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Preparation and Spectroscopic Studies of the Stereoisomers of $[Co(acac)_2(R^1R^2NCH_2CH_2NR^3R^4$ or *o*-Phenylenediamine)]$^+$ (R^1—R^4= H, CH_3, or C_6H_5; acac=2,4-Pentanedionate ion) and Isomer Distribution at Equilibrium

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A series of complexes of the type, $[Co(acac)_2L]^+$, where acac=2,4-pentanedionate ion and L denotes $R^1R^2NCH_2CH_2NR^3R^4$ (R^1—R^4=H or CH_3), *N*-phenylethylenediamine, *N,N'*-diphenylethylenediamine, and *o*-phenylenediamine were prepared and the isomers separated. The absorption spectra and the distributions of the isomers at equilibrium were determined and the results are discussed.

York *et al.*[1] reported that the *N,N,N',N'*-tetramethylethylenediamine (Me_4en) ligand in $[Co(acac)_2(Me_4en)]^+$ (acac=2,4-pentanedionate ion) has a very low ligand field strength comparable to that of the oxygen donors of acac. Akamatsu and Shimura[2] showed that the ligand field strength of the tertiary amine end of *N,N*-dimethylethylenediamine (*N,N*-Me_2en) is weaker than those of oxalato and carbonato ligands. Thus the ligand field strength of ethylenediamine (en) is considerably reduced by the introduction of methyl groups on the nitrogen. In this paper, we report the preparation of $[Co(acac)_2(R^1R^2NCH_2CH_2NR^3R^4)]^+$ (R^1—R^4=H or CH_3), the separation of the isomers, the distributions of the isomers at equilibrium, and the absorption spectra of the isomers. Very recently Ito[3] reported the absorption spectra of bis(acac)-cobalt(III) complexes with *N*-methylated ethylenediamine, however, the complexes were not separated into the isomers.

A cobalt(III) complex with an *N*-phenyl-substituted ethylenediamine ligand will be less stable than the corresponding en complex for both steric and electronic reasons.[4] The two acac ligands seem to stabilize the *N*-phenyl-substituted amine-cobalt(III) system; we have obtained $[Co(acac)_2$(Ph-en, *N,N'*-Ph_2en, or opd)]$^+$ (Ph-en=*N*-phenylethylenediamine, *N,N'*-Ph_2en=*N,N'*-diphenylethylenediamine, opd=*o*-phenylenediamine).

Experimental

Λ(R),Δ(S)-[Co(acac)$_2$(Me-en)]ClO$_4$·0.5H$_2$O and Λ(S),Δ(R)-[Co(acac)$_2$(Me-en)]ClO$_4$(Me-en=N-Methylethylenediamine).* To a solution of $[Co(acac)_3]$ (3.0g, 8.4mmol) in methanol (300cm^3) were added Me-en (0.69g, 9.3mmol) and active charcoal (0.5g). The mixture was stirred for 30min and then filtered. The purple filtrate was diluted with water (3dm^3), and applied on a column (ϕ4.5cm×20cm) of SP-Sephadex C-25. By elution with 0.05 moldm^{-3} NaCl, a purple and a red band developed in this order. The eluate containing the purple band was collected and evaporated to a small volume. To the concentrate sodium perchlorate was added to yield purple crystals, which were recrystallized from water (50°C). Yield: 1.5g. The crystals were a mixture of the two racemic pairs of diastereomers, and they were separated by a column chromatographic method. About 0.3g of the mixture was dissolved in a small amount of water and the solution was applied on a column (ϕ2.2cm×50cm) of SE-Toyopearl[5] HW-40 (fine; eluent: 0.05 moldm^{-3} NaCl). A recycling-chromatographic technique was employed. After three times of recycling, the column showed two purple bands, M-I (*Λ(R)*, *Δ(S)*) and M-II (*Λ(S)*, *Δ(R)*), in the order of elution with the ratio of 1:3. From each eluate the perchlorate of the diastereomer was obtained by the same method as that described above. Anal. (*Λ(R)*, *Δ(S)*, $C_{13}H_{25}N_2ClCoO_{8.5}$) C, H, N. Anal. (*Λ(S)*, *Δ(R)*, $C_{13}H_{24}N_2ClCoO_8$) C, H, N.

