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Isomers of the (2,4-Pentanedionato)bis(*N*-phenylethylenediamine)cobalt(III) Ion

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Synopsis. By reaction of $[Co(acac)_2(Ph\text{-}en)]^+$ (acac=2,4-pentanedionate ion, Ph-en=*N*-phenylethylenediamine) with Ph-en in methanol in the presence of active charcoal, three racemic pairs of diastereomers, $\Delta(SS)\Lambda(RR)$-, $\Delta(SR)\Lambda(RS)$-, and $\Delta(RR)\Lambda(SS)$-*trans*(*N*-Ph,*N*-Ph)-$[Co(acac)(Ph\text{-}en)_2]^{2+}$ were obtained. The isomers epimerize in water, methanol, and ethanol to give an equilibrium mixture of the isomers.

Cobalt(III) complexes with *N*-phenyl-substituted amines are usually unstable because of both steric and electronic reasons.[1] However, in a previous paper,[2] we reported that such amines form stable cobalt(III) complexes with two acac (acac=2,4-pentanedionate ion) ligands.

In this paper, we report the preparation and characterization of $[Co(acac)(Ph\text{-}en)_2]^{2+}$ (Ph-en=*N*-phenylethylenediamine) where only one acac ligand is contained.

Experimental

Three Isomers of trans(N-*Ph*,N-*Ph*)-$[Co(acac)(Ph\text{-}en)_2]^{2+}$. To a methanol solution ($150\,cm^3$) of $[Co(acac)_2(Ph\text{-}en)]ClO_4$[2] (3.0 g, 5.4 mmol) were added active charcoal (0.5 g), acetic acid ($1\,cm^3$) and a methanol solution ($10\,cm^3$) of Ph-en (1.6 g, 11.6 mmol). The mixture was stirred for 6 d at room temperature and then filtered. The purple filtrate was diluted with $0.01\,mol\,dm^{-3}$ HCl ($2\,dm^3$) and applied on a column ($\phi 4.5\,cm \times 30\,cm$) of SP-Sephadex C-25. By elution with $0.3\,mol\,dm^{-3}$ NaCl–$0.04\,mol\,dm^{-3}$ HCl, the column showed five bands; purple, red, brown, green, and brown in the order of elution. The fastest-moving purple band contained unreacted $[Co(acac)_2(Ph\text{-}en)]^+$, and the slowest-moving brown band a mixture of highly-charged species. Sodium perchlorate was added to the eluate containing the green band (G) and the mixture was cooled to yield a green precipitate. It was collected by filtration, washed with cold water, and air dried. Yield (isomer G: $\Delta(SS)\Lambda(RR)$): 0.14 g (4%). Found: C, 39.73; H, 4.91; N, 8.63%. Calcd for $C_{21}H_{31}N_4Cl_2CoO_{10}=[Co(acac)(Ph\text{-}en)_2](ClO_4)_2$: C, 40.08; H, 4.97; N, 8.90%. From each of the brown (B) and the red (R) eluates, the perchlorate of the complex was obtained by the same method as that for isomer G. Each product was dissolved in acetone–0.1 mol dm^{-3} HCl, and the acetone was slowly evaporated to yield crystals. Yield (isomer B: $\Delta(SR)\Lambda(RS)$): 0.61 g (18%). Found: C, 39.99; H, 4.96; N, 8.73%. Calcd for $C_{21}H_{31}N_4Cl_2CoO_{10}=[Co(acac)(Ph\text{-}en)_2](ClO_4)_2$: C, 40.08; H, 4.97; N, 8.90%. Yield (isomer R, $\Delta(RR)\Lambda(SS)$): 0.021 g (0.6%). Found: C, 38.78; H, 5.10; N, 8.61%. Calcd for $C_{21}H_{33}N_4Cl_2CoO_{11}=[Co(acac)(Ph\text{-}en)_2](ClO_4)_2\cdot H_2O$: C, 38.96; H, 5.14; N, 8.66%.

