Co(acac)(dmpe)$_2$]$^{2+}$ (orange-yellow) were eluted accompanying with a few very small brown bands. The effluent of the second orange-red band was collected and evaporated to dryness under reduced pressure. To the residue was added a small amount of methanol to extract the complex. On addition of excess NaPF$_6$ (200 mg) in water (5 cm^3) the extract gave orange-

red crystals, which were filtered, washed with cold water, and air-dried. Yield: 40 mg (4%). Found: C, 23.90; H, 5.16; N, 4.13%. Calcd for $C_{13}H_{33}N_2CoF_{12}O_3P_4 = [Co(acac)(en)(dmpe)](PF_6)_2\cdot H_2O$: C, 24.13; H, 4.83; N, 4.33%. The complex is soluble in methanol, ethanol, and acetonitrile, but hardly soluble in water.

Known complexes, $[Co(acac)_3]$,[7] $[Co(acac)_2(en)]ClO_4$,[6] $[Co(acac)(en)_2]I_2$.[8] $[Co(en)_3](ClO_4)_3$,[5] $[Co(acac)_2(dmpe)]PF_6$,[2] and $[Co(dmpe)_3](ClO_4)_3$[3] were prepared by the literature methods.

Optical Resolution of Complexes. $[Co(en)_2(dmpe)]^{3+}$: The complex was resolved by a chromatographic method with a column (ϕ3.5 cm × 120 cm) of SP-Sephadex C-25 and an eluent of 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$. $[Co(en)_2(dmpe)]Br_3\cdot H_2O$ (*ca.* 30 mg) charged on the top of the column was resolved completely by elution with the eluent. From each effluent, the optically active complex was isolated as bromide by the same method as that for the racemate. The slow-moving enantiomer has been determined to be Λ-$(+)_{589}$-$[Co(en)_2(dmpe)]Br_3\cdot 1/2\,H_2O$ by X-ray analysis.[9]

$[Co(acac)(en)(dmpe)]^{2+}$: The complex was resolved by the same chromatographic method as the above. However, a poor separation between the bands of enantiomers was observed. The fractions having a constant value of $\Delta\varepsilon/\varepsilon$ were collected, diluted five times with water, and poured on a small column (ϕ1 cm × 10 cm) of SP-Sephadex C-25. The complex adsorbed was eluted with 0.2 mol dm^{-3} $NaPF_6$, and the effluent was used for the measurements of CD spectra without isolating the complex. The concentration of the complex was determined by reference to the ε values of the racemate. The active complex hexafluorophosphate is much more soluble in water than the racemic salt.

Other Complexes. The $[Co(en)(dmpe)_2]^{3+}$ and $[Co(acac)_2(dmpe)]^+$ complexes were resolved partially by the same chromatographic method as the above. No fractions having a constant value of $\Delta\varepsilon/\varepsilon$ were obtained. The column chromatographic method becomes less effective as the number of acac or dmpe ligand increases in the complex. No resolution was achieved for $[Co(acac)(dmpe)_2]^{2+}$.

Results and Discussion

Mixed complexes in the series of $[Co(acac)_{3-n}(en)_n]^{n+}$ can be easily prepared from the parent complexes by substitution reactions in fairly good yields; $[Co(acac)_2(en)]^+$ is prepared from $[Co(acac)_2(NO_2)_2]^-$ and en,[6] and $[Co(acac)(en)_2]^{2+}$ from $[CoCO_3(en)_2]^+$[8] or $[CoCl(H_2O)(en)_2]^{2+}$[10] and acac. However, most reactions of dmpe with a cobalt(III) complex accompany disproportionation or ligand scrambling, affording many complexes formed with dmpe and ligands contained in the starting complex. The reaction of $[Co(en)_3]^{3+}$ with dmpe in the ratio of 1:1 yields all complexes of the series, $[Co(en)_{3-n}(dmpe)_n]^{3+}$, and $[Co(en)_2(dmpe)]^{3+}$ is obtained in 16% yield. The formation of $[Co(en)(dmpe)_2]^{3+}$ is very small, and $[Co(dmpe)_3]^{3+}$ decomposes during the experiment of column chromatography. The reaction of *trans*-$[CoCl_2(en)_2]^+$ with dmpe also forms $[Co(en)_2(dmpe)]^{3+}$, but the yield is very poor, $[Co(en)_3]^{3+}$ and *trans*-$[CoCl_2(dmpe)_2]^+$ being formed in large amounts. The other mixed complex, $[Co(en)(dmpe)_2]^{3+}$ is obtained in 18% yield by the reaction of *trans*-$[CoCl_2(dmpe)_2]^+$ with excess en. The reaction with an equimolar amount of en is very slow, and on heating $[Co(en)_3]^{3+}$ and $[Co(dmpe)_3]^{3+}$ are formed as the major product. The (2-aminoethyl)dimethylphosphine (edmp) ligand also forms all complexes of the series, $[Co(en)_{3-n}(edmp)_n]^{3+}$ by reaction with *trans*-$[CoCl_2(en)_2]^+$.[11]