(−)$_{589}$-Λ(S)- and (−)$_{589}$-Λ(R)-[Co(acac)$_2$(Me-en)]ClO$_4$. A suspension of *Λ(S)*, *Δ(R)*-$[Co(acac)_2(Me\text{-}en)]ClO_4$ (0.866g, 2.0mmol) and Dowex 1×8 (Cl^- form, *ca.* 3g) in 30cm^3 of water was stirred for 20min, filtered, and the exchanger washed with water (5cm^3×2). To the combined filtrate and washings was added a hot (*ca.* 70°C) solution containing sodium di-*O*-benzoyl-*d*-tartrate (0.402g, 1.0mmol) and di-*O*-benzoyl-*d*-tartaric acid monohydrate (0.376g, 1.0mmol) in 100cm^3 of water. The mixture was allowed to stand overnight at room temperature and recrystallized from hot water (70cm^3). Yield: 0.30g. The diastereomer was dissolved in water and applied on a column (ϕ2cm×5cm) of SP-Sephadex C-25. The column was washed with water, and the complex (*Λ(S)*-isomer) was eluted with 0.2 moldm^{-3} NaCl. The complex was isolated as the perchlorate and recrystallized in the same way as for the racemate. Yield: 80mg. Anal. ($C_{13}H_{24}N_2ClCoO_8$) C, H, N.

The *Λ(S)*-isomer (60mg) was epimerized in 0.1 moldm^{-3} NaOH (20cm^3, pH *ca.* 13) at room temperature. After 1h, the reaction mixture was applied on a column (ϕ2.2cm×50cm) of SE-Toyopearl HW-40 (fine). By elution with 0.05 moldm^{-3} NaCl, two purple bands developed. From the eluate containing the faster-moving band the perchlorate of the *Λ(R)*-isomer was obtained as described for the racemate. Yield: 20mg. Anal. ($C_{13}H_{24}N_2ClCoO_8$) C, H, N. The *Λ(S)*-isomer was recovered from the slower-moving band.

[Co(acac)$_2$(N,N-Me$_2$en)]ClO$_4$. This complex was prepared by a method analogous to that described for the corresponding Me-en complexes. Column chromatography on SP-Sephadex C-25 (eluent: 0.05 moldm^{-3} NaCl) showed two purple bands. From the eluate containing the faster-moving band the complex was isolated as the perchlorate by the same method as for the Me-en complex, and recrystallized from chloroform by the addition of diethyl ether. Yield: 60%.

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Anal. ($C_{14}H_{26}N_2ClCoO_8$) C, H, N. The slower-moving band seemed to contain $[Co(acac)(N,N\text{-}Me_2en)_2]^{2+}$ but this complex was not isolated.

Λ(RR),Δ(SS)- and Λ(SR),Δ(RS)-[Co(acac)₂(N,N′-Me₂en)]ClO₄, and Λ(SS),Δ(RR)-[Co(acac)₂(N,N′-Me₂en)]ClO₄·H₂O (N,N′-Me₂*en*=N,N′-*Dimethylethylenediamine*). These complexes were prepared in the same way as that for the Me-en complexes in a 48% yield and separated into the three racemic pairs of diastereomers, *Λ(RR),Δ(SS)*, *Λ(SR),Δ(RS)*, and *Λ(SS),Δ(RR)* in the ratio of 5:1:3 by the same chromatographic method as used for the Me-en complex. Anal. (*Λ(RR)*, *Δ(SS)*, and *Λ(SR)*, *Δ(RS)*, $C_{14}H_{26}N_2ClCoO_8$) C, H, N. Anal. (*Λ(SS)*, *Δ(RR)*, $C_{14}H_{28}N_2ClCoO_9$) C, H, N.

Λ(R),Δ(S)- and Λ(S), Δ(R)-[Co(acac)₂(Me₃en)]ClO₄(Me₃en=N,N,N′-*Trimethylethylenediamine*). These complexes were prepared by the same method as that described for the Me-en complexes in a total yield of 78%. The two racemic pairs of diastereomers, *Λ(R)*, *Δ(S)* and *Λ(S)*, *Δ(R)* were obtained as the perchlorate salts in the ratio 10:1 from the mixture of the isomers. Anal. (*Λ(R)*, *Δ(S)*, and *Λ(S)*, *Δ(R)*, $C_{15}H_{28}N_2ClCoO_8$) C, H, N.

