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Preparation, Racemization, and Deuteration of 2-(Methylthio)propionato-*S,O* and 2-Sulfinatopropionato-*S,O* Complexes of Cobalt(III)

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(Received April 28, 1983)

$(+)_{589}$-$[Co\{SCH(CH_3)COO\}(tren)]^+$, $(-)_{589}$-$[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$, and $(+)_{589}$-$[Co\{S(O)_2$-$CH(CH_3)COO\}(tren)]^+$ (tren=tris(2-aminoethyl)amine) were prepared and assigned to the trans (*tertiary amine nitrogen, S*) isomer with the *R* carbon atom on the basis of the absorption, CD, and ^{1}H NMR spectra. Racemization of the complexes was studied in aqueous solutions with ionic strength of 0.1, 0.2, or 1.0 ($NaClO_4$) in the pH and temperature ranges of 5.96—6.86 and 19.9—49.5 °C, respectively. The $CH_3SCH(CH_3)COO^-$ and $^-O_2SCH(CH_3)$-COO^- complexes follow the rate law, $R=k_r[OH^-][complex]$. The second-order rate constants (k_r) for the former and the latter complexes are 4.6×10^3 (35.3 °C) and 7.8×10^3 (35.2 °C) mol^{-1} dm^3 s^{-1}, respectively. The $^-SCH(CH_3)COO^-$ complex did not racemize under these conditions. Deuteration of the methine protons in the complexes was found to proceed simultaneously with the racemization. The differences in reactivity to racemization and proton exchange among three complexes were accounted for by the difference in electron-withdrawing effect of the ^-S–, $S(CH_3)$–, and $^-S(O)_2$– groups, and by the difference in net charge of the complex ions.

It is known that methine or methylene groups of α-amino acids become reactive on chelation to metals. The activation leads to such reactions as deuteration of the methine or methylene protons,[1–3] racemization at the α-carbon atom,[2] and condensation with aldehydes to afford α-substituted amino acids.[4] Activation of methylene groups of ethylenediaminetetraacetato[1] and malonato[5,6] metal chelates has also been demonstrated. All these reactions are base-catalyzed and occur at methine or methylene groups located between two electron-withdrawing groups. 2-(Methylthio)propionato-*S,O* and 2-sulfinatopropionato-*S,O* chelates both of which contain two electron-withdrawing groups are also expected to have similar reactivity. Recently Adzamli *et al.*[7] reported that the methylene protons of *S,O* chelates in $[Co\{S(O)_nCH_2COO\}(en)_2]^+$ (n=0, 1, 2; en: ethylenediamine) undergo deuterium exchange in basic D_2O solutions. However, no kinetic studies have been done. It is of interest to compare quantitatively the activity of methylene groups of such *S,O* chelates with that of amino acidato-*N,O* and dicarboxylato-*O,O* chelates.

This paper reports kinetic studies on racemization and deuteration of optically active $CH_3SCH(CH_3)$-COO^- and $^-O_2SCH(CH_3)COO^-$ chelates in tris(2-aminoethyl)amine(tren) cobalt(III) complexes as well as deuteration of $CH_3SCH_2COO^-$ and $^-O_2SCH_2COO^-$ chelates in some related complexes. Preparation, stereochemistry, and circular dichroism (CD) spectra of these tren complexes are also described in this paper.

Experimental

$(+)_{589}$-$[Co\{SCH(CH_3)COO\}(tren)]ClO_4$. To an aqueous solution (30 cm^3) of $[CoCl_2(tren)]Cl$[8] (1.24 g, 4 mmol) was added an aqueous solution (30 cm^3) of 2-mercaptopropionic acid (0.24 g, 4 mmol). The pH of the solution was adjusted to *ca.* 9 with Na_2CO_3, and the mixture was stirred for 1 h at 65 °C. The color of the solution changed from violet to dark brown. The solution was cooled and then mixed with $NaClO_4$ to yield brown crystals of the complex perchlorate, which were filtered and washed with ethanol. Yield: 1.1 g. No evidence indicative of the presence of the other isomer was obtained in both the ^{1}H NMR spectrum of the isolated complex and chromatography (SP-Sephadex C-25, 0.1 mol dm^{-3} NaBr) of the reaction mixture. The sparingly soluble perchlorate was converted into chloride by use of Dowex 1×8 (Cl^- form). Brown crystals were obtained by adding ethanol to the concentrate of the complex chloride. Yield: 85%. The complex was resolved as follows: To an aqueous solution (9 cm^3) of the complex chloride (2.68 g, 7.78 mmol) was added an aqueous solution (9 cm^3) of $(+)_{546}$-$Na[Co(C_2O_4)_2(en)]\cdot3.5H_2O$[9] (1.48 g, 3.89 mmol). The solution was mixed with 10 cm^3 of ethanol and allowed to stand overnight at room temperature. The dark purple crystals precipitated were collected by filtration and recrystallized six times from water–ethanol. Yield: 0.72 g. The crystals were dissolved in water, and the solution was passed through a column (ϕ1.5 cm×5 cm) of SP-Sephadex C-25 (Na^+ form). After washing the column with water the complex adsorbed was eluted with 0.5 mol dm^{-3} $NaClO_4$. The crystalline $(+)_{589}$-isomer was obtained by further addition of $NaClO_4$ to the effluent, filtered, and washed with ethanol. Yield: 0.37 g. Found: C, 26.30; H, 5.44; N, 13.73%. Calcd for $C_9H_{22}N_4ClCoO_6S$: C, 26.45; H, 5.42; N, 13.71%.