The $[Co(acac)(dmpe)_2]^{2+}$ complex is obtained in good yield by the reaction of *trans*-$[CoCl_2(dmpe)_2]^+$ with Li(acac) in the ratio of 1:1. The reaction takes place rapidly and gives no other complexes in detectable amount. The reaction of dmpe with $[Co(acac)_3]$ in the ratio of 1:1 yields all complexes of the series, $[Co(acac)_{3-n}(dmpe)_n]^{n+}$, the main product being $[Co(acac)_2(dmpe)]^+$.[2] Similar reactions of diphenylphosphine-type chelate ligands such as (2-aminoethyl)diphenylphosphine (edpp) or 1,2-bis(diphenylphosphino)ethane (dppe) with $[Co(acac)_3]$ give only bis(acac) complex, and no bis(edpp or dppe) complex is formed even in the presence of active charcoal.[12] The dmpe ligand is more reactive to Co(III) than edpp and dppe.

The $[Co(acac)(en)(dmpe)]^{2+}$ complex is obtained in 4% yield by the reaction of dmpe with $[Co(acac)_2(en)]^+$. The reaction between dmpe and $[Co(acac)(en)_2]^{2+}$ yields further less amount of the complex. In either reaction, $[Co(en)_3]^{3+}$, $[Co(acac)(dmpe)_2]^{2+}$, and $[Co(acac)_2(dmpe)]^+$ are formed in larger amounts.

While solid $[Co(dmpe)_3](ClO_4)_3$ is rather unstable in the air,[3] all of the dmpe complexes prepared in this study are stable in the solid state. Both $[Co(en)(dmpe)_2]^{3+}$ and $[Co(en)_2(dmpe)]^{3+}$ in aqueous solution are stable at room temperature, but decompose slowly on heating over 60 °C. The former complex in water in the presence of excess NaCl changes to *trans*-$[CoCl_2(dmpe)_2]^+$ by heating, but the latter complex decomposes to give Co(II) species under the same conditions. The $[Co(dmpe)_3]^{3+}$ complex in methanol containing excess Cl^- or Br^- also changes easily to *trans*-$[Co(Cl\text{ or }Br)_2(dmpe)_2]^+$.[3] In contrast to the en complexes, no changes occur for both $[Co(acac)(dmpe)_2]^{2+}$ and $[Co(acac)_2(dmpe)]^+$ in aqueous solution by heating at *ca.* 70 °C for several hours. Thus the acac ligand seems to stabilize more dmpe complexes than the en ligand does. An aqueous solution of $[Co(acac)(en)(dmpe)]^{2+}$ gives a small amount of Co(II) species and $[Co(acac)(dmpe)_2]^{2+}$ by heating.

In Fig. 1 are shown absorption spectra of $[Co(en)_{3-n}(dmpe)_n]^{3+}$ (n=0,1,2,3) together with those of related edmp complexes,[11] and in Fig. 2 absorption spectra of $[Co(acac)_{3-n}(en)_n]^{n+}$ (n=0,1,2,3), $[Co(acac)_{3-n}(dmpe)_n]^{n+}$ (n=1,2,3), and $[Co(acac)(en)(dmpe)]^{2+}$. In the Figures, short vertical lines are positions of the first absorption bands calculated by Yamatera's rule[13] using the observed values of the first absorption bands of $[Co(acac)_3]$, $[Co(en)_3]^{3+}$, and $[Co(dmpe)_3]^{3+}$. Table 1 lists spectral data in the d-d band region for ten complexes of the series, $[Co(acac)_x(en)_y(dmpe)_z]^{n+}$. The observed first absorption band maxima appear to agree with the calculated values for the series of $[CoN_nP_{6-n}]$, where *trans*-$[CoN_4P_2]$, *mer*-$[CoN_3P_3]$, *trans*-$[CoN_2P_4]$, and $[CoNP_5]$ are missing. Many attempts to prepare complexes of these types have been unsuccessful. The first three types have a *trans*(P,P) configuration which would make the complex unstable by the trans effect of a phosphine li-