Isomer Distribution at Equilibrium. Each isomer (*ca.* 0.1 g) was dissolved in water, methanol, or ethanol ($5\,cm^3$) at 20 °C. Portions of the reaction mixture were withdrawn at timed intervals, diluted with $0.1\,mol\,dm^{-3}$ HCl, and the absorption spectra were measured. The experiments were carried out until the mixture attained equilibrium and no change in the spectra was observed. The equilibrated reaction mixture was diluted with $0.04\,mol\,dm^{-3}$ HCl ($30\,cm^3$), and the solution was subjected to column chromatography on SP-Sephadex C-25 (column: ϕ 0.9 $cm \times 25\,cm$; eluent: $0.3\,mol\,dm^{-3}$ NaCl–$0.04\,mol\,dm^{-3}$ HCl) in order to examine the distribution of the isomers.

Measurements. Absorption spectra in dil $HClO_4$ solutions (pH *ca.* 1.2) were recorded on a Hitachi 323 or a JASCO 610B spectrophotometer and ^1H NMR spectra in acetone-d_6 solutions on a JEOL PMX 60 spectrometer using TMS as an internal reference.

Results and Discussion

The $[Co(acac)(Ph\text{-}en)_2]^{2+}$ complex was prepared from $[Co(acac)_2(Ph\text{-}en)]ClO_4$ and Ph-en in methanol in the presence of active charcoal. The complex was separated into three isomers (G, B, and R) by column chromatography on SP-Sephadex C-25. In the course of the separation, the complex was found to isomerize in water to give an equilibrium mixture of the three isomers. In order to avoid the isomerization, the aqueous solutions were kept acidic ($pH<1.5$). When isomer G is dissolved in water, the color of the solution changes from green to greenish brown, and the solution attained equilibrium in *ca.* 10 min. The rate is dependent upon pH; the lower the pH, the slower the reaction. The isomer distribution at equilibrium at 20 °C was analyzed by column chromatographic technique, the ratio being isomer R : isomer B : isomer G=5 : 78 : 17. The runs starting from any isomer gave the same result within the experimental error (*ca.* ±3%). The isomerization was also observed for methanol and ethanol solutions, and the isomer distributions at equilibrium were the same as that for the aqueous solution. In methanol the complex attained equilibrium in *ca.* 10 min. However, in $0.8\,mol\,dm^{-3}$ *p*-toluenesulfonic acid–methanol, the isomers showed no detectable change in the absorption spectra over 40 h at room temperature. A rate of inversion at coordinated secondary amine nitrogen ($M\text{-}NHR^1R^2$; R^1,R^2: alkyl substituent) is known to be proportional to hydroxide ion concentration.[3,4] Recemization (inversion at $N\text{-}CH_3$) of *trans,trans*-$[Co(NO_2)_2(CH_3NHCH_2CH_2NH_2)_2]^+$ in methanol has been reported to obey a rate law of the form $R=[complex]\cdot[CH_3O^-]$.[5] Thus the isomerization of the present complex is suggested to be epimerization caused by inversion at the chiral nitrogen atoms remaining the geometrical configuration of the donor atoms unchanged.

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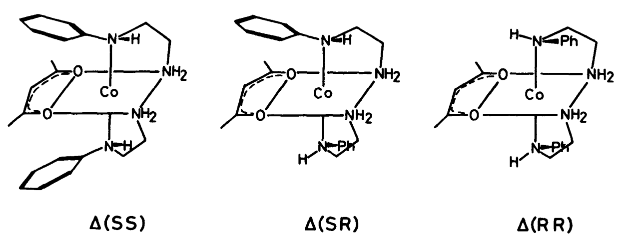

Δ(SS) Δ(SR) Δ(RR)

Fig. 1. Schematic structures of the three isomers of *Δ*-*trans(N*-Ph,*N*-Ph*)*-[Co(acac)(Ph-en)$_2$]$^{2+}$.

