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Preparation and Resolution of a Series of Cobalt(III) Complexes Containing 2,2′-Biimidazole and Ethylenediamine

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A new series of cobalt(III) complexes of the type $[Co(H_2biim)_n(en)_{3-n}]^{3+}$ ($H_2biim = 2,2'$-biimidazole; $n = 1$—3) was obtained. All of the complexes were resolved into their antipodes by SP-Sephadex column chromatography. The absorption, circular dichroism, and ^1H NMR spectra of the complexes in aqueous solutions were dependent on the pH due to deprotonation of the imino protons of H$_2$biim. The pK_{a1} and pK_{a2} values for $[Co(H_2biim)(en)_2]^{3+}$ were obtained as 5.9 and 9.9, respectively, from the absorption spectra in aqueous solutions. The optically active deprotonated complexes, $(-)_{589}$-$[Co(Hbiim)_3]\cdot 2H_2O$ and $(-)_{589}$-$Ba_{1.5}[Co(biim)_3]\cdot 2H_2O$, were also isolated from weakly and strongly basic aqueous solutions, respectively, of $(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3\cdot H_2O$.

A bidentate ligand, 2,2′-biimidazole (H$_2$biim)[1)] forms an almost planar chelate ring as confirmed by X-ray analyses of such complexes as *trans*-$[Ni(H_2biim)_2(H_2O)_2]\,(NO_3)_2$[2)] and $[Fe(H_2biim)_3]\,CO_3$.[3)] Although H$_2$biim is known to form complexes with many kinds of metal ions,[3—8)] no optically active complex has ever been known. This paper reports on the preparation and properties of optically active cobalt(III) complexes containing H$_2$biim.[9)] To our knowledge, no cobalt(III) complex with H$_2$biim has been reported.[10)]

The H$_2$biim ligand has two imino protons and can coordinate to a metal ion as a neutral molecule (H$_2$biim), a monoanion (Hbiim$^-$), and a dianion (biim^{2-}) by deprotonation of the imino proton(s). Although a number of multinuclear complexes with biim^{2-} acting as a bridging ligand were isolated,[7,8,11,12)] only a few mononuclear complexes containing biim^{2-} have been isolated.[7)] This paper also describes the isolation of the optically active deprotonated complexes, $[Co(Hbiim)_3]$ and $[Co(biim)_3]^{3-}$.

Experimental

Preparation of 2,2′-Biimidazole (H$_2$biim). This ligand was prepared according to the literature method.[5)] The free ligand is soluble in *N,N*-dimethylformamide (DMF) and ethylene glycol, but hardly soluble in water. The ligand was converted into the sulfate, which is soluble in water. A 2 mol dm^{-3} H_2SO_4 solution (100 cm^3) of H$_2$biim (10 g) was mixed with acetone (100 cm^3). The mixture was cooled in an ice bath to give crystals, which were collected by filtration, washed with a mixture of acetone and water (1 : 1) and then acetone, and air-dried. Recrystallization from a mixture of acetone and water (1 : 1) gave colorless needles of $H_2biim\cdot H_2SO_4\cdot 2H_2O$. Found: C, 27.10; H, 4.29; N, 20.79%. Calcd for $C_6H_{12}N_4O_6S$: C, 26.86; H, 4.52; N, 20.89%.

Preparation and Resolution of the Complexes. **$[Co(H_2biim)_3]^{3+}$.** A solution containing $K_3[Co(CO_3)_3]$[13)] (10 mmol) and $H_2biim\cdot H_2SO_4\cdot 2H_2O$ (9.5 g, 35 mmol) in a mixture of DMF (75 cm^3) and water (150 cm^3) was kept at 80 °C for 3 h with stirring. The resulting orange solution was diluted with 10^{-2} mol dm^{-3} HNO$_3$ (5 dm^3) and poured on a column ($\phi 3.5\times 15$ cm) of SP-Sephadex C-25. The adsorbed species were eluted with a 1 mol dm^{-3} NH$_4$NO$_3$ (pH 2, HNO$_3$) solution. The orange eluate was concentrated to ca. one-third of its original volume under reduced pressure at 50 °C. Upon storing the concentrate in a refrigerator for 2 d, orange crystals were formed, collected by filtration, washed with methanol, and then air-dried. The complex was recrystallized from 10^{-2} mol dm^{-3} HNO$_3$ (70 °C). Yield: 5.3 g (82%). Found: C, 33.30; H, 2.72; N, 32.30%. Calcd for $[Co(H_2biim)_3](NO_3)_3 = C_{18}H_{18}N_{15}O_9Co$: C, 33.39; H, 2.81; N, 32.46%.

