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Preparation and Some Properties of Tetraamine Cobalt(III) Complexes with Monodentate Thiolate or Sulfinate Ligands

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Tetraamine cobalt(III) complexes with monodentate thiolate ligands, $[Co(RS)_2(amine)_4]^+$, were newly prepared, where R is CH_3 or C_2H_5 and $(amine)_4$ is bis(ethylenediamine) ($(en)_2$), triethylenetetramine (trien), or tris(2-aminoethylamine) (tren). The $(en)_2$ and trien thiolato complexes selectively formed the *cis* and *cis*-α isomers, respectively. The oxidation reactions of $[Co(RS)_2\{(en)_2 \text{ or } (trien)\}]^+$ with use of excess H_2O_2 gave the corresponding S-bonded sulfinato complexes $[Co(RSO_2\text{-}S)_2\{(en)_2 \text{ or } (trien)\}]^+$ with retention of the initial geometries, while $[Co(CH_3SO_2\text{-}S)_2(tren)]^+$ was not formed by the same oxidation reaction of $[Co(CH_3S)_2(tren)]^+$. The *cis*-$(en)_2$ and *cis*-α-trien complexes were optically resolved by the fractional crystallization or column chromatography. The obtained isomers were characterized on the basis of the absorption, CD, and ^{13}C NMR spectra. The thiolato complexes exhibited absorption spectral changes with time in aqueous solutions, which are ascribed to the replacement of the thiolate ligands by H_2O.

Cobalt(III) complexes with polydentate thiolate ligands have been extensively investigated because of spectrochemical and stereochemical interest.[1—18] It has been shown that these complexes with two or three thiolato sulfur donor atoms tend to prefer the *cis(S)* geometry;[8—12,14—16] only a few *trans(S)*-type complexes have been presented.[13,14] In order to clarify the geometrical preference it is desirable to synthetically investigate cobalt(III) complexes with monodentate thiolate ligands. The present work is concerned with the first preparation of $[Co(RS)_2(amine)_4]^+$-type complexes, together with that of $[Co(RSO_2\text{-}S)_2(amine)_4]^+$-type complexes, where R is CH_3 or C_2H_5 and $(amine)_4$ is bis(ethylenediamine) ($(en)_2$), triethylenetetramine (trien), or tris(2-aminoethylamine) (tren). These complexes were characterized from the absorption, CD, and ^{13}C NMR spectra in comparison with those of $[Co\{S(CH_2)_nS\}(trien)]^+$ ($n=2$ or 3).[17,18] The selective formation of the *cis(S)*-type isomers is described.

Experimental

Preparation of Complexes. ***cis*-α-$[Co(CH_3S)_2(trien)]ClO_4$ (1).** To an ice-cold solution containing 3.1 g (0.01 mol) of *cis*-α-$[CoCl_2(trien)]Cl$[19] in 60 cm^3 of water was added an ice-cold solution containing 1.4 g (0.02 mol) of $NaSCH_3$ in 40 cm^3 of water. The mixture was stirred for 30 min in an ice bath (ca. 0°C). After removing insoluble materials by filtration, to the dark-brown filtrate was added an equal volume of a saturated $NaClO_4$ solution. The solution was stored in a refrigerator overnight and the resulting greenish-brown precipitate was collected by filtration. This complex was recrystallized from water in an ice bath. Yield: 65%. Found: C, 23.36; H, 6.16; N, 13.61%. Calcd for $C_8H_{24}N_4O_4S_2ClCo\cdot 0.5H_2O$: C, 23.56; H, 6.18; N, 13.74%.

This complex was also prepared using *trans*-$[CoCl_2(trien)]Cl$[19] as the starting complex instead of *cis*-α-$[CoCl_2(trien)]Cl$. When *cis*-β-$[CoCl_2(trien)]Cl$[19] was used as the starting complex, the desired complex $[Co(CH_3S)_2(trien)]^+$ could not be obtained.