The [Co(acac)(Ph-en)$_2$]$^{2+}$ ion has three possible geometrical isomers with respect to the arrangement of two *N*-Ph groups. When the presence of three asymmetric centers, one at the cobalt atom and the others at the asymmetric nitrogen atoms, are taken into consideration, the number of isomers increases to ten racemic pairs. However, some of the isomers can be ruled out for steric reasons. Examination of molecular models indicates that only the *trans*(*N*-Ph,*N*-Ph) configuration can form three stable racemic pairs of diastereomers (Fig. 1). The structures of three isomers obtained in this study were assigned on the basis of the ^{1}H NMR and absorption spectra. In the *Δ*(*SS*)*Λ*(*RR*) configuration, the two phenyl groups are placed over and under the acac chelate ring and the methine proton will be strongly shielded by the phenyl groups. The resonance at a high field, δ=4.18 of isomer G can be assigned to the shielded methine proton, and the isomer is assigned to the *Δ*(*SS*)*Λ*(*RR*) configuration. Isomer R which exhibits the methine proton signal at a low field (δ=6.10) is assigned to the *Δ*(*RR*)*Λ*(*SS*) configuration in which the acac ligand is not shielded by the phenyl groups. The signal of methyl protons of isomer G (δ=1.77) is also observed at a higher field than that of isomer R (δ=2.13). Isomer B gives two methyl singlets (δ=1.88 and 1.90) and the methine singlet (δ=5.21) in the region between the corresponding signals of isomers G and R. Thus isomer B is assigned to the *Δ*(*SR*)*Λ*(*RS*) configuration where only one of the phenyl groups is placed over the acac chelate ring.

Figure 2 shows absorption spectra of the three isomers. All the isomers show the first absorption band, $^1A_{1g}\rightarrow{}^1T_{1g}$ (O_h) in the region of 16900 to 17950 cm^{-1} (isomer G: 16900 (2.71), isomer B: 17570 (2.56), isomer R: 17950 (2.54) in cm^{-1} (log ε)). The second absorption band, $^1A_{1g}\rightarrow{}^1T_{2g}$ (O_h) is almost hidden by strong charge-transfer bands. These first absorption bands are shifted largely to lower energy and become more intense compared to that of [Co(acac)(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$]$^{2+}$ (20100 cm^{-1}, log ε=2.14).⁶⁾ Similar differences in absorption spectra are observed between [Co(acac)$_2$(Ph-en)]$^+$ and [Co(acac)$_2$(NH$_2$CH$_2$CH$_2$NH$_2$)]$^+$.²⁾ For the [Co(acac)$_2$(Ph-en)]$^+$²⁾ and [Co(acac)$_2$(PhNHCH$_2$CH$_2$NH·Ph)]$^+$⁷⁾ complexes, the isomer in which the phenyl group is placed over an acac chelate ring has been observed to exhibit the first absorption band at lower energy than those of the other isomers. These observations in absorption spectra lead to the assignments that isomers G, R, and B have the *Δ*(*SS*)*Λ*(*RR*), *Δ*(*RR*)-*Λ*(*SS*), and *Δ*(*SR*)*Λ*(*RS*) configurations, respectively. These assignments are in accord with those obtained on the basis of ^{1}H NMR spectra.

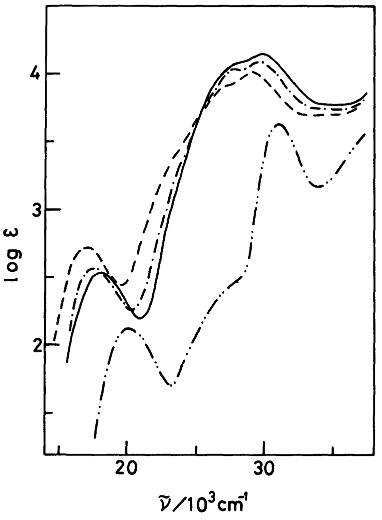

Fig. 2. Absorption spectra of isomer G *(Δ(SS)Λ(RR))* (— —), isomer B *(Δ(SR)Λ(RS))* (—·—), and isomer R *(Δ(RR)Λ(SS))* (——) of [Co(acac)(Ph-en)$_2$]$^{2+}$ in dil HClO$_4$ (pH *ca.* 1.2) and of [Co(acac)(NH$_2$CH$_2$CH$_2$NH$_2$)$_2$]$^{2+}$ (—··—) in water.

As stated previously, the complex in solution exists in three isomers R (*Δ*(*RR*)*Λ*(*SS*)), B (*Δ*(*SR*)*Λ*(*RS*)), and G (*Δ*(*SS*)*Λ*(*RR*)) in the molar ratio of 5:78:17, respectively at equilibrium (20 °C). The most abundant is isomer B where only one of the phenyl groups is placed over the acac chelate ring. It is not clear whether the interaction between the phenyl and pseudoaromatic acac groups is attractive or repulsive.

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