The complex was completely resolved by column chromatography. An aqueous solution of the complex (0.5 g) was applied on a column ($\phi 3.5\times 70$ cm) of SP-Sephadex. Elution with a 0.15 mol dm^{-3} $Na_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$ solution gave two separate bands of $(+)_{589}$- and $(-)_{589}$-isomers in the order of elution. Each eluate of the bands was diluted with 10^{-2} mol dm^{-3} HNO$_3$ (10 dm^3), and poured again on a small column ($\phi 2.2\times 7$ cm) of SP-Sephadex. The adsorbed complex was eluted with a 1 mol dm^{-3} NH$_4$NO$_3$ (pH 2, HNO$_3$) solution. The eluate was concentrated under reduced pressure and stored in a refrigerator to yield crystals of the optically active complex, which were recrystallized from 10^{-2} mol dm^{-3} HNO$_3$ (70 °C). Found for the $(-)_{589}$-isomer: C, 32.52; H, 2.78; N, 31.71%. Calcd for $[Co(H_2biim)_3](NO_3)_3\cdot H_2O = C_{18}H_{20}N_{15}O_{10}Co$: C, 32.49; H, 3.03; N, 31.58%.

$(-)_{589}$-$[Co(Hbiim)_3]\cdot 2H_2O$. To an aqueous solution (80 cm^3) of $(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3\cdot H_2O$ (2.1 g) was added 28% aqueous ammonia (50 cm^3) with stirring to yield orange crystals quantitatively. The crystals were collected by filtration, washed with warm water (60 °C), and then dried over P_4O_{10}. Yield: 1.5 g (96%). Found: C, 43.42; H, 3.69; N, 34.01%. Calcd for $C_{18}H_{19}N_{12}O_2Co$: C, 43.73; H, 3.87; N, 34.00%. The complex is hardly soluble in water and common organic solvents, but slightly soluble in ethanol. This Hbiim$^-$ complex was also obtained from $(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3\cdot H_2O$ dissolved in an ammonium chloride–aqueous ammonia buffer solution of pH 8.

$(-)_{589}$-$Ba_{1.5}[Co(biim)_3]\cdot 2H_2O$. $(-)_{589}$-$[Co(Hbiim)_3]\cdot 2H_2O$ (1.5 g, 3 mmol) was dissolved in 2 mol dm^{-3} NaOH (60 cm^3). To the resulting yellow solution was added an aqueous solution (40 cm^3) of $BaCl_2\cdot 2H_2O$ (1.2 g, 5 mmol) with stirring to yield yellow crystals, which were collected, washed with warm water (60 °C), and then dried over P_4O_{10}. Yield: 1.9 g (90%). Found: C, 31.13; H, 2.50; N, 23.81%. Calcd for $C_{18}H_{16}N_{12}O_2Ba_{1.5}Co$: C, 31.00; H, 2.31; N, 24.10%. The complex is soluble in ethanol, but hardly soluble in water.

$[Co(H_2biim)_2(en)]^{3+}$. A solution containing $K[Co(CO_3)_2(en)]\cdot H_2O$[13] (0.9 g, 3 mmol) and $H_2biim\cdot H_2SO_4\cdot 2H_2O$ (1.7 g, 6.3 mmol) in a mixture of DMF (15 cm^3) and water (30 cm^3) was kept at 60 °C for 24 h with stirring. The resulting solution was diluted with 10^{-2} mol dm^{-3} HCl (1 dm^3) and applied on a column (ϕ2.2×140 cm) of SP-Sephadex. Elution with 0.2 mol dm^{-3} Na_2SO_4 (pH 2, H_2SO_4) gave two orange bands. The faster moving small band was found to contain $[Co(H_2biim)_3]^{3+}$. The eluate of the slower moving band was diluted with 10^{-2} mol dm^{-3} HCl, and then poured again on a small column (ϕ2.2×5 cm) of SP-Sephadex. The adsorbed complex was eluted with 2 mol dm^{-3} HCl. The eluate was concentrated to a small volume under reduced pressure and then mixed with acetone to give orange crystals. They were collected, washed with acetone, and then air-dried. The complex was recrystallized from a mixture of 10^{-2} mol dm^{-3} HCl and acetone (1 : 3). Yield: 0.9 g (55%). Found: C, 30.49; H, 4.76; N, 25.60%. Calcd for $[Co(H_2biim)_2(en)]Cl_3\cdot 3H_2O = C_{14}H_{26}N_{10}O_3Cl_3Co$: C, 30.70; H, 4.78; N, 25.57%.

