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SEPARATION AND CHARACTERIZATION OF TWO COBALT(III) DIASTEREOMERS DUE TO CHIRAL *O*-BONDED SULFINATE

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Two diastereomers due to the chiral *O*-bonded sulfinate in Λ-$[Co(NH_2CH_2CH_2SO_2$-*N*,*O*)$(en)_2](ClO_4)_2$ were separated and characterized by the visible-UV absorption, circular dichroism(CD), and ^{13}C NMR spectra. The absolute configurations were determined by comparison of the CD spectra with that of the corresponding *O*-bonded Λ-*R*-seleninato complex. The racemization of the chiral sulfinato moiety proceeded at a relatively slow rate, which is responsible for the successful separation of the diastereomers.

When 2-aminoethanesulfinate $NH_2CH_2CH_2SO_2^-$(aesi) acts as a bidentate ligand, there is the possibility of two coordination modes, aesi-*N*,*S* and aesi-*N*,*O*. Most of its cobalt(III) complexes take only the former coordination mode.$^{1)}$ The thermodynamically unstable linkage isomer $[Co(aesi$-*N*,*O*$)(en)_2]^{2+}$ has been recently prepared photochemically by Mäcke et al.$^{2)}$ In this complex, two kinds of chiral centers, cobalt and sulfur atoms exist and therefore two diastereomeric pairs of enantiomers, (Λ-*R*, Δ-*S*) and (Λ-*S*, Δ-*R*), are possible. We report here the first separation and characterization of two diastereomers(Fig. 1) in Λ-$[Co(aesi$-*N*,*O*$)(en)_2](ClO_4)_2$.

The mixture of *O*-bonded sulfinato cobalt(III) isomers were prepared according to the reference.$^{2)}$ To a solution of Λ-$[Co(NH_2CH_2CH_2S)(en)_2](ClO_4)_2$(500 mg)$^{3)}$ was added an excess of 30% H_2O_2 solution and then the resulting solution was exposed to sun light for 7 d, accompanied by a color change from yellow to red. The red solution was poured onto a column of SP-Sephadex C-25 (Na^+ form, ϕ4×60 cm) and eluted with 0.15 mol dm^{-3} Na_2SO_4. Five colored bands appeared. Absorption spectral measurements confirmed that the red fourth(f1 isomer) and the red fifth(f2 isomer) band are the desired *O*-bonded sulfinato species. The formation ratio f1/f2 was almost close to unity. Each eluate was concentrated to small volume and after repeated removal of Na_2SO_4 deposited, an equivolume of saturated $NaClO_4$ solution was added to the filtrate, which was cooled in a refrigerator for 2 d to give the red crystals.

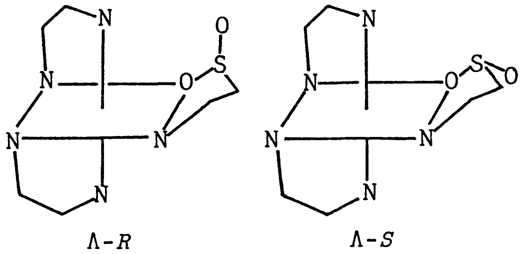

Fig. 1. Two diastereomers of Λ-$[Co(aesi$-*N*,*O*$)(en)_2]^{2+}$.