[Co(acac)₂(Me₄en)]ClO₄. This complex was prepared analogous to the Me-en complex. Column chromatography of the reaction mixture on SP-Sephadex C-25 (eluent: 0.05 mol dm^{-3} NaCl) developed three bands; brown, pink, and green in the order of elution. From the green eluate the complex was isolated as the perchlorate. Yield: 20%. Anal. ($C_{16}H_{30}N_2ClCoO_8$) C, H, N. York *et al.*[1] prepared this complex by the reaction of *trans*-$Na[Co(NO_2)_2(acac)_2]$ with Me_4en in the presence of active charcoal.

Λ(R),Δ(S)- and Λ(S),Δ(R)-[Co(acac)₂(Ph-en)]ClO₄. To a solution of $[Co(acac)_3]$ (3 g, 8.4 mmol) in methanol (100 cm^3) were added a solution of Ph-en (1.27 g, 9.3 mmol) in methanol (50 cm^3), active charcoal (0.5 g), and acetic acid (2 cm^3). The mixture was stirred for 3 h and then filtered. The filtrate diluted with water (3 dm^3) was applied on a column of SP-Sephadex C-25 by the same procedure as for the Me-en complex to give a single band. From the purple eluate the complex was isolated as the perchlorate. Yield: 75%. By fractional crystallization from chloroform, the complex was separated into the two racemic pairs of diastereomers, *Λ(S)*, *Δ(R)* and *Λ(R)*, *Δ(S)*. The *Λ(S)*, *Δ(R)*-pair is less soluble and the more soluble *Λ(R)*, *Δ(S)*-pair was obtained from the mother liquor by the addition of diethyl ether, the ratio of the former to the latter being *ca.* 1:7. Both pairs were recrystallized from acetonitrile by the addition of diethyl ether. Found for the *Λ(S)*, *Δ(R)*-pair: C, 43.49; H, 5.72; N, 5.58%. Found for the *Λ(R)*, *Δ(S)*-pair: C, 43.74; H, 5.28; N, 5.69%. Calcd for $C_{18}H_{26}N_2ClCoO_8$: C, 43.87; H, 5.32; N, 5.68%. The complexes were converted into the more soluble chlorides by means of Dowex 1×8 (Cl^- form) before the determination of the isomer distribution.

Λ(RR),Δ(SS)-[Co(acac)₂(N,N′-Ph₂en)]ClO₄·0.5H₂O. This complex was prepared analogous to the Ph-en complexes except that the reaction mixture was stirred for a longer time (60 h). Column chromatography on SP-Sephadex C-25 (eluent: 0.05 mol dm^{-3} NaCl) resulted in three bands, green, violet, and red in the order of elution. From the green band, the complex was isolated as the perchlorate in the same way as for the Me-en complexes. Yield: 85%. When the preparation was carried out without the addition of acetic acid, the reaction proceeded slowly; about half of the starting complex remained unreacted after 60 h. The complex isolated was the *Λ(RR)*, *Δ(SS)*-pair as confirmed by the ^1H NMR spectrum (*vide infra*). Anal. ($C_{24}H_{30}N_2ClCoO_8$) C, H, N. No fraction indicative of other isomers was obtained in column chromatography. The violet and the red band do not contain the desired complex.

[Co(acac)₂(opd)]ClO₄. To a solution of $[Co(acac)_3]$ (1 g, 2.8 mmol) in methanol (50 cm^3) was added active charcoal (0.5 g). The mixture was deoxygenated with nitrogen, and then mixed with a deoxygenated solution of opd (0.33 g, 3.1 mmol) in methanol (20 cm^3). The mixture was stirred for 1 h and filtered. The purple filtrate was diluted with 0.01 mol dm^{-3} HCl (1 dm^3) and applied on a column (ϕ4.5 cm×30 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} NaCl-0.01 mol dm^{-3} HCl, two bands, purplish red and violet appeared in this order. The eluate containing the purplish red band was collected and evaporated to a small volume, and to the concentrate was added an excess of $NaClO_4$ to yield the perchlorate of the complex. It was recrystallized from 0.02 mol dm^{-3} $HClO_4$ (50 °C). Yield: 35%. Anal. ($C_{16}H_{22}N_2ClCoO_8$) C, H, N. This complex is unstable in neutral or alkaline solution.