$(-)_{589}$-$[Co\{CH_3SCH(CH_3)COO\}(tren)](ClO_4)_2\cdot H_2O$. To a stirred suspension of $(+)_{589}$-$[Co\{SCH(CH_3)COO\}$-$(tren)]ClO_4$ (0.80 g, 1.96 mmol) in dimethyl sulfoxide (20 cm^3) was added CH_3I (2.78 g, 19.6 mmol) in dimethyl sulfoxide (20 cm^3). An orange solution was obtained within a few minutes. After a day the solution was diluted with 0.01 mol dm^{-3} HCl (200 cm^3), excess CH_3I was extracted with $CHCl_3$ (300 cm^3), and the orange aqueous phase was passed through a column (ϕ1.5 cm×3 cm) of SP-Sephadex C-25. The Sephadex charged with the product was placed on the top of a column (ϕ6 cm×30 cm) of SP-Sephadex C-25, and the product was eluted with 0.2 mol dm^{-3} NaCl adjusted to pH 2 with HCl. The column showed only one band. The effluent was diluted twenty times with 0.01 mol dm^{-3} HCl and passed again through an SP-Sephadex C-25 column (ϕ1.5 cm×3 cm). After washing the column with 0.01 mol dm^{-3} $HClO_4$, the complex adsorbed was eluted with 0.7 mol dm^{-3} $NaClO_4$ adjusted to pH 2 with $HClO_4$. The effluent was evaporated to a small volume under reduced pressure to yield orange crystals of the $(-)_{589}$-isomer, which were filtered, washed with ethanol, and recrystallized from 0.01 mol dm^{-3} $HClO_4$. Yield: 0.65 g. Found: C, 22.24; H, 4.68; N, 10.59%. Calcd for $C_{10}H_{27}N_4Cl_2CoO_{11}S$: C, 22.19; H, 5.03; N, 10.35%.

$(+)_{589}$-$[Co\{S(O)_2CH(CH_3)COO\}(tren)]ClO_4\cdot H_2O$. To

a suspension of $(+)_{589}$-$[Co\{SCH(CH_3)COO\}(tren)]ClO_4$ (0.82 g, 2 mmol) in 0.1 mol dm^{-3} $HClO_4$ (20 cm^3) was added 35% aqueous H_2O_2 (1.94 g, 20 mmol) in 0.1 mol dm^{-3} $HClO_4$ (30 cm^3) with stirring. The color of the mixture changed from purple to orange, and the starting material dissolved completely in 10 min. After a day $NaClO_4$ was added to the resulting solution to yield yellow crystals, which were filtered and washed with ethanol. No other complex was formed. Yield: 0.53 g. Found: C, 23.57; H, 5.16; N, 12.44%. Calcd for $C_9H_{24}N_4ClCoO_9S$: C, 23.56; H, 5.27; N, 12.21%.

$(-)_{589}$-$[Co\{S(O)CH(CH_3)COO\}(tren)]^+$. This complex was less stable than the above sulfinato complex and could not be isolated as the pure solid. To a solution of $(+)_{589}$-$[Co\{SCH(CH_3)COO\}(tren)]ClO_4$ (8.2 mg, 0.02 mmol) in 0.01 mol dm^{-3} $HClO_4$ (10 cm^3) was added 35% aqueous H_2O_2 (2.1 mg, 0.022 mmol) in 0.01 mol dm^{-3} $HClO_4$ (25 cm^3). The color of the solution changed immediately from purple to orange. After 30 min the solution showed an absorption band at 365 nm characteristic of the S-bonded sulfenato moiety.[7] The solution was used for CD measurements without isolating the complex.

$[Co(SCH_2COO)(tren)]ClO_4$, $[Co(CH_3SCH_2COO)(tren)](ClO_4)_2$, and $[Co\{S(O)_2CH_2COO\}(tren)]ClO_4$. These complexes were prepared by the same methods as those for the corresponding 2-mercaptopropionate, and its derivative complexes. Found: C, 24.32; H, 5.13; N, 14.22%. Calcd for $C_8H_{20}N_4ClCoO_6S = [Co(SCH_2COO)(tren)]ClO_4$: C,24.34; H, 5.11; N, 14.19%. Found: C, 21.17; H, 4.55; N, 10.95%. Calcd for $C_9H_{23}N_4Cl_2CoO_{10}S = [Co(CH_3SCH_2COO)(tren)](ClO_4)_2$: C, 21.23; H, 4.55; N, 11.00%. Found: C, 22.81; H, 4.85; N, 13.14%. Calcd for $C_8H_{20}N_4ClCoO_8S = [Co\{S(O)_2CH_2COO\}(tren)]ClO_4$: C, 22.52; H, 4.72; N, 13.13%. Each complex was confirmed to yield only one isomer by column chromatography on SP-Sephadex and ^{1}H NMR spectra.

p- *and* t-*$[Co(CH_3SCH_2CH_2NH_2)(tren)](ClO_4)_3 \cdot H_2O$.* These complexes were prepared from CH_3I and the corresponding isomers of $[Co(SCH_2CH_2NH_2)(tren)]ZnCl_4$[10] by a method similar to that for $(-)_{589}$-$[Co\{CH_3SCH(CH_3)COO\}(tren)](ClO_4)_2 \cdot H_2O$. Found for the *p*-isomer: C, 17.56; H, 4.51; N, 11.39%. Found for the *t*-isomer: C, 17.58; H, 4.70; N, 11.57%. Calcd for $C_9H_{29}N_5Cl_3CoO_{13}S$: C, 17.64; H, 4.77; N, 11.43%.