TABLE 1. ABSORPTION AND CD SPECTRAL DATA OF $[Co(acac)_x(en)_y(dmpe)_z]^{n+}$ IN THE d-d BAND REGION

Complex	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)	Solvent
$[Co(acac)_3]$	16.90(2.13)	15.4(−2.3), 17.4(+6.1)$^{1)}$	a
$[Co(acac)_2(en)]^+$	18.60(2.17)	16.7(+1.1), 19.7(+4.2)$^{2)}$	a
$[Co(acac)(en)_2]^{2+}$	20.00(2.14)	20.2(+2.4), 26.8(−1.3)$^{3)}$	b
$[Co(acac)_2(dmpe)]^+$	19(2.4)^{sh}, 23.4(2.9)^{sh}	17.4(+), 19.8(−), 24.0(+)*	a
$[Co(acac)(dmpe)_2]^{2+}$	23.25(3.08)	—	a
$[Co(acac)(en)(dmpe)]^{2+}$	21(2.4)^{sh}, 23.40(2.85)	19.0(+1.0), 21.1(−1.55) 24.6(+1.95)	a
$[Co(en)_3]^{3+}$	21.30(1.94), 29.40(1.90)	20.3(+1.89), 23.4(−0.16)$^{4)}$ 28.5(+0.25)	b
$[Co(en)_2(dmpe)]^{3+}$	23.87(2.62), 29.58(2.37)	20.5(+1.50), 22.7(−1.55) 25.5(+0.55), 29.2(+0.40)	b
$[Co(en)(dmpe)_2]^{3+}$	24.75(2.86), 29.40(2.84)	22.2(+), 24.8(−), 29.2(+)*	b
$[Co(dmpe)_3]^{3+}$	26.00(2.97), 30.5(3.3)^{sh}	—	c

1) I. Jonas and B. Norden, *J. Inorg. Nucl. Chem.*, **12**, 43(1976). 2) Ref. 19. 3) Ref. 20. 4) Ref. 1. sh: shoulder. *: Qualitative data (see the text). a: CH_3OH. b: H_2O. c: $(CH_3)_2SO$.

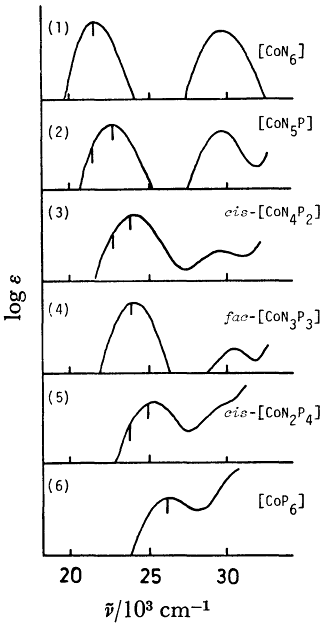

Fig. 1. Absorption spectra of (1) $[Co(en)]^{3+}$, (2) $[Co(en)_2(edmp)]^{3+}$, (3) $[Co(en)_2(dmpe)]^{3+}$, (4) *fac*-$[Co(edmp)_3]^{3+}$, (5) $[Co(en)(dmpe)_2]^{3+}$, and (6) $[Co(dmpe)_3]^{3+}$. Short vertical lines show the calculated band positions (see the text).

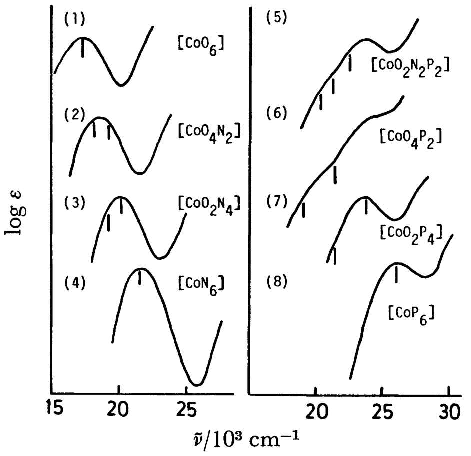

Fig. 2. Absorption spectra of (1) $[Co(acac)_3]$, (2) $[Co(acac)_2(en)]^+$, (3) $[Co(acac)(en)_2]^{2+}$, (4) $[Co(en)_3]^{3+}$, (5) $[Co(acac)(en)(dmpe)]^{2+}$, (6) $[Co(acac)_2(dmpe)]^+$, (7) $[Co(acac)(dmpe)_2]^{2+}$, and (8) $[Co(dmpe)_3]^{3+}$. Short vertical lines show the calculated band positions (see the text).

gand.[11,14] For example, the reaction of edmp with *trans*-$[CoCl_2(dmpe)_2]^+$ did not yield $[Co(edmp)(dmpe)_2]^{3+}$ of the $[CoNP_5]$-type, giving *fac*-$[Co(edmp)_3]^{3+}$ and $[Co(dmpe)_3]^{3+}$ by disproportionation.