Isomer Distribution at Equilibrium. A racemic pair of diastereomers of Me-en, *N,N′*-Me_2en, or Me_3en complex (*ca.* 1 mg) was epimerized in 0.1 mol dm^{-3} Na_3PO_4 (pH 12.1, 2 cm^3) at 25 °C. Portions (0.2 cm^3) of the reaction mixture were withdrawn at timed intervals, neutralized with dilute acetic acid, and chromatographed (sample volume: 4×10^{-3} cm^3) on a JASCO FINE SIL C_{18} column (ϕ4.6 mm×30 cm) with 0.01 mol dm^{-3} sodium 1-heptanesulfonate in 97.5% MeOH–2.5% H_2O as the eluent (flow rate: 0.5 cm^3 min^{-1}). The chromatographic procedures were carried out with a JASCO TRI ROTAR HPLC system, and the complexes were detected by a JASCO UVIDEC 100-IV spectrophotometric detector at 240 nm. The areas of the bands on the chromatograms were determined by weighing paper cutouts matching the bands. The experiments were carried out until the mixture attained equilibrium and no change in the elution curve was observed.

The isomer distribution of the Ph-en complex was determined by a ^1H NMR method. The chloride of the *Λ(S)*, *Δ(R)* (or *Λ(R)*, *Δ(S)*) pair (*ca.* 0.2 g) was dissolved in 0.1 mol dm^{-3} Na_3PO_4 (20 cm^3, pH 12.1) at 25 °C. Portions (4 cm^3) of the reaction mixture were withdrawn every 2 h and mixed with a solution of $NaClO_4$ (*ca.* 2 mol dm^{-3}) in 0.1 mol dm^{-3} $HClO_4$. The perchlorate of the complex which precipitated was collected by filtration, air dried, and the ^1H NMR spectrum was measured in CD_3CN. The distribution of the isomers was determined by measuring the intensities of the methine proton signals of the acac chelate rings (*vide infra*).

Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. ^1H NMR spectra were measured with a JEOL PMX-60 spectrometer. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter.

Results and Discussion

Preparation and Characterization of the Isomers. All the complexes, $[Co(acac)_2(diamine)]^+$ were prepared from $[Co(acac)_3]$ and the diamine ligand in methanol in the presence of active charcoal. The opd complex was prepared under a nitrogen atmosphere.

By the preparations of the Ph-en and *N,N'*-Ph_2en complexes, acetic acid was added to promote the reaction (Experimental). The two acac ligands seem to stabilize the *N*-phenyl-substituted amine–cobalt(III) system. A cobalt(III) complex with an *N*-phenyl-substituted amine ligand is usually unstable and difficult to prepare. For example, although the preparation of $[Co(opd)_3]^{3+}$ has been reported,[6] we could not repeat the results in spite of many attempts. Redox reaction between the phenyl group and the cobalt(III) ion seems to be related to the instability. All the complexes prepared in the present study were purified by column chromatography on SP-Sephadex C-25, and isolated as the perchlorates. The complexes containing a chiral nitrogen atom were separated into the racemic pairs of diastereomers by SE-Toyopearl column chromatography. It has been found that this exchanger is more effective than SP-Sephadex in the separation of diastereomers of uni- and dipositive cobalt(III) complexes.[7,8] However, the separation of the pairs *Λ*(*R*), *Δ*(*S*) and *Λ*(*S*), *Δ*(*R*) of $[Co(acac)_2(Ph\text{-}en)]^+$ was not achieved by the chromatographic method, but by fractional crystallization of their perchlorates. The *Λ*(*S*),*Δ*(*R*)-$[Co(acac)_2(Me\text{-}en)]^+$ pair was resolved by the chemical method with hydrogen di-*O*-benzoyl-*d*-tartrate. The *Λ*(*S*)-isomer formed the less soluble diastereomeric salt which was converted into the perchlorate. The *Λ*(*S*)-isomer was epimerized to give a mixture of the *Λ*(*S*)- and *Λ*(*R*)-isomers which were separated by column chromatography on SE-Toyopearl.

