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Preparation and Characterization of the Stereoisomers of $[Co(acac)_2$(*N*-phenylethylenediamine or *N,N'*-diphenylethylenediamine)$]^+$ (acac = 2,4-Pentanedionate Ion) and Isomer Distribution at Equilibrium

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Abstract

The $[Co(acac)_2$(*N*-phenylethylenediamine)$]^+$ (acac = 2,4-pentanedionate ion) and $[Co(acac)_2$(*N,N'*-diphenylethylenediamine)$]^+$ complexes were separated into two and three racemic pairs of the diastereomers, respectively, by means of column chromatography, and the diastereomers were resolved by the chemical method. The diastereomers are stable in acidic water (pH < 2.5), but easily epimerize in neutral or basic water. The isomer distributions at equilibrium were determined and the results compared with those of the corresponding *N*-methyl-substituted ethylenediamine complexes.

Introduction

Cobalt(III) complexes with *N*-phenyl-substituted diamines are usually unstable because of both steric and electronic reasons [1]. In a previous paper [2], we reported that *N*-phenylethylenediamine (Ph-en) and *N,N'*-diphenylethylenediamine (*N,N'*-Ph_2en) form stable cobalt(III) complexes of the type $[Co(acac)_2L]^+$ (acac = 2,4-pentanedionate ion; L = Ph-en, *N,N'*-Ph_2en). The acac ligand seems to stabilize the *N*-phenyl-substituted amine–cobalt(III) system. Because of the presence of chiral nitrogen atoms, two and three diastereomers are possible for the Ph-en and *N,N'*-Ph_2en complexes, respectively (Fig. 1).

In this paper, we describe the preparation and resolution of the diastereomers of $[Co(acac)_2(Ph\text{-}en)]^+$ and $[Co(acac)_2(N,N'\text{-}Ph_2en)]^+$, distributions of the diastereomers at equilibrium, and absorption and circular dichroism (CD) spectra of these diastereomers.

Experimental

Δ(R)Λ(S)- and Δ(S)Λ(R)-[Co(acac)₂(Ph-en)] ClO₄

$[Co(acac)_2(Ph\text{-}en)]ClO_4$ was prepared as described earlier [2] and separated into two isomers (Δ(R)Λ(S) and Δ(S)Λ(R)) by a chromatographic method. A methanol solution (200 cm^3) of a mixture of the isomers (1.0 g) was allowed to stand for 1 h at room temperature to give an equilibrium mixture of the isomers. The solution was diluted with 0.02 mol dm^{-3} HCl (2 dm^3) and applied on a column (ϕ 4.5 cm × 30 cm) of SP-Toyopearl 650 M†. By elution with 0.18 mol dm^{-3} NaCl–0.02 mol dm^{-3} HCl, a purple (Δ(R)Λ(S)) and a gray (Δ(S)Λ(R)) band developed in this order in the ratio of 4:6. The eluate

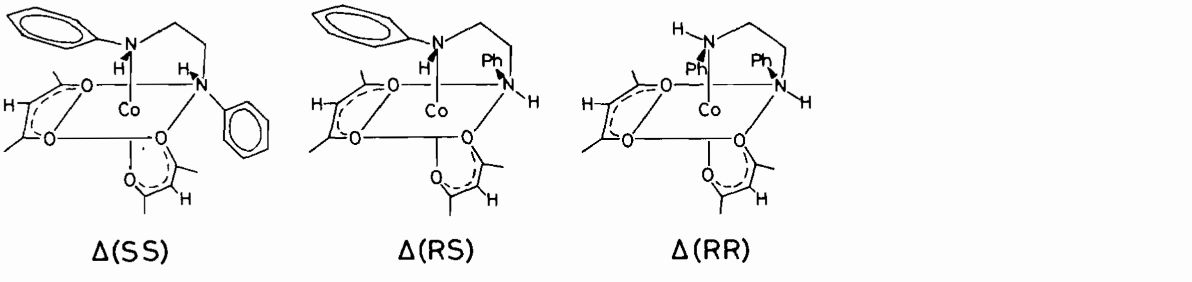

Fig. 1. Schematic structures of the three isomers of Δ-$[Co(acac)_2(N,N'\text{-}Ph_2en)]^+$.