The complex (0.1 g) was completely resolved by a method similar to that for $[Co(H_2biim)_3]^{3+}$ using a column (ϕ2.2×140 cm) of SP-Sephadex. The $(-)_{589}$-isomer was eluted faster. The optically active complex was isolated as the chloride by a method similar to that for the racemate. Found for the $(-)_{589}$-isomer: C, 30.58; H, 4.52; N, 25.71%. Calcd for $(-)_{589}$-$[Co(H_2biim)_2(en)]Cl_3\cdot 3H_2O$: C, 30.70; H, 4.78; N, 25.57%.

$[Co(H_2biim)(en)_2]^{3+}$. A solution containing $[Co(CO_3)(en)_2]Cl\cdot H_2O$[13] (2.9 g, 10 mmol) and $H_2biim\cdot H_2SO_4\cdot 2H_2O$ (2.7 g, 10 mmol) in a mixture of DMF (75 cm^3) and water (150 cm^3) was kept at 60 °C for 24 h with stirring. The resulting solution was diluted with 10^{-2} mol dm^{-3} HCl (5 dm^3) and poured on a column (ϕ3.5×15 cm) of SP-Sephadex. The adsorbed species were eluted with a 2 mol dm^{-3} HCl solution. The eluate of a large orange band was collected and concentrated to a small volume under reduced pressure. The concentrate was mixed with acetone to give orange crystals. They were collected, washed with acetone, and then air-dried. The complex was recrystallized from a mixture of 10^{-2} mol dm^{-3} HCl and ethanol (1 : 4). Yield: 3.0 g (69%). Found: C, 27.35; H, 5.53; N, 25.22%. Calcd for $[Co(H_2biim)(en)_2]Cl_3\cdot H_2O = C_{10}H_{24}N_8OCl_3Co$: C, 27.44; H, 5.53; N, 25.60%.

The optically active complex was obtained as the chloride by the same method as that for $[Co(H_2biim)_2(en)]^{3+}$. The $(-)_{589}$-isomer was eluted faster from the column. Found for the $(-)_{589}$-isomer: C, 27.27; H, 5.58; N, 25.43%. Calcd for $(-)_{589}$-$[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$: C, 27.44; H, 5.53; N, 25.60%.

Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Shimadzu MPS-50L spectrophotometer and a JASCO J-40 spectropolarimeter, respectively. Optical rotations were measured with a Union PM-101 polarimeter. ^{1}H NMR spectra in D_2O solutions were recorded on a Varian EM-390 spectrometer using sodium 2,2′-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.

Spectrophotometric titration for $[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$ was carried out in aqueous solutions at 25 °C using a Shimadzu MPS-50L spectrophotometer. The pH of the solutions was adjusted with aqueous solutions of HCl or NaOH, or buffer solutions.[14] The pH measurements were made with a Horiba F-8L pH meter. Ionic strengths ($I = 1.0$) of the solutions were adjusted with an aqueous solution of NaCl. The concentrations of the complex were about 3 mmol dm^{-3}.

Results and Discussion

Three new cobalt(III) complexes, $[Co(H_2biim)_n(en)_{3-n}]^{3+}$ (n=1—3), were prepared from $[Co(CO_3)_n(en)_{3-n}]^{(3-2n)+}$ and $H_2biim\cdot H_2SO_4\cdot 2H_2O$ in a mixture of water and DMF. All of the H_2biim complexes were completely resolved into their antipodes by SP-Sephadex column chromatography using $Na_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$ as an eluent.

The complexes were identified by ^{1}H NMR spectroscopy. Table 1 lists the chemical shifts of the free H_2biim ligand and the complexes in the region of the imidazole ring CH protons. Each signal in NaOD solutions was observed at a higher magnetic field than the corresponding one in DCl solutions. The complexes in both acidic and basic aqueous solutions showed no change in the spectra after 2 d at room temperature. In the spectrum of the tris(H_2biim) complex, one of the resonances of the imidazole CH protons is observed at a higher field. Molecular models indicate that one of two imidazole CH protons in the complex is placed above the adjacent H_2biim ligand and is shielded by its ring current. The bis(H_2biim) complex also showed a high field shift. A similar high field shift was reported for [Si(1,1′-dimethyl-2,2′-biimidazole)$_3$]I_4.[15]

Figure 1 shows that the absorption spectra of $[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$ depend on the pH of solutions. The spectral changes can be divided into two steps corresponding to different isosbestic points at 392 and 430 nm. Thus, two stepwise acid-base equilibria are involved in the solutions. Figure 2 shows plots of the absorbances at 330 or 500 nm. The equilibria can be shown as Scheme 1. The pK_{a1} and pK_{a2} values were obtained as 5.9±0.1 and 9.9±0.1 at 25 °C, respectively. The results indicate that the H_2biim ligand in this complex acts as a neutral molecule (H_2biim), a monoanion ($Hbiim^-$),