The structures of the isomers were assigned on the basis of the ^1H NMR and CD spectra. Four isomers, *Λ*(*R*), *Λ*(*S*), *Δ*(*R*), and *Δ*(*S*) are possible for $[Co(acac)_2(Me\text{-}en)]^+$ (Fig. 1). In the *Δ*(*R*) and *Λ*(*S*) configurations, the *N*-methyl group is placed over one of the two acac chelate rings and the methyl protons will be shielded by the acac ring. Thus, pair M-I (Experimental) which shows a doublet assignable to the *N*-methyl protons at a higher magnetic field (1.80, Table 1) is assigned to the racemic pair of diastereomers, *Δ*(*R*) and *Λ*(*S*). The structures of the complexes with *N,N'*-Me_2en and Me_3en were assigned in the same way (Table 1). Examination of molecular models indicates that in *Δ*(*S*)- and *Λ*(*R*)-$[Co(acac)_2(Ph\text{-}en)]^+$, the phenyl group strongly shields the methine proton of one of the two acac chelate rings. The resonance at δ 4.88 of the more soluble racemic pair can safely be attributed to the shielded methine proton, and thus the pair is assigned to the racemic pair of diastereomers, *Δ*(*S*) and *Λ*(*R*). The *N,N'*-Ph_2en complex which shows a singlet (2H, 4.86 ppm) attributable to the shielded methine protons is assigned to the racemic pair of the *Δ*(*SS*) and *Λ*(*RR*) isomers.

The absolute configurations, *Λ* or *Δ*, of the optically active Me-en complexes were assigned on the basis of the CD spectra (Fig. 2). In general, the optical activity of a metal complex is explained as a superposition of the configurational and the vicinal effects, the former being usually larger than the latter.[9,10] The two isomers in Fig. 2 show a similar CD pattern and exhibit a main positive CD band in the region of the first absorption band. Thus both isomers are assigned to the *Λ* configuration. Half the sum of the two CD spectra should give the *Λ* configurational effect. In fact, the calculated CD curve is quite similar to the reported CD spectrum of *Λ*-$[Co(acac)_2(en)]^+$[11] where no vicinal effect exists. This result shows that the additivity between the two effects holds for the two isomers, and confirms the above assignments.

Absorption Spectra. The absorption data for the complexes are listed in Table 2, and the representative spectra are shown in Figs. 3 and 4. All the complexes show the first absorption band, $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) in the

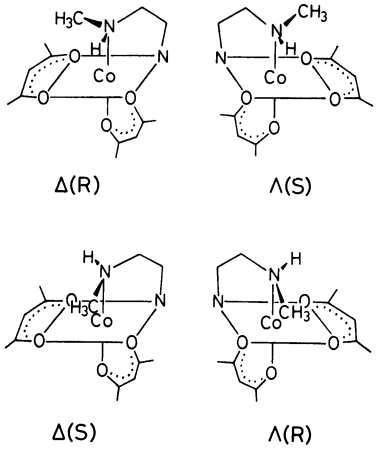

Fig. 1. The four isomers of $[Co(acac)_2(Me\text{-}en)]^+$.

TABLE 1. ^1H NMR DATA FOR $[Co(acac)_2L]^+$ AND THE DISTRIBUTIONS OF THE ISOMERS AT EQUILIBRIUM (25 °C)

L	Assignment	^1H NMR (*N*-methyl or acac methine signal, δ)	Relative Abundance, %
Me-en	*Λ*(*R*), *Δ*(*S*)	2.10d[a]	55
	Λ(*S*), *Δ*(*R*)	1.80d[a]	45
N,N'-Me_2en	*Λ*(*RR*), *Δ*(*SS*)	2.02d[a]	52
	Λ(*SS*), *Δ*(*RR*)	1.77d[a]	30
	Λ(*SR*), *Δ*(*RS*)	1.78d, 2.06d[a]	18
Me_3en	*Λ*(*R*), *Δ*(*S*)	1.87s, 2.02d, 2.07s[a]	64
	Λ(*S*), *Δ*(*R*)	1.73d, 1.78s, 2.07s[a]	36
Ph-en	*Λ*(*R*), *Δ*(*S*)	4.88s, 5.52s[b]	*ca.* 60
	Λ(*S*), *Δ*(*R*)	5.53s, 5.63s[c]	*ca.* 40
N,N'-Ph_2en	*Λ*(*RR*), *Δ*(*SS*)	4.86s[b]	*ca.* 100

a) The chloride in D_2O. b) The perchlorate in $CDCl_3$. c) The perchlorate in CD_3CN.