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†Toyopearl, the product of Toyo Sofa Mfg. Co., Ltd. (Tokyo, Japan) is the same material as Fractogel TSK available from E. Merck (Darmstadt, F.R.G.).

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containing the purple band was collected and evaporated to a small volume under reduced pressure. To the concentrate, sodium perchlorate was added to yield purple crystals, which were recrystallized from acetonitrile by the addition of diethyl ether. From the gray band, the perchlorate of the Δ(S)-Λ(R)-isomer was obtained by the same method as that for the Δ(R)Λ(S)-isomer. The complex could be separated into the isomers by fractional crystallization from chloroform [2]. The isomers obtained by either method gave identical absorption and ^{1}H NMR spectra.

Δ(R)-[Co(acac)$_2$(Ph-en)]ClO$_4$ and Δ(S)-[Co(acac)$_2$-(Ph-en)]ClO$_4$·0.5H$_2$O

A column (*ϕ* 1.2 cm × 10 cm) of Dowex 1 X8 (200–400 mesh) in the (–)$_{546}$-[Co(edta)]$^-$ (edta = ethylenediaminetetraacetate ion) form was prepared by passing an aqueous solution of (–)$_{546}$-K[Co(edta)]·2H$_2$O [3] through the column in the Cl$^-$ form. An aqueous solution (200 cm^3) of [Co(acac)$_2$(Ph-en)]ClO$_4$ (1.0 g, 2.0 mmol; a mixture of the isomers) was applied on the column, and the column was washed with water (20 cm^3). The combined purple eluate and washing were evaporated to *ca.* 5 cm^3 under reduced pressure, and to the concentrate acetone was added dropwise to give a purple precipitate. It was recrystallized from 0.01 mol dm^{-3} HCl by adding acetone. Purple needles were collected by filtration and washed with acetone. Yield: 0.2 g. No change in the Δϵ value was observed by repeated recrystallization. The diastereomeric salt (Δ(R)-[Co(acac)$_2$(Ph-en)](–)$_{546}$-[Co(edta)]) was dissolved in 0.01 mol dm^{-3} HCl and applied on a column (*ϕ* 1.2 cm × 3 cm) of Dowex 1 X8 (Cl$^-$ form, 200–400 mesh). The column was washed with 0.01 mol dm^{-3} HCl, and from the eluate and washing, the Δ(R)-isomer was isolated as the perchlorate and recrystallized in the same way as for the racemate. Yield: 80 mg. *Anal.* Calc. for $C_{18}H_{26}N_2ClCoO_8$: C, 43.70; H, 5.32; N, 5.68. Found: C, 43.80; H, 5.23; N, 5.73%.

The Δ(R)-isomer (60 mg) was epimerized in 0.025 mol dm^{-3} KH$_2$PO$_4$–0.025 mol dm^{-3} Na$_2$HPO$_4$ (pH 6.8, 20 cm^3) at room temperature. After 1 h, the reaction mixture was diluted with 0.01 mol dm^{-3} HCl (200 cm^3) and applied on a column (*ϕ* 1.5 cm × 20 cm) of SP-Toyopearl 650 M. By elution with 0.15 mol dm^{-3} NaCl–0.03 mol dm^{-3} HCl, two bands, purple and gray, developed. From the eluate containing the slower-moving gray band, the perchlorate of the Δ(S)-isomer was obtained as described for the racemate. Yield: 20 mg. *Anal.* Calc. for $C_{18}H_{27}N_2ClCoO_{8.5}$: C, 43.08; H, 5.42; N, 5.58. Found: C, 43.28; H, 5.18; N, 5.65%. The Δ(R)-isomer was recovered from the faster-moving purple band.

