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Preparation and Characterization of Triammine Cobalt(III) Complexes with (*R*)-2-(Carboxymethylthio)propionate and Its Derivative

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Synopsis. Two complexes of *fac*(*NH*$_3$)-[Co(L)(NH$_3$)$_3$]$^+$ type (where L denotes (*R*)-2-(carboxymethylthio)propionate and (*R*)-2-(2-carboxyethylthio)propionate) were newly prepared and separated into two isomers, *R*(*S*), *R*(*C*) and *S*(*S*), *R*(*C*), by column chromatography. The absolute configurations of the isomers are suggested on the basis of the ^{13}C NMR spectra.

(*R*)-2-(Carboxymethylthio)propionate (*R*-cmtp) and (*R*)-2-(2-carboxyethylthio)propionate (*R*-cetp) function as terdentate-*O*,*S*,*O* ligands. When this type of ligand coordinates to a cobalt(III) ion and three ammonia molecules occupy the remaining three coordination sites, the resulting complexes have one chirality due to the coordinated sulfur atom (*R*(*S*) or *S*(*S*) configuration) and another due to the asymmetric carbon atom (*R*(*C*) configuration). There have been only a few works on such kinds of chirality due to the rigid chiral sulfur atom.[1)] This note is concerned with the preparation and isolation of diastereomers, *R*(*S*),*R*(*C*) and *S*(*S*),*R*(*C*), of the *fac*(*NH*$_3$) triammine cobalt(III) complexes with *R*-cmtp and *R*-cetp ligands. The ^{13}C NMR and CD spectra for the four isomers are presented.

Experimental

R-H$_2$cmtp was prepared by the well-established procedure,[2)] using (*S*)-2-bromopropionic acid and mercaptoacetic acid. The $[\alpha]_D^{23}=+87.6°$ (*c* 2.2, CHCl$_3$) for the *R*-H$_2$cmtp·0.1NaBr in this work agreed with the value in the literature.[3)]

R-H$_2$cetp was prepared by the same procedure as that of *R*-H$_2$cmtp,[2)] using 3-mercaptopropionic acid instead of mercaptoacetic acid. This reaction proceeds without racemization.[2,4)] Found: C, 40.17; H, 5.58%. Calcd for *R*-H$_2$cetp: C, 40.44; H, 5.56%. $[\alpha]_D^{23}=+64.1°$ (*c* 4.4, water) and $[\alpha]_D^{23}=+106.1°$ (*c* 2.2, CHCl$_3$).

*[Co(*R*-cmtp)(NH$_3$)$_3$]Cl.* This complex was prepared by the reaction of *R*-H$_2$cmtp (5 g) with [Co(NO$_3$)$_3$(NH$_3$)$_3$][5)] (5 g) in 40 cm^3 of water at 50 °C for 1.5 h. The reaction mixture was filtered and the filtrate was poured onto a column of Dowex 50W-X8 (H$^+$ form, 3×40 cm). After the column had been swept with water, the adsorbed band was eluted with 0.1 mol dm^{-3} aqueous solution of sodium chloride, of which the pH was adjusted to 3 by addition of concentrated hydrochloric acid. Two red-violet bands, F1 and F2 (the formation ratio of F1 to F2 was *ca.* 46 : 54), were eluted in this order. Each eluate was concentrated to *ca.* 10 cm^3 with a rotary evaporator. The deposited NaCl was filtered off and the filtrate was passed through a column of Sephadex G-10 (2×150 cm). The solution eluted with water was concentrated to a small volume again and kept in a refrigerator overnight. The crystals obtained were collected by filtration. Found for F1: C, 19.93; H, 4.88; N, 13.56%. Found for F2: C, 19.48; H, 4.88; N, 13.77%. Calcd for [Co(*R*-cmtp)(NH$_3$)$_3$]Cl=CoC$_5$H$_{15}$N$_3$O$_4$SCl: C, 19.51; H, 4.92; N, 13.66%.