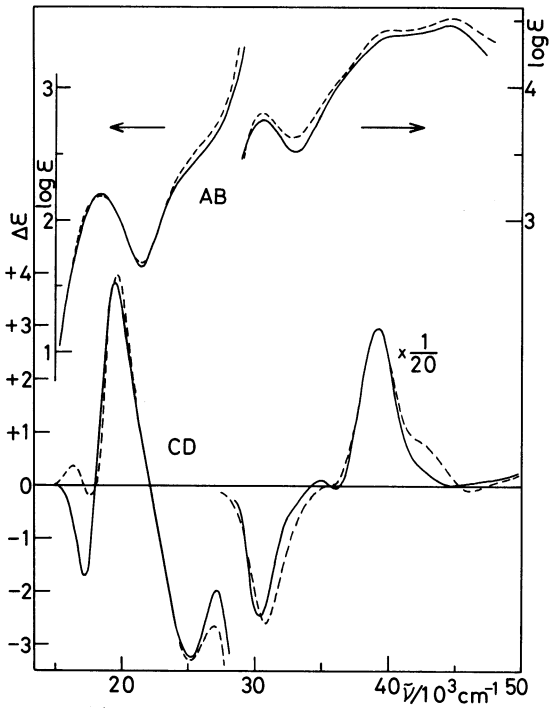

Fig. 2. Absorption and CD spectra of $(-)_{589}$-$A(R)$-(——) and $(-)_{589}$-$A(S)$-$[Co(acac)_2(Me\text{-}en)]ClO_4$(----) in water.

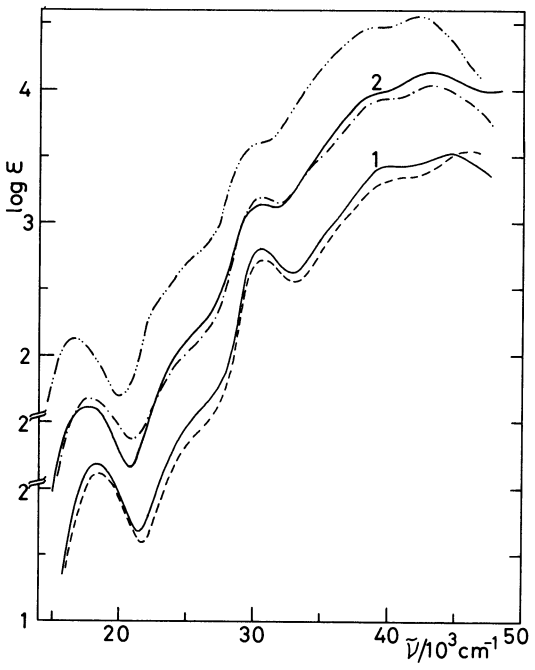

Fig. 3. Absorption spectra of $[Co(acac)_2L]^+$ in methanol. L=en (----), Me-en ($A(S)$,$A(R)$-pair, ——1), N,N-Me_2en (-·-·), Me_3en ($A(S)$,$A(R)$-pair, ——2), and Me_4en (-···-).

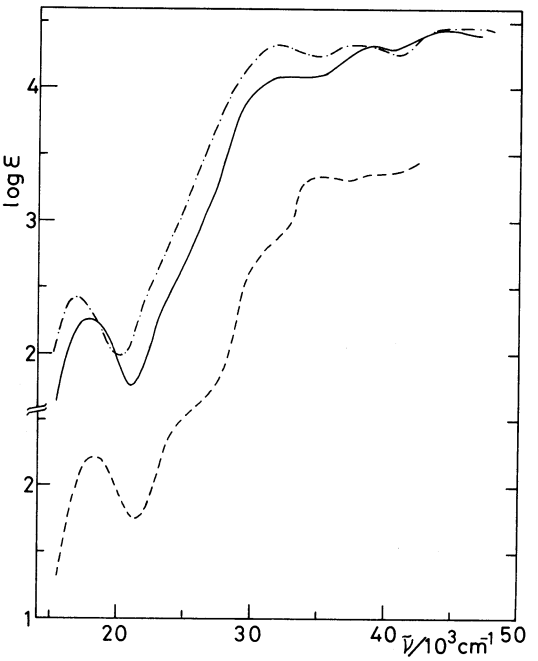

Fig. 4. Absorption spectra of $[Co(acac)_2L]^+$ in methanol. L=Ph-en ($A(S)$,$A(R)$-pair, ——), N,N'-Ph_2en (-·-·-), and opd (---).