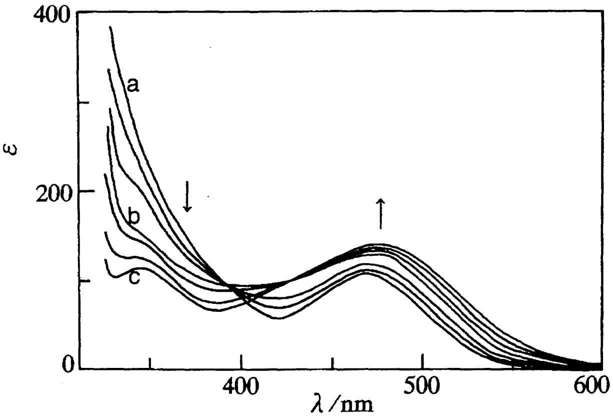


Fig. 1. Absorption spectra of $[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$ at 25 °C in aqueous solutions at various pH; in 0.1 mol dm^{-3} HCl (a), pH 5.5, 6.0, 7.9 (b), 9.5, 10.2, and in 0.1 mol dm^{-3} NaOH (c).

Table 1. ^{1}H NMR Data in the Region of the Imidazole Ring CH Protons (δ from DSS)

Compounds	In 0.1 mol dm^{-3} DCl	In 1 mol dm^{-3} NaOD
H_2biim[a)]	7.87(s)	
[Co(H_2biim)(en)$_2$]$^{3+}$	7.57(q, 4H)[b)]	7.19(q, 4H)[c)]
[Co(H_2biim)$_2$(en)]$^{3+}$	6.39(d, 2H),[d)] 7.37(d, 2H),[d)] 7.79(br, 4H)	5.82(d, 2H),[e)] 6.71(d, 2H),[e)] 7.24(d, 2H),[f)] 7.33(d, 2H)[f)]
[Co(H_2biim)$_3$]$^{3+}$	6.72(br, 6H), 7.61(br, 6H)	6.20(br, 6H), 6.90(br, 6H)

a) Insoluble in 1 mol dm^{-3} NaOD. b) AB quartet; $J = 1.86$ Hz. c) AB quartet; $J = 1.20$ Hz. d) $J = 1.56$ Hz. e) $J = 0.84$ Hz. f) $J = 1.08$ Hz.

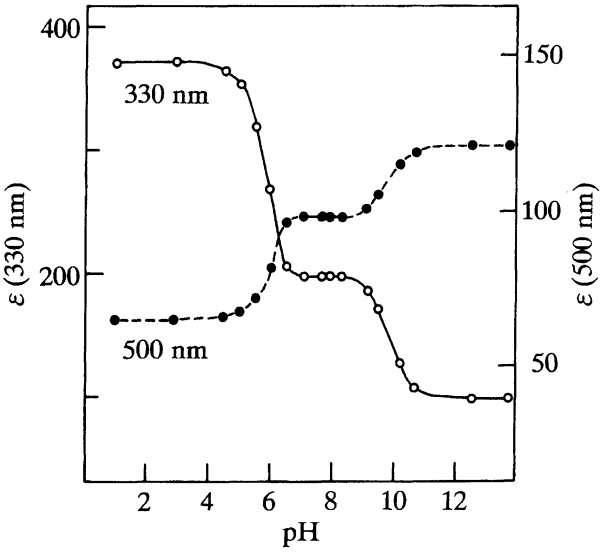
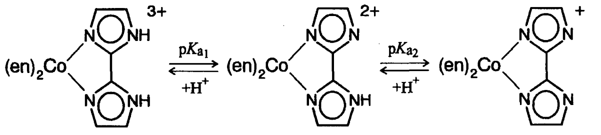


Fig. 2. Spectrophotometric titration curves for [Co(H_2biim)(en)$_2$]$Cl_3 \cdot H_2O$ in aqueous solutions at 25 °C.