***cis*-$[Co(CH_3S)_2(en)_2]ClO_4$ (2) and $[Co(CH_3S)_2(tren)]ClO_4$ (3).** These complexes were prepared by the same procedure as that used for **1**, using *cis*-$[CoCl_2(en)_2]Cl$[21] (2.85 g, 0.01 mol) or $[CoCl_2(tren)]Cl\cdot H_2O$[20] (3.3 g, 0.01 mol) instead of *cis*-α-$[CoCl_2(trien)]Cl$.

$(en)_2$ complex: Yield: 35%. Found: C, 19.19; H, 5.92; N, 14.96%. Calcd for $C_6H_{22}N_4O_4S_2ClCo$: C, 19.33; H, 5.94; N, 15.03%.

tren complex: Yield: 30%. Found: C, 23.66; H, 5.81; N, 13.81%. Calcd for $C_8H_{24}N_4O_4S_2ClCo$: C, 24.09; H, 6.06; N, 14.04%.

2 was also prepared using *trans*-$[CoCl_2(en)_2]Cl$[20] as the starting complex.

***cis*-α-$[Co(C_2H_5S)_2(trien)](ClO_4)$ (4).** This complex was prepared by the same procedure as that used for **1**, using an ice-cold solution containing C_2H_5SH (1.24 g, 0.02 mol) in a mixture of 1 mol dm^{-3} NaOH aqueous solution (20 cm^3) and methanol (20 cm^3). Yield: 26%. Found: C, 27.82; H, 6.57; N, 13.00%. Calcd for $C_{10}H_{28}N_4O_4S_2ClCo$: C, 28.14; H, 6.61; N, 13.13%.

***cis*-α-$[Co(CH_3SO_2\text{-}S)_2(trien)]ClO_4$ (5).** To a brown solution containing 0.5 g of **1** in 40 cm^3 of water was added 8 cm^3 of 5% H_2O_2 and 1 cm^3 of 30% $HClO_4$. The mixture was stirred for 1 h in an ice bath, followed by storing in a refrigerator overnight. The resulting orange-yellow solution was concentrated to a small volume with a rotary evaporator below 25 °C. To this was added 2 cm^3 of an ethanol–ether (2 : 1) mixture, which gave a yellow precipitate. This complex was recrystallized from water by adding an appropriate amount of ethanol in an ice bath. Yield: 82%. Found: C, 20.15; H, 5.33; N, 11.42%. Calcd for $C_8H_{24}N_4O_8S_2ClCo\cdot H_2O$: C, 19.98; H, 5.45; N, 11.65%.

When the orange-yellow reaction solution was chromatographed on a Dowex 50W-X8 column (200—400 mesh, Na^+ form), only one yellow band containing **5** was eluted with a 0.05 mol dm^{-3} Na_2SO_4 aqueous solution.

***cis*-$[Co(CH_3SO_2\text{-}S)_2(en)_2]ClO_4$ (6) and *cis*-α-$[Co(C_2H_5SO_2\text{-}S)_2(trien)](ClO_4)$ (7).** These complexes were prepared by the same procedure as that used for **5**, using **2** or **4** instead of **1**.

CH_3SO_2 complex: Yield: 78%. Found: C, 16.50; H, 5.12; N, 12.84%. Calcd for $C_6H_{22}N_4O_8S_2ClCo$: C, 16.50; H, 5.08; N, 12.83%.

$C_2H_5SO_2$ complex: Yield: 76%. Found: C, 23.04; H, 6.08; N, 10.93%. Calcd for $C_{10}H_{28}N_4O_8S_2ClCo\cdot 1.5H_2O$: C, 23.19; H, 6.06; N, 10.82%.