As shown in Fig. 1, the first absorption bands of $[CoN_nP_{6-n}]$ are shifted to the high energy side by replacing N with P, while the positions of the second absorption bands remain almost unchanged. As the result the energy difference between the two d-d bands becomes small as the number of P increases. The difference of *ca.* 3500 cm^{-1} for $[Co(dmpe)_3]^{3+}$ is only 43% of that for $[Co(en)_3]^{3+}$ (8100 cm^{-1}). When the decrease in energy difference is assumed to occur by an increasing covalent character of bonds between the phosphine ligand and Co(III),[15] it is concluded that the Co^{3+}–P bond has extremely strong covalent character as compared with the Co^{3+}–N bond. Some Co(III)-phosphite complexes have also small energy difference between the two d-d bands, $[Co\{P(OCH_2)_3CCH_3\}_6]^{3+}$ and $[Co\{P(OCH_3)_3\}_6]^{3+}$ being 5000 and 3300 cm^{-1}, respectively.[16]

While each of $[Co(acac)_{3-n}(en)_n]^{n+}$ (n=1,2) shows the first absorption band at nearly the same position as that expected from Yamatera's rule, $[Co(acac)_2(dmpe)]^+$ and $[Co(acac)(en)(dmpe)]^{2+}$ give spectra fairly different from those expected from the rule in this region (Fig. 2). Both complexes exhibit a peak around 23400 cm^{-1} on the high energy side of the expected positions. The $[Co(acac)(dmpe)_2]^{2+}$ complex also shows the absorption maximum at nearly the same position (23250 cm^{-1}), although the position coincides with that expected from the rule. The spectra of *cis*-$[Co(acac)_2(P)_2]^+$ (P=$P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$) resemble that of $[Co(acac)_2(dmpe)]^+$.[2] The reason for these spectral properties remains unknown.

Figure 3 shows CD spectra of $[Co(en)_{3-n}(dmpe)_n]^{3+}$

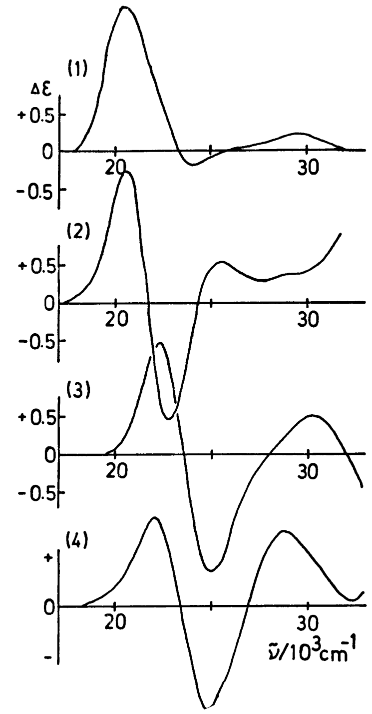

Fig. 3. CD spectra of (1) Λ-[Co(en)$_3$]$^{3+}$, (2) Λ-[Co(en)$_2$(dmpe)]$^{3+}$, (3) Λ-*fac*-[Co(edmp)$_3$]$^{3+}$, and (4) (+)$_{589}$-[Co(en)(dmpe)$_2$]$^{3+}$ (qualitative data, see the text).