Scheme 1.

and a dianion (biim^{2-}) in acidic, near neutral, and basic aqueous solutions, respectively. In fact, the deprotonated neutral and anionic complexes, $(-)_{589}$-[Co(Hbiim)$_3$]$\cdot 2H_2O$ and $(-)_{589}$-$Ba_{1.5}$[Co(biim)$_3$]$\cdot 2H_2O$ were isolated from $(-)_{589}$-[Co(H_2biim)$_3$]$(NO_3)_3 \cdot H_2O$ in buffer solutions of pH 8 and in strongly basic aqueous solutions, respectively (see Experimental). These deprotonated complexes gave again the protonated complex, $(-)_{589}$-[Co(H_2biim)$_3$]$^{3+}$ in 0.1 mol dm^{-3} HCl. Recently, Rillema et al.[12)] reported the values of pK_{a1} and pK_{a2}, 7.2 and 12.1, respectively, for [Ru(H_2biim)(bpy)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine).[8)] Variations of pK_a values among different metal centers were observed for a similar deprotonation of [M(2,2′-bibenzimidazole)(bpy)$_2$]$^{n+}$ (M = Os(III), Os(II), Ru(II)).[16)]

Figure 3 compares the absorption and CD spectra for the series of $(-)_{589}$-[Co(H_2biim)$_n$(en)$_{3-n}$]$^{3+}$ (n = 1—3) in 0.1 mol dm^{-3} HCl solutions. The spectral data are listed in Table 2. The first ligand field band ($^1T_{1g} \leftarrow {}^1A_{1g}$) of [Co($H_2$biim)$_n(en)_{3-n}$]$^{3+}$ at ca. 21500 cm^{-1} scarcely shifts by replacing en with H_2biim, indicating similar ligand field strength (10 Dq) of H_2biim to that of en. The second ligand field band ($^1T_{2g} \leftarrow {}^1A_{1g}$) seems to overlap other bands. For the [Ru(H_2biim)$_3$]$^{2+}$ [12)] and [M(H_2biim)$_2$]$^{2+}$ (M = Cu(II) and Zn(II))[17)] complexes, a band around at ca. 26000 cm^{-1} was assigned to involve the ligand to metal charge-transfer transition. In the region of 30000 to 38000 cm^{-1}, the new cobalt(III) complexes exhibit strong absorptions, and the intensities are related to the number of the H_2biim ligand. In the same region, almost the same absorptions were observed for the above Ru(II), Cu(II), and Zn(II) complexes, and were assigned to the $\pi^* \leftarrow \pi$ transitions of the coordinated H_2biim ligand.[12,17)]

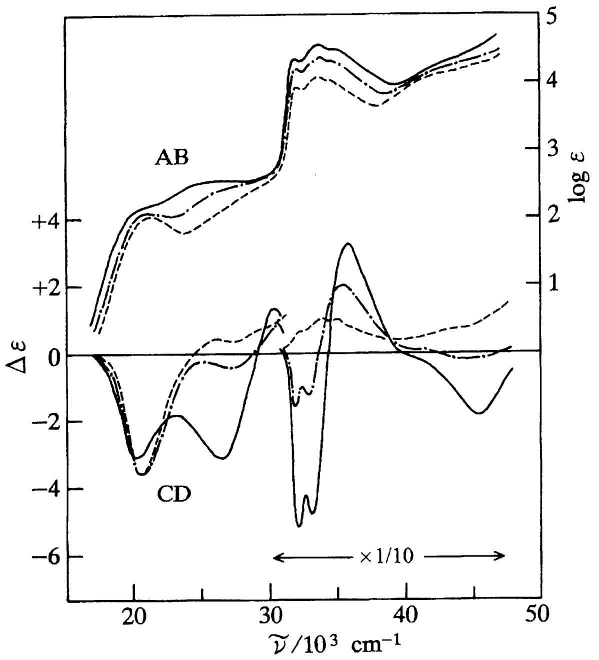


Fig. 3. Absorption and CD spectra of $(-)_{589}$-[Co(H_2biim)$_3$]$^{3+}$ (——), $(-)_{589}$-[Co(H_2biim)$_2$(en)]$^{3+}$ (–••–), and $(-)_{589}$-[Co(H_2biim)(en)$_2$]$^{3+}$ (- - -) in 0.1 mol dm^{-3} HCl.

As Fig. 3 shows, all of the $(-)_{589}$-isomers in 0.1 mol dm^{-3} HCl solutions exhibit negative CD in the region of the first ligand field band, and are assigned to have the Δ configuration on the basis of an empirical rule.[18)] The $(-)_{589}$-[Co(H_2biim)$_3$]$^{3+}$ complex shows a strong negative CD band at ca. 25000 cm^{-1} corresponding to the broad absorption band in this region. The band can possibly be assigned to a charge-transfer in origin. Alternatively, the strong CD may be re-