*[Co(*R*-cetp)(NH$_3$)$_3$]Cl.* This complex was prepared and separated into two isomers, G1 and G2 (the formation ratio of G1 to G2 was *ca.* 44 : 56), by a procedure similar to that for [Co(*R*-cmtp)(NH$_3$)$_3$]Cl complex, using *R*-H$_2$cetp instead of *R*-H$_2$cmtp. Found for G1: C, 21.98; H, 5.33; N, 12.86%. Calcd for [Co(*R*-cetp)(NH$_3$)$_3$]Cl·0.25H$_2$O=CoC$_6$H$_{17}$N$_3$O$_4$SCl·0.25H$_2$O: C, 22.09; H, 5.42; N, 12.88%. Found for G2: C, 21.29; H, 5.64; N, 12.22%. Calcd for [Co(*R*-cetp)(NH$_3$)$_3$]Cl·H$_2$O: C, 21.21; H, 5.65; N, 12.37%.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra, with a JASCO J-20 spectropolarimeter. The ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature in a D$_2$O solvent. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference.

Results and Discussion

Two geometrical isomers, *fac*(*NH*$_3$) and *mer*(*NH*$_3$), are possible for [Co(terdentate-*O*,*S*,*O*)(NH$_3$)$_3$]$^+$, as shown in Fig. 1(a). The two isomers for each of the *R*-cmtp and *R*-cetp complexes isolated show the similar absorption spectra over the whole region, and the pattern of their first absorption bands is in line with that of the *s-cis*(*O*)-*fac*-(thiodiacetato)(diethylenetriammine)cobalt(III) complex (Fig. 2).[6)] Therefore, it is possible to assign the present isomers to be *fac*(*NH*$_3$).

The *fac*(*NH*$_3$) complexes have two chiral centers at carbon and sulfur atoms. Namely, two diastereomers due to the chirality of the sulfur atom are possible for each of the complexes, since the chiral carbon atom has the *R*(*C*) configuration (Fig. 1(b)). In the ^{13}C NMR spectra, the methyl, methylene, and methine carbons of F2 resonate at higher magnetic field than those of F1, as shown in Fig. 3. When the chiral sulfur atom takes the *R*(*S*) configuration, the interaction between a methyl group of a coordinated *R*-cmtp ligand and another chelate ring of the same ligand is probable (Fig. 1(b)). On the contrary, there is no spatial crowd for the methyl group of the *S*(*S*),*R*(*C*) isomer (Fig. 1(b)). Taking the steric effects for the chemical shift of carbon into consideration,[7)] the ^{13}C NMR spectra seem to suggest that F1 takes the *S*(*S*),*R*(*C*) configuration and F2 the *R*(*S*),*R*(*C*) one. In the same manner, G1 is assigned to

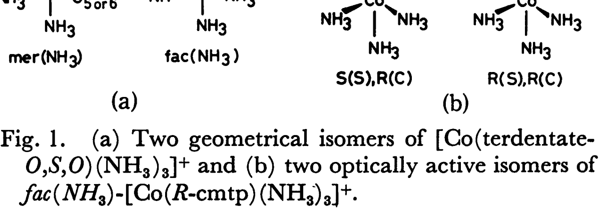

Fig. 1. (a) Two geometrical isomers of [Co(terdentate-*O*,*S*,*O*)(NH$_3$)$_3$]$^+$ and (b) two optically active isomers of *fac*(*NH*$_3$)-[Co(*R*-cmtp)(NH$_3$)$_3$]$^+$.