region of 16600 to 18300 cm^{-1}. Most of the spectra show a weak shoulder around 25000 cm^{-1}. The corresponding en complex shows a shoulder at *ca.* 24000 cm^{-1} and the transition has been assigned by Boucher to the second d-d absorption band, $^1A_{1g} \rightarrow {}^1T_{2g}$ (O_h)[11]. As seen in Fig. 5 the first absorption band shifts to lower energy as the number of the substituents (CH_3 or C_6H_5) on the nitrogen atom increases. York *et al.*[1] pointed out that the Me_4en ligand in $[Co(acac)_2(Me_4en)]^+$ has a ligand field strength comparable to that of the oxygen donors of acac; the complex shows the first absorption band (16640 cm^{-1}) at nearly the same position as that of $[Co(acac)_3]$ (16750 cm^{-1}). The low ligand field strength of the Me_4en ligand was ascribed to the steric repulsions which occur in the complex.[1] The $[Co(acac)_2(N,N\text{-}Me_2en)]^+$ complex exhibits the first absorption band at lower energy than those of any of the isomers of the corresponding N,N'-Me_2en complex. When the methyl group attached to the nitrogen atom is replaced by a phenyl group, the d-d absorption band shifts to lower energy. Thus the ligand field strengths of the diamines studied here decrease in the order of en>Me-en>N,N'-Me_2en>N,N-Me_2en~Ph-en>Me_3en>N,N'-Ph_2en>Me_4en. The first absorption band of the opd complex (18250 cm^{-1}) is at nearly the same position as those of the Me-en complexes (18250 and 18300 cm^{-1}, respectively). Except for the Me_3en complex, the isomer in which the substituent attached to the nitrogen atom is placed over an acac chelate ring exhibits the first absorption band at lower energy than the other isomers.

The complexes containing an N-methyl-substituted ethylenediamine show a band assignable to a Co^{III}-to-acac $d\pi \rightarrow \pi^*$ transition[12] at 30600—30300 cm^{-1}. For the en complex the corresponding transition occurs at 30700 cm^{-1}. The position shifts slightly to lower energy with an increasing number of methyl groups. On the other hand, the positions of a shoulder (38500—39500 cm^{-1}) which is assigned to another $d\pi \rightarrow \pi^*$ transition,[12] and the $\pi \rightarrow \pi^*$ transition of acac[12]

TABLE 2. ABSORPTION SPECTRAL DATA FOR $[Co(acac)_2L]^+$ IN METHANOL AND CD SPECTRAL DATA OF THE Me-en ISOMERS IN WATER

L	Configuration	$\tilde{\nu}_{max}/10^3\,cm^{-1}(\log\varepsilon)$, $\tilde{\nu}_{ext}/10^3\,cm^{-1}(\Delta\varepsilon)$
en		18.45(2.20) 30.70(3.82) 40.0(4.26)[a] 46.00(4.64)
Me-en	$\Lambda(R)$	18.30(2.19) 30.60(3.75) 39.5(4.45)[a] 44.40(4.58)
	CD:	17.30(−1.72) 19.57(+3.82) 25.12(−3.23) 30.49(−49) 35.00(+2.1) 36.10(−1.0) 39.20(+60)
	$\Delta(S)$	18.25(2.18) 30.60(3.76) 39.5(4.42)[a] 44.40(4.55)
	CD:	16.39(+0.39) 17.70(−0.23) 19.70(+3.98) 25.19(−3.28) 30.77(−52) 39.22(+59) 42.60(+15)[a] 46.30(−2.0)
N,N-Me_2en		17.80(2.16) 30.50(3.68) 39.5(4.42)[a] 43.40(4.52)
N,N'-Me_2en	$\Lambda(RR)$, $\Delta(SS)$	18.05(2.17) 30.50(3.71) 39.5(4.45)[a] 43.70(4.54)
	$\Lambda(SS)$, $\Delta(RR)$	17.90(2.14) 30.50(3.69) 39.5(4.41)[a] 43.80(4.52)
	$\Lambda(SR)$, $\Delta(RS)$	17.95(2.16) 30.50(3.68) 39.5(4.46)[a] 43.75(4.58)
Me_3en	$\Lambda(R)$, $\Delta(S)$	17.30(2.15) 30.45(3.65) 39.0(4.51)[a] 43.30(4.65)
	$\Lambda(S)$, $\Delta(R)$	17.35(2.11) 30.45(3.63) 39.0(4.47)[a] 43.00(4.63)
Me_4en		16.60(2.12) 30.30(3.59) 38.5(4.45)[a] 42.40(4.54)
Ph-en	$\Lambda(R)$, $\Delta(S)$	17.80(2.32) 32.30(4.11) 39.40(4.36) 44.60(4.51)
	$\Lambda(S)$, $\Delta(R)$	17.90(2.26) 32.25(4.08) 39.10(4.32) 44.40(4.45)
N,N'-Ph_2en	$\Lambda(RR)$, $\Delta(SS)$	16.95(2.42) 31.85(4.32) 37.90(4.33) 44.40(4.45)
opd		18.25(2.20) 25.0(2.50)[a] 31.0(3.78)[a] 35.10(4.32) 39.40(4.34)