Table 2. Absorption and CD Spectral Data in 0.1 mol dm^{-3} HCl

Absorption		CD	
$\tilde{\nu}_{max}/10^3$ cm^{-1} (log ε)		$\tilde{\nu}_{ext}/10^3$ cm^{-1} ($\Delta\varepsilon$)	
	$H_2biim\cdot H_2SO_4\cdot 2H_2O$		
36.50(4.17)			
	$(-)_{589}$-$[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$		
21.32(2.02),	29.5(2.5)sh,[a]	20.66(−3.57),	26.32(+0.34),
32.10(3.93),	33.3(4.0)sh,	32.26(+5.85),	34.13(+9.65),
33.78(4.10),	34.66(4.05),	34.90(+9.34),	42.4(+5.4)sh
44.0(4.2)sh			
	$(-)_{589}$-$[Co(H_2biim)_2(en)]Cl_3\cdot 3H_2O$		
21.39(2.08),	29.0(2.6)sh,	20.62(−3.67),	27.03(−0.38),
32.10(4.19),	33.4(4.3)sh,	30.67(+0.96),	31.95(−16.9),
33.84(4.37),	34.72(4.33),	32.84(−12.0),	35.65(+20.4),
44.0(4.2)sh		44.44(−1.68)	
	$(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3\cdot H_2O$		
21.7(2.2)sh,	26.46(2.54),	20.20(−3.16),	26.39(−3.20),
32.10(4.36),	33.0(4.5)sh,	30.58(+1.33),	32.15(−52.9),
33.78(4.54),	34.66(4.51),	33.11(−48.4),	35.84(+32.9),
43.5(4.3)sh		45.25(−18.5)	

a) sh: Shoulder.

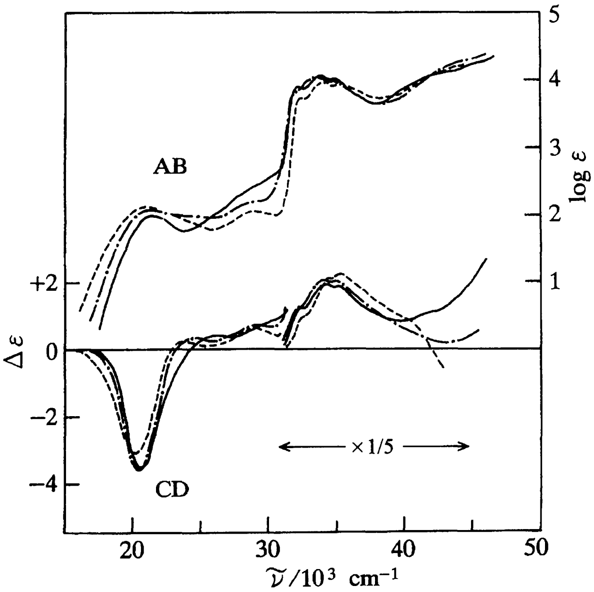


Fig. 4. Absorption and CD spectra of $(-)_{589}$-$[Co(H_2biim)(en)_2]Cl_3\cdot H_2O$ in 0.1 mol dm^{-3} HCl (——), in an ammonium chloride–aqueous ammonia buffer solution of pH 7.9 (– • –), and in 0.1 mol dm^{-3} NaOH (- - -).

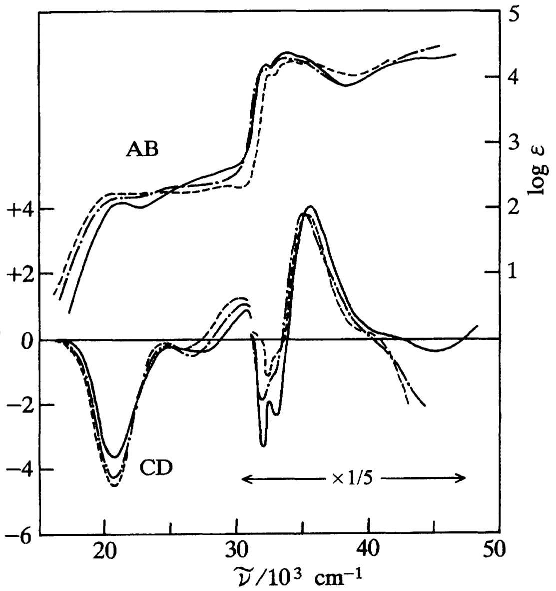


Fig. 5. Absorption and CD spectra of $(-)_{589}$-$[Co(H_2biim)_2(en)]Cl_3\cdot 3H_2O$ in 0.1 mol dm^{-3} HCl (——), in an ammonium chloride–aqueous ammonia buffer solution of pH 7.9 (– • –), and in 0.1 mol dm^{-3} NaOH (- - -).