Resolution of Complexes. A yellow solution containing 0.2 g of **5** in 20 cm^3 of water was poured onto a Dowex 50W-X8 column (200—400 mesh, Na$^+$ form, 2.5 cm×15 cm). The adsorbed band was separated into two bands by eluting with a 0.075 mol dm^{-3} $K_2[Sb_2(R,R\text{-tartrate})_2]\cdot 3H_2O$ aqueous solution. After complete separation into two bands, each adsorbed band was eluted with a 0.15 mol dm^{-3} $NaClO_4$ aqueous solution. It was found from the CD spectral measurements that the earlier moving band contained the $(+)^{\mathrm{CD}}_{480}$ isomer and the later one contained the $(-)^{\mathrm{CD}}_{480}$ isomer. Each eluate was concentrated to a small volume with a rotary evaporator below 25 °C, followed by storing in a refrigirator overnight. The resulting $(+)^{\mathrm{CD}}_{480}$-**5** and $(-)^{\mathrm{CD}}_{480}$-**5** were collected by filtration.

6 and **7** were also completely resolved by the same Dowex 50W-X8 column chromatography. The earlier moving band contained the $(+)^{\mathrm{CD}}_{480}$ isomer and the later one contained the $(-)^{\mathrm{CD}}_{480}$ isomer.

An excess amount (1.0 g) of $Na_2[Sb_2(R,R\text{-tartrate})_2]\cdot 5H_2O$ was added with stirring to a solution containing 0.2 g of **1** in 20 cm^3 of water. After the mixture was stirred at room temperature for a few minutes, 5 cm^3 of ethanol was added in an ice bath. The resulting brown precipitate, which showed a positive CD value at 500 nm, was collected by filtration. In the region of 260—650 nm, the aqueous solution of the precipitate and the filtrate showed CD spectra which were enantiomeric to each other. The H_2O_2 oxidation reaction of the $(-)^{\mathrm{CD}}_{500}$ filtrate gave an orange yellow solution, which showed an identical CD spectral pattern with $(-)^{\mathrm{CD}}_{480}$-**5**, though the CD intensity was much smaller.

2 was also partially resolved by the same procedure as that used for **1**. The precipitate and filtrate showed positive and negative CD values at 500 nm, respectively.

Measurements. The electronic absorption spectra were recorded on a JASCO UVIDEC-1 or UVIDEC-610 spectrophotometer and the CD spectra on a JASCO J-20 spectropolarimeter. All of the measurements were carried out in aqueous solutions at room temperature. The ^{13}C NMR spectra were recorded in D_2O on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference.

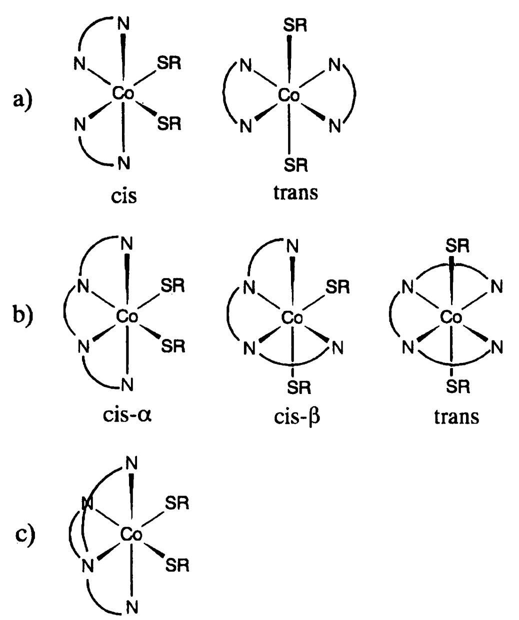

Fig. 1. Geometrical isomers for $[Co(RS)_2(en)_2]^+$ (a), $[Co(RS)_2(trien)]^+$ (b), and $[Co(RS)_2(tren)]^+$ (c).