$[Co(SCH_2COO)(en)_2]ClO_4$, $[Co(CH_3SCH_2COO)(en)_2](ClO_4)_2$, and $[Co\{S(O)_2CH_2COO\}(en)_2]Cl \cdot H_2O$. These complexes were prepared by literature procedures.[7,11—13]

$[Co\{S(O)_2C(CH_2OH)_2COO\}(en)_2]ClO_4 \cdot 0.5CH_3OH$. To a mixture of $[Co\{S(O)_2CH_2COO\}(en)_2]Cl \cdot H_2O$ (0.68 g, 2 mmol) and Na_2CO_3 (0.12 g, 1 mmol) in water (25 cm^3) was added an aqueous solution (25 cm^3) containing 8 mmol of formaldehyde. The mixture was stirred for a day at room temperature and filtered to remove a small amount of precipitate. The filtrate was chromatographed using a column (ϕ3 cm × 40 cm) of SP-Sephadex C-25 and an eluent of 0.2 mol dm^{-3} $NaClO_4$. The effluent of the fast-moving main band was collected and evaporated to a small volume under reduced pressure. On addition of methanol the concentrate gave large orange crystals, which were filtered, washed with methanol, and recrystallized from water–methanol. Yield: 0.13 g. The presence of 0.5 mol of methanol in the complex salt was confirmed by the ^{1}H NMR spectrum. Found: C, 21.22; H, 5.06; N, 11.86%. Calcd for $C_{8.5}H_{24}N_4ClCoO_{10.5}S$: C, 21.41; H, 5.07; N, 11.75%.

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter. ^{1}H NMR spectra were obtained in D_2O or DCl–D_2O solutions with a JEOL PMX-60 spectrometer using sodium 3-(trimethylsilyl)propionate-d_4 or sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal reference.

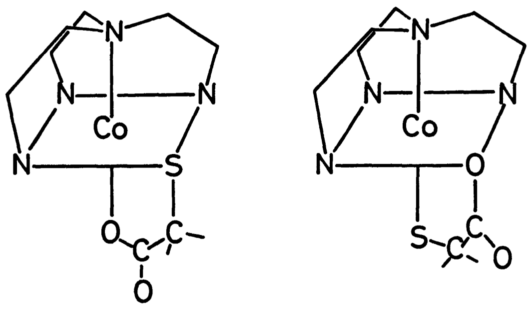
Racemization Studies. Racemization rates were followed by monitoring CD strength changes at 465 nm ($[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$) or at 420 nm ($[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$) as a function of reaction time. All experiments were carried out in aqueous solutions with ionic strength of 0.1, 0.2, or 1.0 ($NaClO_4$) in the pH and temperature ranges of 5.96—6.86 ($NaCH_3COO$-HCl) and 19.9—49.5 °C, respectively. The complex concentrations were in the range of $(2.5—9.6) \times 10^{-3}$ mol dm^{-3}. The absorption spectra were also measured to check the stability of the complexes toward decomposition.

Deuteration Studies. Deuteration rates were followed by monitoring signal changes in ^{1}H NMR spectra. The complex perchlorates were converted into chlorides with a Dowex 1×8 anion exchanger in the chloride form in order to increase the solubility. The complex concentrations were 0.21—0.25 mol dm^{-3}, and no attempt was made to keep ionic strength constant. The samples in NMR tubes were placed in a thermostat at 34.5 °C, and the spectra were recorded at timed intervals at 34.5 °C. The peak areas of signals were determined by weighing paper cutouts maching the peak areas. The $pD = pH + 0.4$,[14] and $[OD^-] = 2.89 \times 10^{-15} [D^+]^{-1}$ [15] formulae were used to evaluate $[D^+]$ and $[OD^-]$, respectively.

Results and Discussion

Preparation and Characterization of the Complexes. The thiolato complexes, $[Co\{SCH(CH_3)COO\}(tren)]^+$ and $[Co(SCH_2COO)(tren)]^+$ were prepared from $[CoCl_2(tren)]^+$ and the thiolate ligands in fairly good yields (60—70%). A number of thiolatobis(ethylenediamine)cobalt(III) complexes have been prepared by oxidizing bis(ethylenediamine)cobalt(II) ions with the disulfide derivative of a thiol in the absence of air.[16] However, this method was not effective for the tren complex, no redox reaction taking place between tren-cobalt(II) ions and either disulfide, $(^-OOCCH_2S-)_2$ or $(^-OOCCH(CH_3)S-)_2$. On the other hand, analogous ligands, $(^-OOCCH_2Se-)_2$ and $(NH_2CH_2CH_2S-)_2$ oxidize tren-cobalt(II) ions to yield $[Co(SeCH_2COO)(tren)]^{+}$[19] and $[Co(NH_2CH_2CH_2S)(tren)]^{2+}$,[10] respectively, although the reaction with the latter ligand is slow. Such differences in reactivity may be related with oxidizing strength of these ligands toward the tren-cobalt(II) ion.

Two geometrical (*p*- and *t*-) isomers[18] are possible for



p-isomer **t-isomer**

Fig. 1. Two geometrical isomers of [Co(*S*,*O* chelate)(tren)]$^{n+}$.