Δ(RR)Λ(SS)-[Co(acac)$_2$(N,N'-Ph$_2$en)]ClO$_4$, Δ(RS)-Λ(SR)-[Co(acac)$_2$(N,N'-Ph$_2$en)]ClO$_4$·0.5H$_2$O, and Δ(SS)Λ(RR)-[Co(acac)$_2$(N,N'-Ph$_2$en)]ClO$_4$·0.5CHCl$_3$

Δ(SS)Λ(RR)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]ClO$_4$ was prepared as described earlier [2]. This isomer was epimerized in methanol and separated into three isomers (Δ(RR)Λ(SS), Δ(RS)Λ(SR), and Δ(SS)-Λ(RR)) by a method analogous to that for the corresponding Ph-en complexes. Column chromatography on an SP-Sephadex C-25 (eluent: 0.08 mol dm^{-3} NaCl–0.02 mol dm^{-3} HCl) showed three green bands, **I** (Δ(RR)Λ(SS)), **II** (Δ(RS)Λ(SR)), and **III** (Δ(SS)Λ(RR)), in the order of elution in the ratio of 2:1:8. From eluate **I**, the Δ(RR)Λ(SS)-isomer was isolated as the perchlorate by the same method as for the Ph-en complex, and recrystallized from acetonitrile by the addition of diethyl ether. *Anal.* Calc. for $C_{24}H_{30}N_2ClCoO_8$: C, 50.67; H, 5.32; N, 4.92. Found: C, 50.44; H, 5.27, N, 4.85%.

From each eluate of **II** and **III**, the perchlorate of the complex was obtained by the same method as for isomer **I**. *Anal.* Calc. for $C_{24}H_{31}N_2ClCoO_{8.5}$: C, 49.88; H, 5.41; N, 4.85. Found for isomer **II** (Δ(RS)Λ(SR)): C, 49.72; H, 5.24; N, 4.85%. Isomer **III** (Δ(RS)Λ(SR)) was recrystallized from chloroform by adding diethyl ether. *Anal.* Calc. for $C_{24.5}H_{30.5}N_2Cl_{2.5}CoO_8$: C, 46.82; H, 4.89; N, 4.46. Found for isomer **III** (Δ(SS)Λ(RR)): C, 46.88; H, 4.92; N, 4.46%. The presence of chloroform of crystallization was confirmed by the ^{1}H NMR spectrum.

Δ(RR)-, Δ(RS)- and Δ(SS)-[Co(acac)$_2$(N,N'-Ph$_2$en)]$^+$

The Δ(RR)Λ(SS)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]ClO$_4$ isomer was converted into the chloride by use of Dowex 1 X8 (Cl$^-$ form). A suspension of Δ(RR)-Λ(SS)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]ClO$_4$ in 0.01 mol dm^{-3} HCl was stirred with Dowex 1 X8 in the Cl$^-$ form. After filtration, the filtrate was passed through a column of the same resin to ensure the conversion into the chloride. The effluent was evaporated to dryness under reduced pressure to yield a green powder of the chloride of Δ(RR)Λ(SS)-isomer. To a solution of the Δ(RR)Λ(SS)-isomer in 10^{-3} mol dm^{-3} HNO$_3$ was added Ag$_2$[Sb$_2${(R,R)-tartrate}$_2$] in a 2:1 molar ratio. The suspension was stirred for 30 min and filtered. The filtrate was evaporated to yield green needles. They were recrystallized repeatedly from 0.01 mol dm^{-3} HCl until no change in Δϵ value was observed. The diastereomeric salt Δ(RR)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]$_2$-[Sb$_2${(R,R)tartrate}$_2$] thus obtained was dissolved in water (pH 5.5) to give a mixture of the three isomers (Δ(RR), Δ(RS), and Δ(SS)). The isomers were separated by SP-Sephadex column chromatography (eluent; 0.08 mol dm^{-3} NaCl–0.02 mol dm^{-3} HCl). They were not isolated because only very small amounts were formed. The Δϵ values were determined with the aid of the ϵ values of the racemates.