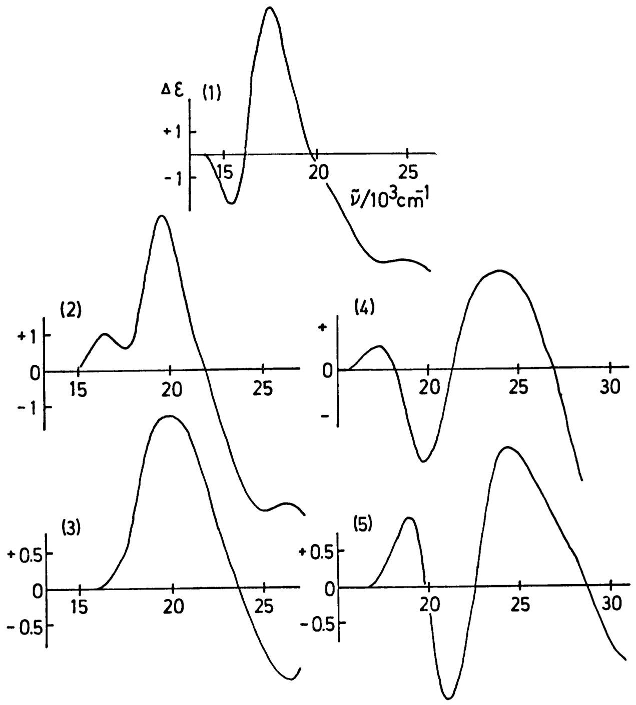

Fig. 4. CD spectra of (1) Λ-[Co(acac)$_3$], (2) Λ-[Co(acac)$_2$(en)]$^+$, (3) Λ-[Co(acac)(en)$_2$]$^{2+}$, (4) (+)$_{589}$-[Co(acac)$_2$(dmpe)]$^+$ (qualitative data, see the text), and (5) (+)$_{589}$-[Co(acac)(en)(dmpe)]$^{2+}$.

(n=0,1,2) and *fac*-[Co(edmp)$_3$]$^{3+}$ [11] in the d-d band region. The spectrum of [Co(en)(dmpe)$_2$]$^{3+}$ is qualitative because of poor resolution. The absolute configurations of [Co(en)$_3$]$^{3+}$,[17] [Co(en)$_2$(dmpe)]$^{3+}$,[9] and *fac*-[Co(edmp)$_3$]$^{3+}$ [12] in the Figure have been determined to Λ by the X-ray method. These Λ-isomers give two CD components with different signs, (+) and (−) from the low energy side in the first absorption band region, although the negative components of the phosphine complexes are very strong as compared with that of Λ-[Co(en)$_3$]$^{3+}$. All the isomers give positive CD in the second absorption band region. The CD spectrum of [Co(en)(dmpe)$_2$]$^{3+}$ in the Figure has such characteristics of the Λ-isomer, and the complex can be assigned to Λ configuration. In column chromatographic resolution by use of SP-Sephadex C-25 and Na$_2$[Sb$_2$(d-tartrate)$_2$], the fast-moving enantiomer is Λ for [Co(en)$_3$]$^{3+}$ and *fac*-[Co(edmp)$_3$]$^{3+}$, while Δ for [Co(en)$_2$(dmpe)]$^{3+}$ and [Co(en)(dmpe)$_2$]$^{3+}$. No resolution has been achieved for [Co(dmpe)$_3$]$^{3+}$.

Figure 4 shows CD spectra of [Co(acac)$_{3-n}$(en)$_n$]$^{n+}$ (n=0,1,2), [Co(acac)$_2$(dmpe)]$^+$, and [Co(acac)(en)(dmpe)]$^{2+}$ in the d-d band region. The latter two complexes are enantiomers eluted faster in column chromatography. The CD spectrum of [Co(acac)$_2$(dmpe)]$^+$ is qualitative because of poor resolution. In the Figure, the absolute configuration of [Co(acac)$_3$] has been determined to Λ by the X-ray method,[18] and those of [Co(acac)$_2$(en)]$^+$ [19] and [Co(acac)(en)$_2$]$^{2+}$ [20] assigned to the same Λ configuration on the basis of the CD spectra. These Λ-isomers as well as Λ-[Co(en)$_3$]$^{3+}$ give a positive main CD band in the first absorption band region. On the other hand, the CD spectra of [Co(acac)$_2$(dmpe)]$^+$ and [Co(acac)(en)(dmpe)]$^{2+}$ differ remarkably from those of Λ-[Co(acac)$_{3-n}$(en)$_n$]$^{n+}$, giving three CD components of (+), (−), and (+) signs from the low energy side in this region. This CD pattern, however, is quite similar to that of Λ-[Co(en)$_{3-n}$(dmpe)$_n$]$^{3+}$ (n=1,2), both of which show a strong negative CD component as seen in Fig. 3. The appearance of the strong negative components in [Co(acac)$_2$(dmpe)]$^+$ and [Co(acac)(en)(dmpe)]$^{2+}$ can also be attributed to the effect of substitution of one en ligand in [Co(acac)$_2$(en)]$^+$ and [Co(acac)(en)$_2$]$^{2+}$, respectively by the dmpe ligand. Thus both acac complexes containing dmpe in Fig. 4 can be assigned to Λ configuration.

This work was supported by the research grant of the Takeda Science Foundation.

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