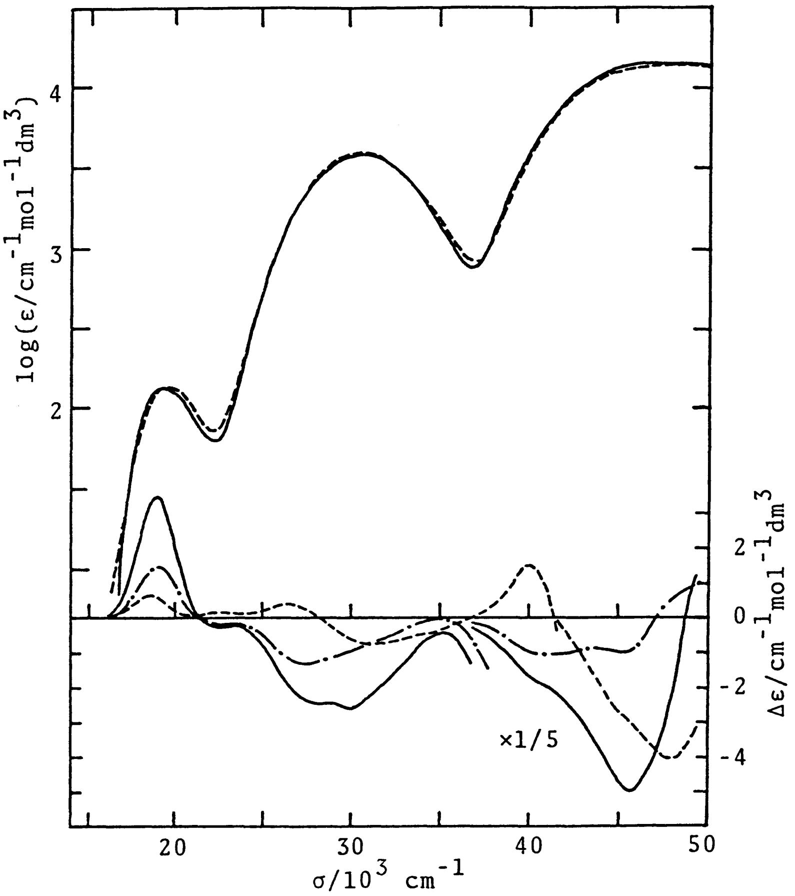

Fig. 2. Absorption and CD spectra of the two diastereomers of Λ-[Co(aesi-*N*,*O*)(en)$_2$](ClO$_4$)$_2$: f1(Λ-*R*) isomer (————), f2(Λ-*S*) isomer (-------), and CD contribution due to the *R*-sulfinate ($\Delta\varepsilon_{f1}$ − $\Delta\varepsilon_{f2}$)/2 = —·—·—·—.

Found for f1 isomer: C, 14.89; H, 4.55; N, 14.31%. Calcd for [Co(aesi)(en)$_2$](ClO$_4$)$_2$ = $C_6H_{22}N_5SO_{10}Cl_2Co$: C, 14.82; H, 4.56; N, 14.41%. Found for f2 isomer: C, 13.93; H, 4.58; N, 13.54%. Calcd for [Co(aesi)(en)$_2$](ClO$_4$)$_2$·H$_2$O·0.1NaClO$_4$ = $C_6H_{24}N_5SO_{11.4}Na_{0.1}Cl_{2.1}Co$: C, 13.95; H, 4.68; N, 13.56%. The visible-UV absorption and circular dichroism(CD) spectra were measured on a Hitachi 330 spectrophotometer and a JASCO MOE-1 spectropolarimeter, respectively. The ^{13}C NMR spectra were recorded with a JEOL FX-90Q NMR spectrometer in D$_2$O containing 1,4-dioxane(δ 67.40 vs. Me$_4$Si) as an internal standard.

The absorption and CD spectra are shown in Fig. 2. Both isomers lacked the intense charge-transfer(CT) band at ∿35000 cm^{-1} characteristic for the starting *S*-bonded sulfinato complex and showed the new CT band at 30600 cm^{-1} in good agreement with the authentic value of the *O*-bonded complex.$^{2)}$ The first spin-allowed d-d absorption band of f1 isomer(19440 cm^{-1}) appeared at somewhat lower energy than that of f2 isomer(19650 cm^{-1}). The ^{13}C NMR spectra showed that each isomer is composed of the single species(Table 1). The oxidation reactions of Λ(or Δ)-