Measurements

Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. ^{1}H NMR spectra were measured with a JEOL PMX-60 spectrometer.

Results and Discussion

Two and three isomers (racemic pairs of diastereomers) are possible for [Co(acac)$_2$(Ph-en)]$^+$ and [Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$, respectively (Fig. 1). The two isomers of the Ph-en complex and one of the three isomers of the *N,N'*-Ph$_2$en complex could be obtained by fractional crystallization of the perchlorates from chloroform [2]. However, as we reported in a previous paper [2], these complexes could not be separated into the isomers by column chromatography under neutral conditions analogous to those for [Co(acac)$_2$(Me-en or *N,N'*-Me$_2$en)]$^+$ (Me-en = *N*-methylethylenediamine, *N,N'*-Me$_2$en = *N,N'*-dimethylethylenediamine). In the study of isomerization (epimerization) of [Co(acac)$_2$(Me-en or Ph-en)]$^+$, it was found that the Ph-en complex isomerizes very rapidly in neutral water to give an equilibrium mixture of the isomers and that the rate is proportional to the hydroxide ion concentration [4]. These observations suggest that under acidic conditions the [Co(acac)$_2$(Ph-en)]$^+$ and [Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$ complexes might be separated into the isomers by a column chromatographic method. In fact, all of the possible isomers were obtained by column chromatography under acidic conditions. The complexes are likely to isomerize in water, and the aqueous solutions had to be kept acidic (pH $<$ 2.5) to avoid the isomerization. The complexes also isomerize in methanol.

To obtain a diastereomeric salt of [Co(acac)$_2$(Ph-en)]$^+$ with $(-)_{546}$-[Co(edta)]$^-$, a conventional chromatographic technique was used. An effluent containing only [Co(acac)$_2$(Ph-en)]$^+$ and $(-)_{546}$[Co(edta)]$^-$ was obtained by applying an aqueous solution of [Co(acac)$_2$(Ph-en)]ClO$_4$ on a column of Dowex 1 X8 in the $(-)_{546}$-[Co(edta)]$^-$ form; a perchlorate ion has a much larger affinity toward the exchanger than $(-)_{546}$-[Co(edta)]$^-$. The diastereomeric salt did not crystallize in the presence of other salts. Of the four isomers (Δ(R), Δ(S), Λ(R), and Λ(S)) of [Co(acac)$_2$(Ph-en)]$^+$, the Δ(R)-isomer formed the least soluble diastereomeric salt with $(-)_{546}$-[Co(edta)]$^-$. The diastereomeric salt was converted into the chloride by use of a column of Dowex 1 X8 (Cl$^-$ form), and then isolated as the perchlorate by adding NaClO$_4$ to the effluent. The Δ(R)-isomer was epimerized to give a mixture of the Δ(R)- and Δ(S)-isomers which were separated by column chromatography on SP-Toyopearl. The Δ(RR)Λ(SS)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$ isomer was resolved by the chemical method with [Sb$_2${(R,R)-tartrate}$_2$]$^{2-}$. The Δ(RR)-isomer formed the less soluble diastereomeric salt. After epimerizing the Δ(RR)-isomer, three optically active isomers (Δ(RR), Δ(RS), and Δ(SS)) were separated by SP-Sephadex column chromatography.