Table 1. Absorption and CD spectral data

Complex	Absorption $\tilde{\nu}_{max}$/cm^{-1}(logε)	CD $\tilde{\nu}_{ext}$/cm^{-1}($\Delta\varepsilon$)
$[Co(SCH_2COO)(tren)]^+$	17000(1.81)[b]	
	20330(2.07)	
	22000(2.03)[b]	
	27500(2.42)[b]	
	34600(4.17)	
	44840(4.18)	
$(+)_{589}$-$[Co\{SCH(CH_3)COO\}(tren)]^+$	17000(1.82)[b]	17150(−0.59)
	20330(2.07)	19880(+3.10)
	22000(2.02)[b]	22990(−2.72)
	27500(2.40)[b]	
	34720(4.18)	34970(+4.63)
	44350(4.16)	41490(−3.05)
$[Co(CH_3SCH_2COO)(tren)]^{2+}$	20620(2.13)	
	28000(2.41)[b]	
	34660(3.99)	
	42830(4.13)	
$(-)_{589}$-$[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$[a]	20640(2 22)	21510(−0 93)
	28000(2.44)[b]	28170(+0.40)
	34970(4.03)	34360(+2 86)
	43290(4.13)	39220(−3.04)
$[Co\{S(O)_2CH_2COO\}(tren)]^+$	23040(2.52)	
	33170(4.09)	
	44740(4.15)	
$(+)_{589}$-$[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$[a]	22990(2.60)	20200(−0.17)
		23920(+0.79)
	33000(4.10)	33220(+4.11)
	44540(4.13)	42020(−1.95)
p-$[Co(CH_3SCH_2CH_2NH_2)(tren)]^{3+}$	20530(2.29)	
	34720(3.88)	
	43200(4.17)	
t-$[Co(CH_3SCH_2CH_2NH_2)(tren)]^{3+}$	20790(2.15)	
	34420(4.05)	
	44540(4.18)	
$[Co\{S(O)_2C(CH_2OH)_2COO\}(en)_2]^+$	22300(2.45)	
	33110(4.01)	
	44740(4.14)	
$[Co\{S(O)_2CH_2COO\}(en)_2]^+$	22300(2.37)	
	33840(3.96)	
	44740(4.15)	

a) Measured in 10^{-2} mol dm^{-3} $HClO_4$. b) Shoulder.

$[Co(SCHRCOO)(tren)]^+$ (R=H, CH_3; Fig. 1). These thiolatocarboxylato complexes form only one geometrical isomer as confirmed by column chromatography and ^1H NMR spectra. The absorption spectra of both complexes are quite similar and the complexes will have the same geometrical configuration. The spectra show a shoulder around 17000 cm^{-1} on the low energy side of the first absorption band, and an intense sulfur-to-cobalt(III) charge-transfer band around 34700 cm^{-1} (Table 1 and Fig. 2). The spectral pattern is characteristic of cobalt(III)-thiolato complexes.[19)]

The $[Co(NH_2CH_2CH_2S)(tren)]^{2+}$ complex forms both *p*- and *t*-isomers. The isomers give the first absorption band at nearly the same position, but the patterns differ remarkably from each other. The spectral pattern of the $^-SCHRCOO^-$ complexes is very similar to that of the *t*-isomer of the $NH_2CH_2CH_2S^-$ complex, showing strong shoulder absorption on the low energy side of the first absorption band (Fig. 2). The *p*-isomer exhibits only weak shoulder in this region. Thus both thiolatocarboxylato complexes can be assigned to the *t*-isomer. This assignment agrees with that obtained from absorption spectra of methylthio complexes derived from the present $^-SCHRCOO^-$ complexes described below.

The sulfenato-, sulfinato-, and methylthio-carboxylato complexes were prepared from the $^-SCHRCOO^-$ complexes by stoichiometric oxidation with H_2O_2,[7,20)] by oxidation with excess H_2O_2,[7,20)] and by methylation with CH_3I in dimethyl sulfoxide,[10,11,21,22)] respectively. These reactions do not involve Co–S cleavage, and geometrical structures of the complexes should be retained.[23,24)] The $[Co(CH_3SCH_2COO)(tren)]^{2+}$ complex thus obtained gives the first absorption band (20620 cm^{-1}) between those of *p*-(20530 cm^{-1}) and *t*-(20790

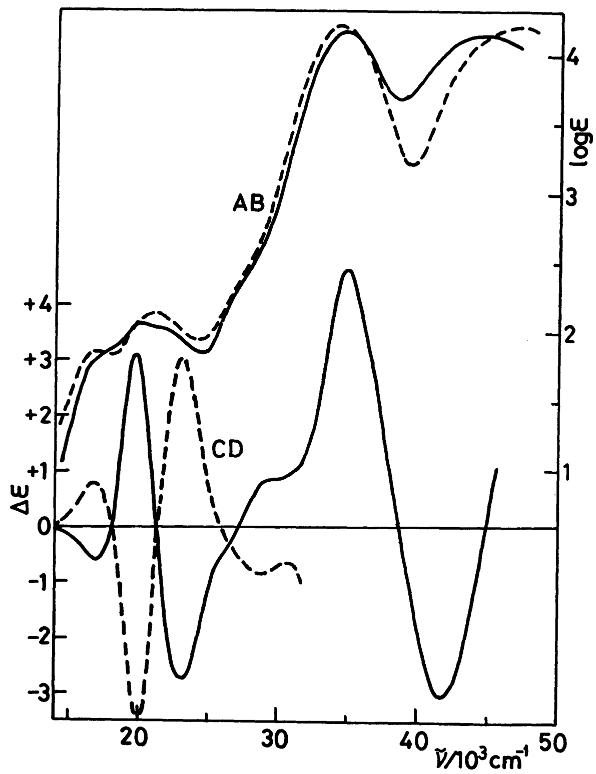


Fig. 2. Absorption and CD spectra of $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$ (——) and *t*-[Co{(*S*)-SCH(CH_3)CH_2NH_2}(tren)]$^{2+}$ (------)[26] in water.

cm^{-1}) isomers of [Co($CH_3SCH_2CH_2NH_2$)(tren)]$^{3+}$ (Table 1). Since $CH_3SCH_2COO^-$ will exert a weaker ligand field than $CH_3SCH_2CH_2NH_2$, the $CH_3SCH_2COO^-$ complex will show the d-d absorption bands at lower energy than those of the $CH_3SCH_2CH_2NH_2$ complex with the same geometrical configuration. Thus [Co(CH_3SCH_2COO)(tren)]$^{2+}$ and all the *S*,*O* chelate complexes obtained in this study can be assigned to the *t*-isomer.