Table 1. Spectral Data

	Absorption[a)] $\sigma_{max}(\log \varepsilon)$	CD[a)] $\sigma_{ext}(\Delta\varepsilon)$	^{13}C NMR[b)] (δ)
f1 isomer	19.44(2.14)	18.98(+3.48)	28.53(1)
(Λ-*R*)	30.58(3.63)	22.7(-0.26)[c)]	43.83(1)
	46.78(4.16)	28.00(-2.48)	45.51(2)
		29.94(-2.58)	45.87(1)
		40.8(-9.6)[c)]	51.77(1)
		45.77(-25.0)	
f2 isomer	19.65(2.14)	18.59(+0.64)	28.78(1)
(Λ-*S*)	30.67(3.63)	22.4(+0.14)	44.48(1)
	45.77(4.20)	26.40(+0.38)	44.97(1)
		31.2(-0.74)	45.62(2)
		40.00(+1.52)	52.20(1)
		48.08(-20.3)	

a) Wave numbers are given in 10^3 cm^{-1} unit and ε or Δε in $cm^{-1}mol^{-1}dm^3$. b) The values in parentheses show the relative intensity. Chemical shift: ppm from Me_4Si. c) Shoulder.

$[Co(NH_2CH_2CH_2S)(en)_2]^{2+}$ and the related complexes with H_2O_2 involved no racemization at the chirality due to the skew pairs of chelate rings[4)] and both the product isomers showed a positive CD band in the first d-d absorption band region. Therefore, it is reasonable to consider that the initial Λ-configuration is retained after the photoisomerization and that f1 and f2 isomers are the diastereomers due to the chiral sulfur atom in the *O*-bonded sulfinate.

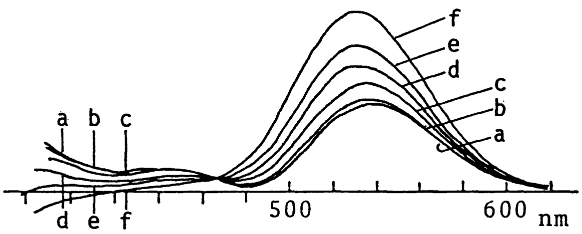

Fig. 3. CD spectral change of f2 isomer with time at 19 °C: a, pure f2 isomer; b, 5 h after dissolution; c, 19 h; d, 43 h; e, 71 h; f, 142 h.

The above discussion is further supported by the following racemization reaction at the chiral sulfur center: f2 isomer exhibited five ^{13}C NMR signals during the first *ca.* 10 h but the additional resonances appeared after 2 d, being identical to those of f1 isomer. The reverse change of f1 to f2 was also confirmed in the ^{13}C NMR spectra. Figure 3 shows the CD change of f2 isomer with time at 19 °C in the first absorption band region. In this case, the increase of the Δε value was observed with the blue shift of the maximum position because f1 isomer($\Delta\varepsilon_{527}$ = +3.48) has the stronger CD than f2 one($\Delta\varepsilon_{538}$ = +0.64). After 142 h the solution contains 70% f2 and 30% f1 species. During this period, the initial absorption spectrum was retained, which removed the possibility of the isomerization into the *S*-bonded sulfinato complex. The aqueous solution of f1 isomer exhibited a gradual decrease of Δε with red shift of the CD peak. These observations indicate that the racemization occurs only at the chiral sulfur atom with the retention of Λ-configuration around the cobalt center. Thus, the successful separation of the two diastereomers Λ-*R* and Λ-*S* is based on the relatively slow rate of racemization.

The absolute configuration of the corresponding *O*-bonded seleninato complex $(-)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(NH_2CH_2CH_2SeO_2}$-$N,O)(\mathrm{en})_2]^{2+}$ was determined by X-ray diffraction study: the asymmetric selenium atom in the Δ-configuration takes the *S* chirality.5) The CD spectral pattern reported for the complex Λ-*R*-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(NH_2CH_2CH_2SeO_2}$-$N,O)$-$(\mathrm{en})_2]^{2+}$ 6) is very similar to that of f1 isomer all over the region measured. Therefore, the absolute configuration Λ-*R* can be assigned to f1 isomer and Λ-*S* to f2 one. The CD contribution due to the chiral sulfur atom was estimated by assuming the additivity rule(Fig. 2). The *R* configuration has a positive and a negative CD contribution in the first d-d and the first CT absorption band region, respectively.

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