The structures of the complexes were assigned on the basis of the ^{1}H NMR and CD spectra. In Δ(SS)- and Λ(RR)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$, the two phenyl groups shield the methine protons of the two acac chelate rings (Fig. 1). The high field resonance at δ = 4.97 (CD$_3$CN) in the ^{1}H NMR spectrum of isomer **III** can be assigned to the shielded methine protons, and the isomer is assigned to the Δ(SS)Λ(RR) configuration. Isomer **I**,which exhibits the signal attributable to the methine protons at a lower magnetic field (δ = 5.55, (CD$_3$)$_2$SO), is assigned to the Δ(RR)Λ(SS) configuration where the acac ligands are not shielded by the phenyl groups. Isomer **II**, which gives two methine signals (δ = 4.83 and 5.68, CD$_3$CN), is assigned to the Δ(RS)-Λ(SR) configuration because of its symmetry; the signal at δ = 4.83 is assigned to the shielded methine proton. The structures of the isomers of [Co(acac)$_2$(Ph-en)]$^+$ have been assigned in the same way [2].

The absolute configurations (Δ,Λ) of the optically active complexes were assigned on the basis of the CD spectra (Figs. 2 and 3). In general, the optical activity of a metal complex is explained as a superposition of the configurational and vicinal effects, the former usually being larger than the latter [5]. The two isomers of [Co(acac)$_2$(Ph-en)]$^+$ in Fig. 2 show a similar CD pattern and exhibit a major negative CD band in the region of the first

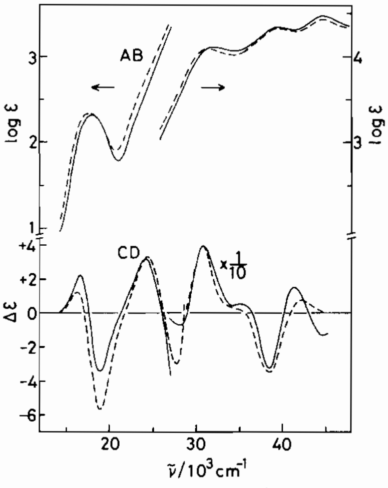

Fig. 2. Absorption (AB) and CD spectra of Δ(R)- (———) and Δ(S)-[Co(acac)$_2$(Ph-en)]$^+$ (-----) in 0.01 mol dm^{-3} HClO$_4$.

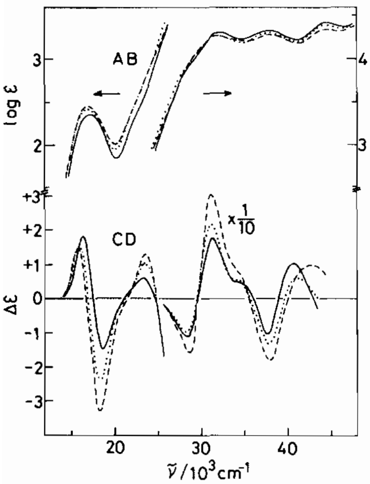

Fig. 3. Absorption and CD spectra of Δ(RR)- (———), Δ(RS)- (·····), and Δ(SS)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$ (-----).

absorption band. This pattern is almost enantiomeric to that of the reported CD spectrum of Λ-[Co(acac)$_2$(en)]$^+$ [6] (en = ethylenediamine). Thus, both isomers of the Ph-en complex in Fig. 2 are assigned to the Δ configuration. The absolute configurations of the three isomers of [Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$ in Fig. 3 were assigned to the Δ configuration in the same way. The CD spectrum of the Δ(RS)-isomer is almost the average of those of the Δ(RR)- and Δ(SS)-isomers in the region of the d–d absorption bands. This suggests that for these isomers the two effects, configurational (Δ, Λ) and vicinal (R, S), are additive. Figure 4 compares the vicinal effect curve ($\Delta\epsilon$(R) = ½{$\Delta\epsilon$[Δ(R)]-$\Delta\epsilon$[Δ(S)]}) obtained from the spectra of Δ(R)- and Δ(S)-[Co(acac)$_2$(Ph-en)]$^+$ with the curve ($\Delta\epsilon$(S)) derived similarly from Λ(R)- and Λ(S)-[Co(acac)$_2$(Me-en)]$^+$ [2]*. Both curves show major positive CD bands in the region of the first absorption band, although the patterns are different.