lated to the adjacent very strong CD bands in the π*←π transition region. But the details are unknown at present. In the π*←π transition region, $(-)_{589}$-$[Co(H_2biim)_3]^{3+}$ exhibits a characteristic CD pattern with strong magnitude, two negative and one positive bands from the lower energy side. In the same region, $(-)_{589}$-$[Co(H_2biim)_2(en)]^{3+}$ also shows nearly the same CD pattern as that of $(-)_{589}$-$[Co(H_2biim)_3]^{3+}$, although the magnitude is reduced. On the other hand, $(-)_{589}$-$[Co(H_2biim)(en)_2]^{3+}$ and Δ-$[Co(en)_3]^{3+}$ [19] show no such a CD pattern. The characteristic strong CD of the tris- and bis (H_2biim) complexes should be assigned to the exciton interaction among the H_2biim ligands as observed for $[M(phen)_3]^{n+}$ (phen = 1,10-phenanthroline) and $[M(bpy)_3]^{n+}$.[18] The absolute configuration of Δ can be assigned to the $(-)_{589}$-$[Co(H_2biim)_3]^{3+}$ complex, since its CD pattern is the same as that of Δ-$[Co(phen)_3]^{3+}$ [20,21] and Δ-$[Co(bpy)_3]^{3+}$. [21,22] The assignment agrees well with that based on the CD sign in the region of the first ligand field

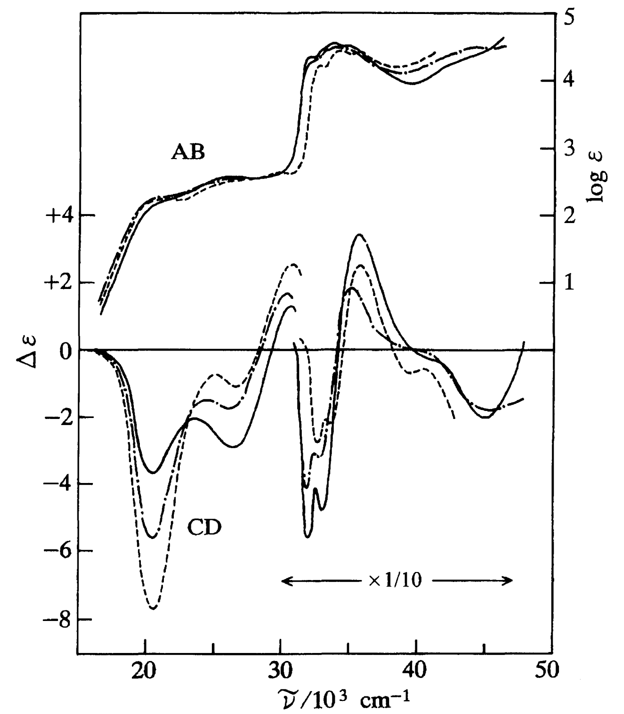


Fig. 6. Absorption and CD spectra of $(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3 \cdot H_2O$ in 50% ethanol solutions containing HCl in 0.1 mol dm^{-3} (——), an ammonium chloride–aqueous ammonia buffer solution of pH ca. 8 (–••–), and NaOH in 0.1 mol dm^{-3} (- - -).

band.

Figure 4 shows the absorption and CD spectra of $(-)_{589}$-$[Co(H_2biim)(en)_2]Cl_3 \cdot H_2O$ in 0.1 mol dm^{-3} HCl, in ammonium chloride–aqueous ammonia buffer of pH 7.9, and in 1 mol dm^{-3} NaOH solutions. The first ligand field band slightly shifts to a lower energy side and broadens by increasing the pH of the solution. In the $\pi^* \leftarrow \pi$ transition, the absorption band slightly shifts to a higher energy side in 1 mol dm^{-3} NaOH solutions. The CD spectra are similar to one another over the whole region, although the spectra show a small change in magnitude and position with an increasing basicity of the solution.