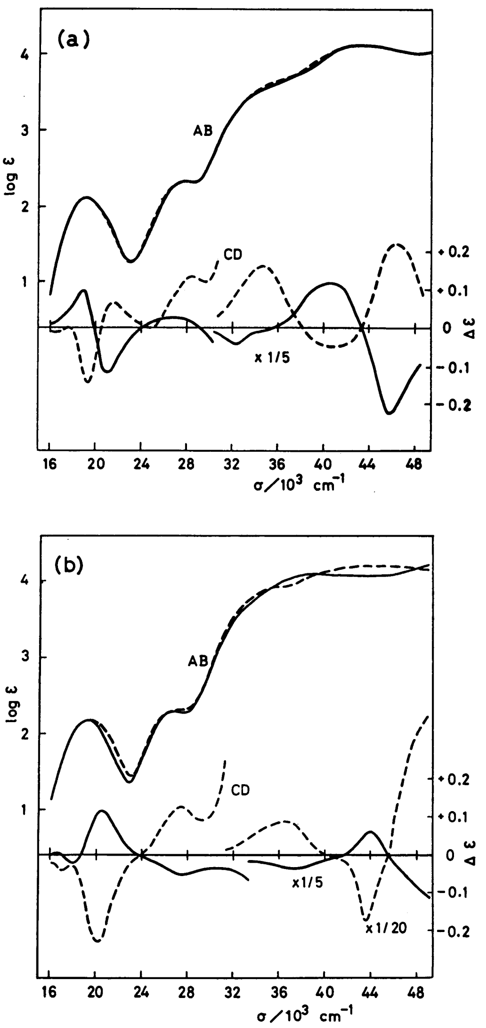

Fig. 2. Absorption and CD spectra of the triammine complexes: (a) F1 (——) and F2 (------) of $[Co(R\text{-}cmtp)(NH_3)_3]^+$, and (b) G1 (——) and G2 (------) of $[Co(R\text{-}cetp)(NH_3)_3]^+$.

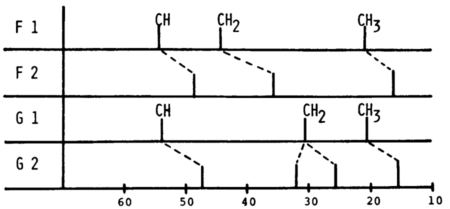

Fig. 3. Distribution of ^{13}C NMR chemical shifts.

the *S*(*S*),*R*(*C*) configuration and G2 to the *R*(*S*),*R*(*C*) one. These assignments are supported by the ^{13}C NMR spectral study of the cobalt(III) complexes with the *N*-(carboxylatomethyl)-L-alaninate ligand which has a similar framework to the *R*-cmtp one.[8]

As shown in Figs. 2(a) and (b), the CD spectra of two isomers for each of the *R*-cmtp and *R*-cetp complexes are almost enantiomeric over the whole region. In the first absorption band region, the *R*(*S*),*R*(*C*) isomer (F2) of the *R*-cmtp complex, which consists of two five-membered chelate rings, shows three CD bands ((−), (−) and (+) from lower energy side) (Fig. 2(a)). The *R*(*S*),*R*(*C*) isomer (G2) of the *R*-cetp complex, which consists of one five- and one six-membered chelate ring, shows almost opposite signs ((−) and (−)) for that of the *R*-cmtp one (Fig. 2(b)), although the two complexes show a similar CD behavior in the region of (32—48) × 10³ cm⁻¹. A similar CD spectral behavior in the first absorption band region was observed for the *R*(*N*),*S*(*C*) triammine cobalt(III) complexes with the *N*-(carboxylatomethyl)-L-alaninate and *N*-(2-carboxylatoethyl)-L-alaninate,[9] which have the chiral nitrogen atoms instead of the sulfur atoms of the *R*-cmtp and *R*-cetp ligands. The CD intensity in the *R*-cmtp and *R*-cetp complexes is very much smaller than that of the mixed cobalt(III) complexes with the 1,1,1-tris(aminomethyl)-ethane (tame) and terdentate-*N*,*S*,*O* such as (2-amino-ethylthio)acetate, which have a similar CD contribution to the present complexes.[1] The CD spectra of the present isomers seem to indicate that the arrangement chirality of the donor atoms in the *R*-cmtp and *R*-cetp complexes little affects the CD spectra, or that the chelate rings of the tame ligand in the tame cobalt(III) complexes[1] are significant for CD contribution.

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