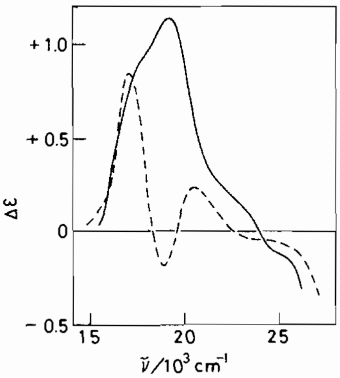

Fig. 4. Vicinal effect CD curves. ——: $\Delta\epsilon$(R), calculated from Δ(R)- and Δ(S)-[Co(acac)$_2$(Ph-en)]$^+$ (½{$\Delta\epsilon$[Δ(R)] − $\Delta\epsilon$[Δ(S)]}); -----: $\Delta\epsilon$(S), calculated from Λ(R)- and Λ(S)-[Co(acac)$_2$(Me-en)]$^+$ (½{$\Delta\epsilon$[Λ(S)] − $\Delta\epsilon$[Λ(R)]}).

The absorption spectral data for [Co(acac)$_2$L]$^+$ (L = Ph-en, *N,N'*-Ph$_2$en) are listed in Table I. All the complexes show the first absorption band, $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ in the region of 16 800–18 000 cm^{-1}. The *N,N'*-Ph$_2$en complexes give the first absorption band at lower energy than either of the Ph-en complexes. As seen in Table I, when the phenyl group attached to the nitrogen atom is placed over an acac chelate ring, the first absorption band shifts to lower energy and becomes more intense. A similar trend

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*According to the rule [7], the notation of the absolute configurations, R and S, for the chiral nitrogen atoms are reversed for apparently the same configurations of Ph-en and Me-en complexes.

TABLE I. Absorption (AB) and CD Spectral Data for the Isomers of [Co(acac)$_2$L]$^+$ (L = Ph-en, *N,N'*-Ph$_2$en)

L	Isomer	$\tilde{\nu}_{max}$ (10^3 cm^{-1}) (log ϵ) ($\tilde{\nu}_{ext}$ (10^3 cm^{-1}) ($\Delta\epsilon$))
Ph-en	Δ(R)	AB^a: 18.0(2.32), 31.9(4.11), 39.4(4.34), 44.6(4.47)
		CD^a: 16.7(+2.26), 18.9(−3.43), 24.3(+3.21), 28.1(−7.29), 30.8(+39.8), 35.1(+5.8), 38.5(−32.1), 41.5(+15.5), 44.8(−13.6)
Ph-en	Δ(S)	AB^a: 17.7(2.35), 31.4(4.09), 39.5(4.32), 44.6(4.43)
		CD^a: 16.4(+1.11), 19.0(−5.71), 24.4(+3.28), 27.7(−2.99), 30.8(+39.3), 38.5(−34.3), 42.2(+7.03)
N,N'-Ph$_2$en	Δ(RR)Λ(SS)	AB^b: 17.1(2.37), 32.1(4.30), 37.7(4.33), 44.3(4.41)
N,N'-Ph$_2$en	Δ(RR)	CD^c: 16.3(+1.84), 18.6(−1.51), 23.4(+0.61), 28.2(−11.1), 31.3(+17.7), 34.2(+5.1)^d, 37.7(−9.9), 40.7(+10.4)
N,N'-Ph$_2$en	Δ(RS)Λ(SR)	AB^b: 16.9(2.42), 31.8(4.28), 38.0(4.30), 44.3(4.38)
N,N'-Ph$_2$en	Δ(RS)	CD^c: 16.0(+1.53), 18.2(−2.39), 23.5(+1.02), 28.3(−9.9), 31.1(+21.5), 33.9(+5.2)^d, 37.7(−12.9), 41.0(+6.2)
N,N'-Ph$_2$en	Δ(SS)Λ(RR)	AB^b: 16.9(2.45), 31.9(4.28), 38.0(4.27), 44.3(4.33)
N,N'-Ph$_2$en	Δ(SS)	CD^c: 15.9(+1.71), 18.2(−3.33), 23.5(+1.26), 28.6(−15.9), 31.2(+30.3), 33.9(+8.7)^d, 37.9(−17.8), 42.6(+9.7)