a) Shoulder.

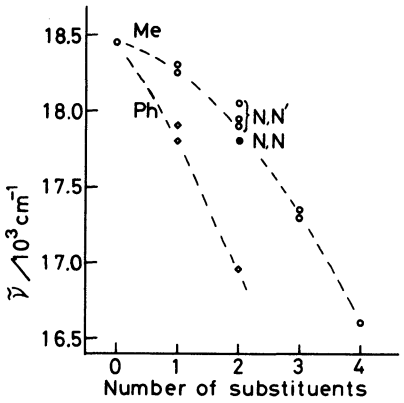

Fig. 5. Correlation between the positions of the first absorption band of $[Co(acac)_2(R^1R^2NCH_2CH_2NR^3R^4)]^+$ (R^1—R^4=H, CH_3, or C_6H_5) and the number of substituents on the nitrogen atoms.

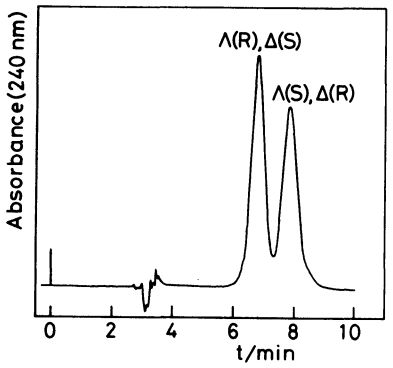

Fig. 6. Elution curve of $[Co(acac)_2(Me\text{-}en)]^+$ equilibrated at pH 12.1 and 25 °C. Chromatographic conditions: column, JASCO FINE SIL C_{18} (ϕ4.6 mm×30 cm); eluent, 0.01 mol dm^{-3} sodium 1-heptanesulfonate in 97.5% MeOH-2.5% H_2O; flow rate, 1 cm^3 min^{-1}; sample volume, 4×10^{-3} cm^{-3} containing *ca.* 4×10^{-9} mol complex.

(42400—44400 cm^{-1}) shift to lower energy to a larger extent as the number of the *N*-methyl groups increases.

Equilibrium Isomer Distribution. The isomers of Me-en, *N,N'*-Me_2en, and Me_3en complexes were equilibrated at pH 12.1 and 25 °C, and the distributions were analyzed by the reversed-phase high performance liquid chromatographic technique.[13] This method has the great advantages of short elution time and micro quantities of samples.[8,14] All the complexes attained equilibrium within one day. Figure 6 shows an example of the Me-en complex and the results are given in Table 1. No decomposition product was observed in column chromatography. The runs starting from any isomer gave the same result within the experimental error (*ca.* ±3%). In general, the more crowded or strained isomer of a metal complex exhibits the d-d absorption bands at lower energy and the abundance is smaller than that of the other isomer.[15] There is, however, no clear relationship between the distribution of the isomers and positions of the absorption bands (Tables 1 and 2).

It was difficult to separate the isomers of the Ph-en complex by HPLC technique, and thus the isomer distribution was determined by the ^1H NMR method. The epimerization was accompanied by a slight decomposition of the complex to cobalt(II), which resulted in a broadening of the ^1H NMR signals. Thus, it was necessary to isolate the cobalt(III) complex after the reaction in order to obtain a well-resolved spectrum. The complex attained equilibrium in 5 h at pH 12.1 and 25 °C. The rate of epimerization seems to be similar to those of the *N*-methyl-substituted diamine complexes. A detailed account of kinetic studies will be reported subsequently.

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