The difference in absorption maxima of the d-d bands between *t*- and *p*-[Co($CH_3SCH_2CH_2NH_2$)(tren)]$^{3+}$ may partly be ascribed to the difference in strain involved in the isomers. Molecular models indicate that the *p*-isomer will be strained by steric hindrance between the methyl group and the tren ligand. On the other hand, the *t*-isomer has no such hindrance around the methyl group. Accordingly the strained *p*-isomer will show the first absorption band at lower energy than that of the *t*-isomer. When the methyl group in the *p*-isomer is replaced by a small hydrogen atom, the hindrance with the tren ligand will be diminished, and the energy difference between the first absorption bands of the *p*- and *t*-isomers will be decreased. In concd H_2SO_4, where the thiolato chelates will be completely protonated,[25] both isomers show the first absorption band at the same position (20640 cm^{-1}). Thus the position of the first absorption band of [Co($RSCH_2CH_2NH_2$)(tren)]$^{3+}$ seems to depend strongly on the steric conditions.

The ^1H NMR spectrum of [Co(CH_3SCH_2COO)(tren)]$^{2+}$ in DCl–D_2O (pD *ca.* 2) gives an AB quartet (3.53—4.22 ppm, $J=18$ Hz, $\Delta\nu=14$ Hz) attributable to the methylene protons of the (methylthio)acetate ligand. The result demonstrates that the inversion at the sulfur atom is slow on the NMR time scale. However, attempts to resolve the complex by column chromatography were unsuccessful, suggesting that the inversion is not so slow as to be resolved by conventional techniques. The ^1H NMR spectrum of [Co{CH_3SCH(CH_3)COO}(tren)]$^{2+}$ shows only one kind of quartet (4.07 ppm) and doublet (1.65 ppm) assignable to the methine and methyl protons of the –CH(CH_3)– group, respectively. From a comparison with the above (methylthio)acetato complex, it is unlikely that the spectrum is brought about by rapid inversion at sulfur (coalesced spectrum) or accidental degeneracies. Thus it is concluded that the disposition of the S–CH_3 group is stereospecific in the (methylthio)propionato complex (*vide post*). In general, sulfur atoms in cobalt(III)-sulfide complexes are labile toward inversion, although the rate is slow on the NMR time scale.[10]

Figure 2 compares the absorption and CD spectra of $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$, which has been assigned to the *t*-isomer, with those of *t*-[Co{(*S*)-SCH(CH_3)CH_2NH_2}(tren)]$^{2+}$.[26] The absorption spectra of both complexes are similar, but the CD spectra are almost enantiomeric to each other in the d-d absorption band region. Thus the carbon atom of $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$ can be assigned to *R* configuration. The absolute configuration of the sulfur atom in $(-)_{589}$-[Co{S(O)CH(CH_3)COO}(tren)]$^+$ which was derived from $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$ can be assigned by comparing the CD spectrum with that of *Δ*-[Co{*S*(S), *R*(C)-cysO}(en)$_2$]$^{+23)}$ whose absolute configuration has been determined by the X-ray method[27] (*S*(S), *R*(C)-cysO=(*S*(S), *R*(C))-2-amino-3-sulfenatopropionate-*N*,*S*). In the Co–S charge-transfer band region (25000—39000 cm^{-1}) the CD pattern of $(-)_{589}$-[Co{S(O)CH(CH_3)COO}(tren)]$^+$ is almost enantiomeric to that of the *Δ*[*S*(S), *R*(C)]-cysO complex, and very similar to that of the *Δ*[*R*(S), *R*(C)]-cysO complex.[23] Thus the sulfur atom in $(-)_{589}$-[Co{S(O)CH(CH_3)COO}(tren)]$^+$ can be assigned to *R* configuration. The oxidation of the sulfur atom in the $^-$SCH(CH_3)COO$^-$ complex will occur selectively at the *anti* position to the methyl group to afford the (*R*(S), *R*(C))- or (*S*(S), *S*(C))-$^-$S(O)CH(CH_3)COO$^-$ complex, since the incoming oxidant to this position has less steric interaction with the methyl group (Fig. 3). Thus the carbon atom in $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$ which gives the (*R*(S))-$^-$S(O)CH(CH_3)COO$^-$ complex should have *R* configuration. This conclusion for the carbon atom agrees with the previous one obtained on the basis of the CD spectrum of the (*S*)-SCH(CH_3)CH_2NH_2 complex.

Very recently, the structure of $(-)_{589}$-[Co{CH_3SCH(CH_3)COO}(tren)]$^{2+}$ which was derived from $(+)_{589}$-[Co{SCH(CH_3)COO}(tren)]$^+$ has been determined by X-ray analysis to have *S*(S), *R*(C) configuration.[28] The disposition of the methyl group on the sulfur atom in this complex is the same as that of the oxygen atom in the above *R*(S), *R*(C)-sulfenato complex, the notation, *R* and *S* for the chiral sulfur atom being reversed between the methylthio and sulfenato complexes.

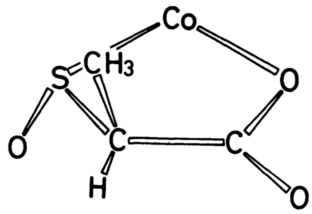


Fig. 3. Proposed structure of the $^{-}$OSCH(CH$_3$)COO^{-} chelate.