^{a}In 0.01 mol dm^{-3} HClO$_4$. ^{b}In CH$_3$CN. ^{c}In 1 mol dm^{-3} NaCl–0.2 mol dm^{-3} HCl. ^{d}Shoulder.

TABLE II. Distributions of the Isomers of Δ-[Co(acac)$_2$L]$^+$ at Equilibrium (25 °C)

L	Isomer	Relative abundance (%)	L	Isomer	Relative abundance (%)
Ph-en	Δ(S)	60	Me-en	Δ(R)	45
	Δ(R)	40		Δ(S)	55
N,N'-Ph$_2$en	Δ(SS)	73	*N,N'*-Me$_2$en	Δ(RR)	30
	Δ(RS)	9		Δ(RS)	18
	Δ(RR)	18		Δ(SS)	52

has been reported for the isomers of [Co(acac)(Ph-en)$_2$]$^{2+}$ [8]. The second absorption band, $^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$, is not observed by overlapping of the strong charge transfer band around 32 000 cm^{-1} which is assignable to a Co^{III}-to-acac $d\pi \rightarrow \pi^*$ transition [9]. The $d\pi \rightarrow \pi^*$ transition is at nearly the same position for all the complexes. On the other hand, the positions of another $d\pi \rightarrow \pi^*$ [9] (37 700–39 500 cm^{-1}) and the $\pi \rightarrow \pi^*$ transition of acac [9] (44 300–44 600 cm^{-1}) shift to lower energy as the number of the *N*-phenyl groups increases.

The isomers of Ph-en and *N,N'*-Ph$_2$en complexes were equilibrated in water at 25 °C and the distributions were analyzed by a column chromatographic technique. The runs starting from each isomer gave the same result within the experimental error. Table II shows the equilibrium isomer distributions for Δ-[Co(acac)$_2$L]$^+$ (L = Ph-en, *N,N'*-Ph$_2$en, Me-en, *N,N'*-Me$_2$en) [2]. In the Me-en and *N,N'*-Me$_2$en complexes, the Δ(R)- and Δ(RR)-isomers have a lower yield than the Δ(S)- and Δ(SS)-isomers. The result may be ascribed to the steric repulsion between the *N*-methyl group and the acac chelate ring; in Δ(R)-[Co(acac)$_2$(Me-en)]$^+$ and Δ(RR)-[Co(acac)$_2$(*N,N'*-Me$_2$en)]$^+$ the methyl groups are placed over the acac chelate rings, and these isomers will involve more steric repulsions than the Δ(S)- and Δ(SS)-isomers. On the other hand, the Ph-en and *N,N'*-Ph$_2$en complexes formed more of the Δ(S)- and Δ(SS)-isomers than the others. In Δ(S)-[Co(acac)$_2$(Ph-en)]$^+$ and Δ(SS)-[Co(acac)$_2$(*N,N'*-Ph$_2$en)], the phenyl groups are placed over the acac chelate rings (Fig. 1), and the steric interactions involved in these complexes will be larger than those in the Δ(R)- and Δ(RR)-isomers. The interaction between the phenyl and pseudoaromatic acac groups seems to be attractive rather than repulsive. It is not clear why the Δ(RS)-isomer is the least stable of the three isomers for both [Co(acac)(*N,N'*-Me$_2$en)]$^+$ and [Co(acac)$_2$(*N,N'*-Ph$_2$en)]$^+$.

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