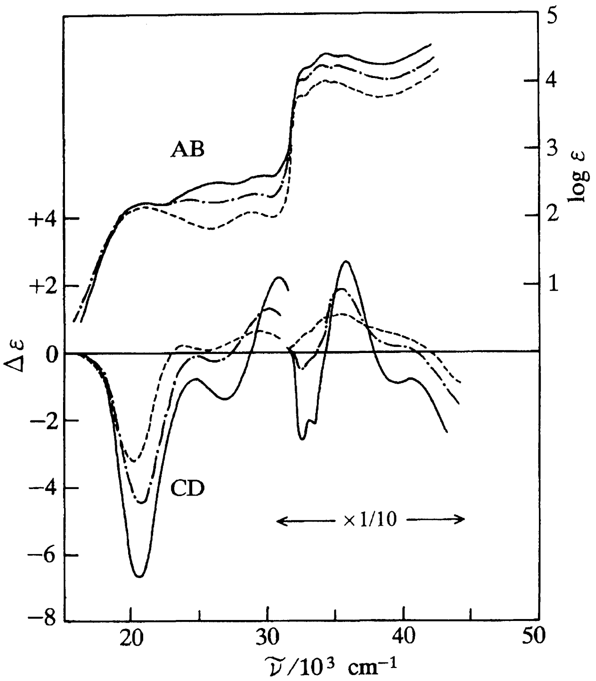


Fig. 7. Absorption and CD spectra of $(-)_{589}$-$[Co(biim)_3]^{3-}$ (——), $(-)_{589}$-$[Co(biim)_2(en)]^-$ (–••–), and $(-)_{589}$-$[Co(biim)(en)_2]^+$ (- - -) in 0.1 mol dm^{-3} NaOH.

As shown in Fig. 5, the absorption spectrum of $(-)_{589}$-$[Co(H_2biim)_2(en)]Cl_3 \cdot 3H_2O$ shows a pH-dependence similar to that of $[Co(H_2biim)(en)_2]^{3+}$. The CD magnitude in the region of the first ligand field band slightly increases with increasing basicity of the solution. In the region of the exciton CD, the magnitudes of the negative components are gradually reduced with increasing basicity of the solution, while the magnitude of the positive one is slightly decreased by deprotonation of the H_2biim ligands.

Figure 6 shows the absorption and CD spectra of $(-)_{589}$-$[Co(H_2biim)_3](NO_3)_3 \cdot H_2O$ in 50% ethanol solutions containing HCl in 0.1 mol dm^{-3}, and ammonium chloride–aqueous ammonia buffer of pH ca. 8, or NaOH in 1 mol dm^{-3}. The solvents were used because $(-)_{589}$-$[Co(Hbiim)_3] \cdot 2H_2O$

Table 3. Absorption and CD Spectral Data in Ethanol

Absorption		CD	
$\tilde{\nu}_{max}/10^3$ cm^{-1} (log ε)		$\tilde{\nu}_{ext}/10^3$ cm^{-1} (Δε)	
$(-)_{589}$-$[Co(Hbiim)_3] \cdot 2H_2O$			
21.5(2.3)sh,[a]	27.0(2.5)sh,	20.45(−5.70),	25.97(−1.81),
31.95(4.30),	33.61(4.47),	30.44(+1.75),	31.90(−42.5),
34.31(4.46),	45.0(4.5)sh	32.79(−32.3),	35.15(+18.8),
		45.25(−19.3)	
$(-)_{589}$-$Ba_{1.5}[Co(biim)_3] \cdot 2H_2O$			
20.75(2.25),	27.0(2.5)sh,	20.56(−7.81),	26.63(−1.21),
29.41(2.60),	32.57(4.21),	30.96(+2.50),	32.57(−27.1),
34.31(4.43),	35.21(4.41),	33.54(−22.5),	35.84(+26.1),
		39.37(−6.58)	

a) sh: Shoulder.

is insoluble in water. The absorption spectra show a pH dependence similar to those of the mono- and bis(H_2biim) complexes. The CD spectra markedly depend on the pH of the solution. The CD magnitude in the region of the first ligand field band increases remarkably with increasing basicity of the solution. In the region of the exciton CD, the spectrum shows a change in magnitude similar to that of the bis(H_2biim) complex, reducing the magnitude with increasing basicity of the solution. Thus the magnitude of the exciton CD of the present cobalt(III) complexes is reduced by the deprotonation of the imino protons of H_2biim. As Table 3 shows, the absorption and CD spectra of $(-)_{589}$-[Co(Hbiim)$_3$]·2H_2O and $(-)_{589}$-Ba$_{1.5}$[Co(biim)$_3$]·2H_2O in ethanol are almost the same as those of $(-)_{589}$-[Co(H_2biim)$_3$]$^{3+}$ in 50% ethanol containing a buffer solution of pH ca. 8 and in 1 mol dm^{-3} NaOH, respectively.

Figure 7 compares the absorption and CD spectra of a series of $(-)_{589}$-$[Co(biim)_n(en)_{3-n}]^{(3-2n)+}$ ($n = 1$—3) in 1 mol dm^{-3} NaOH solutions. These three complexes show the first ligand field band at nearly the same position with similar intensity, while the CD magnitude in this region increases remarkably by replacing en with biim^{2-}. The CD spectra of basic solutions in this region show marked contrast to those of acidic solutions shown in Fig. 3.

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