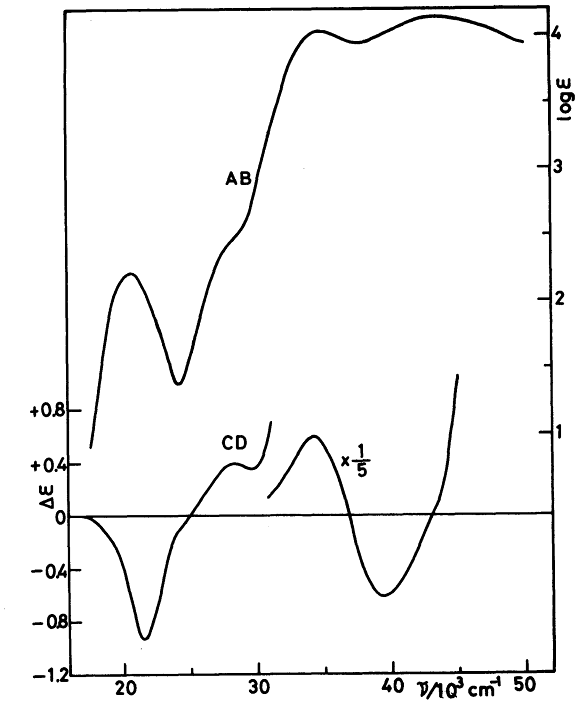


Fig. 4. Absorption and CD spectra of $(-)_{589}$-[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$ in 10^{-2} mol dm^{-3} HClO$_4$.

Kinetics of Racemization and Deuteration Reactions. Absorption and CD spectra of $(-)_{589}$-[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$ in acidic water are given in Fig. 4. The complex which was prepared from $(+)_{589}$-[Co{SCH(CH$_3$)COO}(tren)]$^{+}$ gives a CD extreme at 465 nm (21510 cm^{-1}), and this wavelength was used to follow the racemization rates. Measurements were carried out over the temperature range of 20.0 to 45.3 °C in the pH region of 5.96 to 6.86. In every kinetic run the plot of $\log(\Delta\varepsilon_{465})$ *vs.* time at a constant pH gave a straight line for at least two half-lives. Thus the racemization rate at a constant pH can be expressed as $-d[\text{complex}]/dt = k_{r(\text{obsd})}[\text{complex}]$, where $k_{r(\text{obsd})}$ is the pseudo-first-order rate constant for racemization at a constant pH. The $k_{r(\text{obsd})}/[\text{OH}^-]$ ($=k_r$) values are constant at a given temperature, indicating that the reaction is first-order in [OH$^-$]. The values of $k_{r(\text{obsd})}$ and k_r are listed in Table 2, where the variation of ionic product of water, $k_w = [\text{H}^+][\text{OH}^-]$ with change in temperature[29] was taken into consideration. The average value of k_r is $(4.6\pm0.1)\times10^3$ mol^{-1} dm^3 s^{-1} at 35.3 °C (Table 3). No detectable change in the absorption spectrum was observed during the measurements. The rate was independent of ionic strength in the range of 0.1 to 1.0 (NaClO$_4$). Eyring treatments of $\log(k_r/T)$ *vs.* T^{-1} yielded an activation enthalpy of 46±1 kJ mol^{-1} and an activation entropy of −26±4 J mol^{-1} K^{-1}. The sulfur atom in the complex is also chiral, but racemizes more rapidly than does the carbon atom as stated previously. Thus the racemization observed should be for the carbon atom.

The absorption and CD spectra of $(+)_{589}$-[Co{S(O)$_2$CH(CH$_3$)COO}(tren)]$^{+}$ in 0.01 mol dm^{-3} HClO$_4$ are given in Fig. 5. The complex was also prepared from $(+)_{589}$-[Co{SCH(CH$_3$)COO}(tren)]$^{+}$, and the racemization was studied by the same procedure as the above. The decrease in CD strength also obeyed second-order kinetics; first-order in each of the concentrations of complex and OH$^-$ ions. The results are given in Table 2. The second-order rate constant (k_r) is (7.8±

Table 2. Rate constants for the racemization of $(-)_{589}$-[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$ and $(+)_{589}$-[Co{S(O)$_2$CH(CH$_3$)COO}-(tren)]$^{+}$(I=0.2)

pH	t/°C	$k_{r(\text{obsd})}$/s^{-1}	k_r/mol^{-1} dm^3 s^{-1}
	$(-)_{589}$-[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$		
5.96	24.9	$(2.20\pm0.03)\times10^{-5}$	$(2.41\pm0.05)\times10^{3}$
5.96	35.3	$(9.05\pm0.05)\times10^{-5}$	$(4.74\pm0.12)\times10^{3}$
6.29	35.3	$(1.86\pm0.02)\times10^{-4}$	$(4.57\pm0.10)\times10^{3}$
6.57	20.0	$(4.26\pm0.02)\times10^{-5}$	$(1.68\pm0.04)\times10^{3}$
6.57	25.0	$(9.00\pm0.03)\times10^{-5}$	$(2.42\pm0.05)\times10^{3}$
6.57	30.3	$(1.83\pm0.02)\times10^{-4}$	$(3.35\pm0.08)\times10^{3}$
6.57	35.3	$(3.52\pm0.02)\times10^{-4}$	$(4.53\pm0.11)\times10^{3}$
6.57	40.3	$(6.88\pm0.03)\times10^{-4}$	$(6.37\pm0.13)\times10^{3}$
6.57	45.3	$(1.21\pm0.03)\times10^{-3}$	$(8.12\pm0.17)\times10^{3}$
6.86	35.3	$(6.70\pm0.06)\times10^{-4}$	$(4.44\pm0.12)\times10^{3}$
6.32[a)]	30.3	$(8.83\pm0.05)\times10^{-5}$	$(2.88\pm0.06)\times10^{3}$
6.66[b)]	30.3	$(2.62\pm0.04)\times10^{-5}$	$(3.90\pm0.09)\times10^{3}$
	$(+)_{589}$-[Co{S(O)$_2$CH(CH$_3$)COO}(tren)]$^{+}$		
6.21	19.9	$(3.71\pm0.03)\times10^{-5}$	$(3.37\pm0.06)\times10^{3}$
6.21	25.1	$(8.62\pm0.10)\times10^{-5}$	$(5.32\pm0.16)\times10^{3}$
6.21	30.1	$(1.46\pm0.02)\times10^{-4}$	$(6.13\pm0.14)\times10^{3}$
6.21	35.2	$(2.65\pm0.02)\times10^{-4}$	$(7.82\pm0.18)\times10^{3}$
6.21	39.7	$(4.74\pm0.02)\times10^{-4}$	$(1.00\pm0.03)\times10^{4}$
6.21	40.2	$(5.09\pm0.03)\times10^{-4}$	$(1.08\pm0.03)\times10^{4}$
6.21	42.5	$(6.53\pm0.03)\times10^{-4}$	$(1.13\pm0.03)\times10^{4}$
6.21	45.5	$(8.92\pm0.03)\times10^{-4}$	$(1.37\pm0.03)\times10^{4}$
6.21	49.5	$(1.39\pm0.01)\times10^{-3}$	$(1.57\pm0.03)\times10^{4}$
6.67	25.2	$(2.46\pm0.02)\times10^{-4}$	$(5.26\pm0.08)\times10^{3}$
6.80	25.1	$(3.70\pm0.03)\times10^{-4}$	$(5.86\pm0.10)\times10^{3}$

a) Ionic strength 1.0. b) Ionic strength 0.1.

Table 3. Rate constants for racemization and deuteration

Complex	k/mol^{-1} dm^3 s^{-1} (t/°C)
Racemization	
[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$	$(4.6\pm0.1)\times10^{3}$ (35.3)
[Co{S(O)$_2$CH(CH$_3$)COO}(tren)]$^{+}$	$(7.8\pm0.2)\times10^{3}$ (35.2)
Deuteration	
[Co{CH$_3$SCH(CH$_3$)COO}(tren)]$^{2+}$	$(1.5\pm0.3)\times10^{4}$ (34.5)
[Co{S(O)$_2$CH(CH$_3$)COO}(tren)]$^{+}$	$(4.5\pm0.9)\times10^{4}$ (34.5)
[Co{S(O)$_2$CH$_2$COO}(tren)]$^{+}$	$(3.0\pm0.6)\times10^{5}$ (34.5)
[Co{S(O)$_2$CH$_2$COO}(en)$_2$]$^{+}$	$(4.3\pm0.9)\times10^{5}$ (34.5)

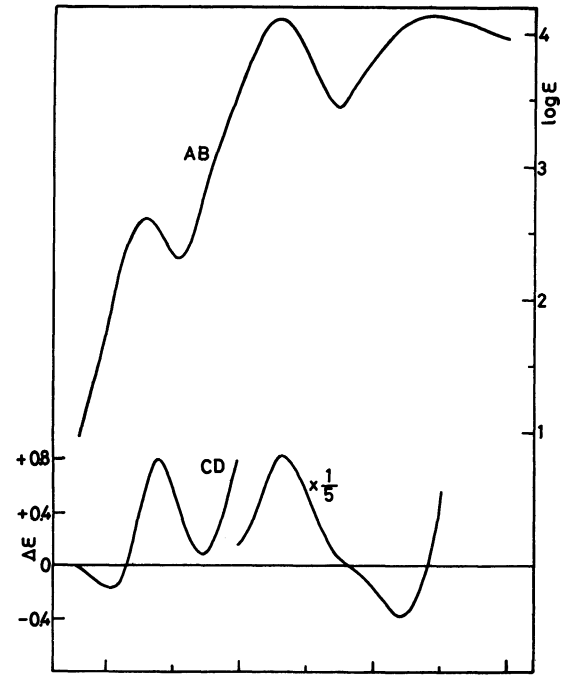


Fig. 5. Absorption and CD spectra of $(+)_{589}$-$[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$ in 10^{-2} mol dm^{-3} $HClO_4$.

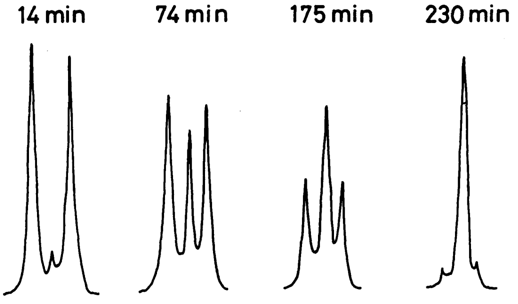


Fig. 6. Signal change of the C–CH_3 of $[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$ in D_2O (pD 5.75, 34.5 °C).

0.2) × 10^3 mol^{-1} dm^3 s^{-1} at 35.2 °C, and the values of activation enthalpy and entropy are 40±1 kJ mol^{-1} and −40±4 J mol^{-1} K^{-1}, respectively.

Deuteration rates of the methine protons of *S,O* chelates in $[Co\{CH_3SCH(CH_3)COO\}(tren)]Cl_2$ and $[Co\{S(O)_2CH(CH_3)COO\}(tren)]Cl$ were obtained by monitoring signal changes in the ^{1}H NMR spectra. The C–CH_3 doublet signals become a singlet by the proton-deuteron exchange (Fig. 6). For both complexes, the plot of log(peak area of the doublet) *vs.* time was linear, from which the pseudo-first-order rate constant for the deuteration $k_{D(obsd)}$ was obtained. The rates for the $CH_3SCH(CH_3)COO^-$ and $^-S(O)_2CH(CH_3)COO^-$ complexes were (7.3±0.5) × 10^{-5} s^{-1} (pD 5.75, 34.5 °C) and (6.4±0.4) × 10^{-5} s^{-1} (pD 6.16, 34.5 °C), respectively. The deuteration was completed in 1 h at pD 7.5 and 34.5 °C for both complexes. The rates are 10^5—10^6-fold greater than that for the methine proton in $[Co(alaninate)(en)_2]^{2+}$ (8.5 × 10^{-11} s^{-1} at pD 5.75 and 34.3 °C, and 2.2 × 10^{-10} s^{-1} at pD 6.16 and 34.3 °C).[30]

Table 4. ^{1}H NMR spectral data for S–CH and S–CH_2 protons in $[CoN_4OS]^{n+}$-type complexes in D_2O, δ[a]

Complex	S–CH	S–CH_2
$[Co\{SCH(CH_3)COO\}(tren)]^+$	3.5(q)[b]	
$[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$	4.07(q)	
$[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$	4.38(q)	
$[Co(SCH_2COO)(en)_2]^+$		3.21(s)
$[Co(CH_3SCH_2COO)(en)_2]^{2+}$		3.85(q_{AB})
$[Co\{S(O)_2CH_2COO\}(en)_2]^+$		4.45(q_{AB})

a) The complexes of which methine or methylene protons are susceptible to deuterium exchange were measured in DCl–D_2O. b) The signal overlapped with those of tren-CH_2, and the chemical shift was determined by the spin decoupling technique. s: singlet, q: quartet, q_{AB}: AB quartet.

As shown previously, the racemization rates of $CH_3SCH(CH_3)COO^-$ and $^-S(O)_2CH(CH_3)COO^-$ chelates in the tren complex are proportional to the concentration of OH^-. The results support that the reactions proceed with a mechanism analogous to that for racemization of α-amino acidato chelates,[2] where the rate-determining step is release of the methine proton by the nucleophilic attack of OH^-. If the proton exchange and the racemization take place simultaneously and there is no isotopic effect between H and D, the ratio of k_D to k_r (k_D/k_r) should be 2. The observed ratios are 3.2 and 5.7 for $[Co\{CH_3SCH(CH_3)COO\}(tren)]^+$ and $[Co\{S(O)_2CH(CH_3)COO\}(tren)]^+$, respectively, at 35 °C, the k_D values being obtained by the formula $k_D = k_{D(obsd)}[D^+]/2.89 \times 10^{-15}$.[15] Although the reliability of these values is uncertain because of difficulty in determining accurate $[D^+]$ values,[14] we assume that both reactions of the proton exchange and the racemization in these tren complexes proceed simultaneously, forming carbanions as intermediate.

Table 4 shows that the NMR signals of the methine or methylene protons adjacent to sulfur shift remarkably to a lower magnetic field in the order of the $^-SCHRCOO^-$, $CH_3SCHRCOO^-$, and $^-S(O)_2CHRCOO^-$ (R=H and CH_3) complexes. Such large lower shifts may be brought about by the increasing electron-withdrawing effect of ^-S–, $S(CH_3)$–, and $^-S(O)_2$– groups. When the electron-withdrawing effect is small, the methine or methylene group will require larger energy in forming a carbanion and will have less reactivity to proton exchange or racemization. In fact, $[Co\{SCH(CH_3)COO\}(tren)]^+$ which has two lone pairs of electrons on the sulfur atom and gives the methine proton signal at 3.5 ppm does not racemize over 6 days at pH 9.22 and 25 °C. The methylene protons of $^-SCH_2COO^-$ in $[Co(SCH_2COO)(tren)]^+$ do not either undergo deuterium exchange over at least a day at pD 10.4 and 30 °C, although Adzamli *et al.*[7] reported that the deuteration occured in basic D_2O solution. The complex decomposes at higher pH. The sulfinato complex is expected to be more labile than the methylthio complex in deuteration or racemization reactions, since the sulfinato group is more electronegative than the methylthio group. However, the rates of $[Co\{S(O)_2CH(CH_3)$-

COO}(tren)]$^+$ in these reactions are similar to those of [Co{$CH_3SCH(CH_3)COO$}(tren)]$^{2+}$. The result may be accounted for by a difference in net charge of the complex ions. It has been reported that reactivity of glycine chelates in cobalt(III) complexes toward base-catalyzed condensation with acetaldehyde decreases with a decreasing positive net charge of the complex ion.[2,31,32]

The [Co{$S(O)_2CH_2COO$}(en)$_2$]$^+$ complex easily reacts with formaldehyde under basic conditions to afford [Co{$S(O)_2C(CH_2OH)_2COO$}(en)$_2$]$^+$ (Experimental). A similar condensation reaction has been reported to occur between [Co(glycinate)(en)$_2$]$^{2+}$ and formaldehyde in aqueous solution saturated with Li_2CO_3.[33]

The free $CH_3SCHRCOO^-$ (R=H, CH_3) ligand is stable to proton exchange. For example, $CH_3SCH(CH_3)COO^-$ does not undergo deuterium exchange for 4 d at pD *ca.* 9 and 30 °C. Thus the cobalt(III) ion activates the methine or methylene protons of these *S,O* chelate ligands. The activity of the protons seems to be much higher than that of the corresponding protons of amino acidato chelates as indicated by the proton exchange or racemization reactions.

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