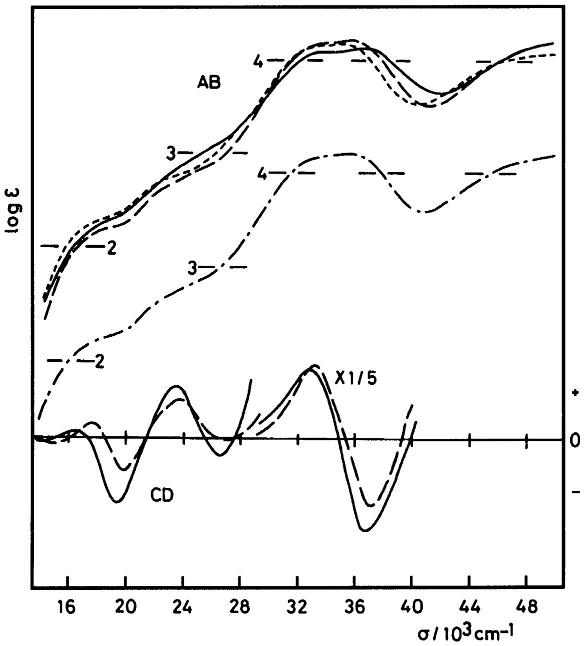

Fig. 2. Absorption and CD spectra of $(-)^{\mathrm{CD}}_{500}$-*cis*-$[Co(CH_3S)_2(en)_2]^+$ (——), $(-)^{\mathrm{CD}}_{500}$-*cis*-α-$[Co(CH_3S)_2(trien)]^+$ (— —), $[Co(CH_3S)_2(tren)]^+$ (- - -), and *cis*-α-$[Co(C_2H_5S)_2(trien)]^+$ (—·—). CD scale is arbitrary.

Results and Discussion

Characterization. Two geometries, *cis(S)* and *trans(S)*, are possible for $[Co(CH_3S)_2(en)_2]^+$ and $[Co(CH_3S \text{ or } C_2H_5S)_2(trien)]^+$, while only *cis(S)* geometry is possible for $[Co(CH_3S)_2(tren)]^+$ (Fig. 1). As shown in Fig. 2 and Table 1, the absorption spectra of $[Co(CH_3S)_2(en)_2]^+$, $[Co(CH_3S)_2(trien)]^+$, $[Co(C_2H_5S)_2(trien)]^+$, and $[Co(CH_3S)_2(tren)]^+$ are quite similar to one another over the entire region, showing vague d–d absorption shoulders in the visible region (ca. 16—26×10^3 cm^{-1}) and an intense SMCT absorption band with two components in the near-UV region (ca. 30—38×10^3 cm^{-1}). This absorption spectral behavior resembles that of $[Co\{S(CH_2)_nS\}(trien)]^+$ (n=2 or 3), which take the *cis(S)* geometry.[17,18] Accordingly, it is assigned that $[Co(CH_3S)_2(en)_2]^+$ and $[Co(CH_3S \text{ or } C_2H_5S)_2(trien)]^+$ obtained in this work take the *cis(S)* geometry. The absorption spectra of $[Co(CH_3SO_2)_2(en)_2]^+$, $[Co(CH_3SO_2)_2(trien)]^+$, and $[Co(C_2H_5SO_2)_2(trien)]^+$, which were derived from the corresponding thiolato complexes by H_2O_2 oxidation, ex-

Table 1. Absorption Spectral Data of Complexes[a)]

Complex	d–d region	SMCT region
cis-$[Co(CH_3S)_2(en)_2]^+$	19.0 (2.30 sh)	33.9 (4.09 sh)
	22.0 (2.66 sh)	36.50 (4.14)
	25.0 (2.98 sh)	
cis-α-$[Co(CH_3S)_2(trien)]^+$	18.5 (2.19 sh)	33.5 (4.17 sh)
	22.5 (2.62 sh)	35.65 (4.21)
	25.0 (2.82 sh)	
$[Co(CH_3S)_2(tren)]^+$	18.5 (2.30 sh)	33.3 (4.15 sh)
	23.0 (2.74 sh)	35.09 (4.17)
cis-α-$[Co(C_2H_5S)_2(trien)]^+$	18.2 (2.24 sh)	33.3 (4.17 sh)
	22.5 (2.66 sh)	35.59 (4.21)
	25.0 (2.86 sh)	
cis-$[Co(CH_3SO_2\text{-}S)_2(en)_2]^+$	22.68 (2.46)	31.9 (4.24 sh)
		33.78 (4.30)
cis-α-$[Co(CH_3SO_2\text{-}S)_2(trien)]^+$	22.62 (2.57)	31.3 (4.20 sh)
		33.11 (4.27)
cis-α-$[Co(C_2H_5SO_2\text{-}S)_2(trien)]^+$	22.32 (2.56)	30.8 (4.22 sh)
		32.68 (4.29)

a) Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} cm^3 cm^{-1}, respectively. The sh label denotes a shoulder.

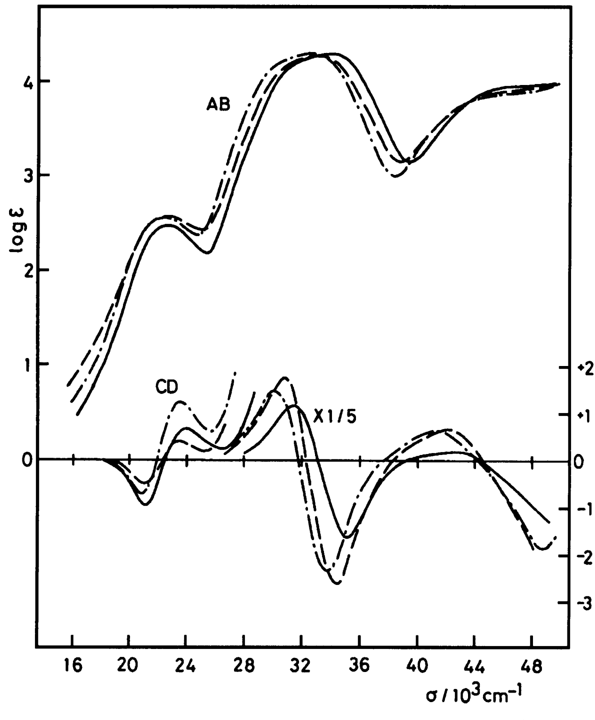

Fig. 3. Absorption and CD spectra of $(-)^{CD}_{480}$-*cis*-$[Co(CH_3SO_2\text{-}S)_2(en)_2]^+$ (——), $(-)^{CD}_{480}$-*cis*-α-$[Co(CH_3SO_2\text{-}S)_2(trien)]^+$ (– – –), and $(-)^{CD}_{480}$-*cis*-α-$[Co(C_2H_5SO_2\text{-}S)_2(trien)]^+$ (—-—).

hibit a well-defined first d–d absorption band at ca. 23×10^3 cm^{-1} and an intense SMCT absorption band with two components in the region 31—34×10^3 cm^{-1} (Fig. 3 and Table 1). This absorption spectral bahavior agrees well with that of the S,S-bonded disulfinato complexes, $[Co\{O_2S(CH_2)_nSO_2\text{-}S,S\}(trien)]^+$ (n=2 or 3),[17,18)] indicating that $[Co(CH_3SO_2)_2(en)_2]^+$ and $[Co(CH_3SO_2$ or $C_2H_5SO_2)_2(trien)]^+$ are S-bonded isomers having a *cis(S)* geometry. The *cis(S)* geometry for the present thiolato and sulfinato complexes is supported by the fact that these complexes were optically resolved.

Two geometrical isomers, *cis*-α (C_2 symmetry) and *cis*-β (C_1 symmetry), are expected for $[Co(CH_3S$ or $C_2H_5S)_2(trien)]^+$ and $[Co(CH_3SO_2\text{-}S$ or $C_2H_5SO_2\text{-}S)_2(trien)]^+$ having a *cis(S)* geometry (Fig. 1). As summarized in Table 2, the ^{13}C NMR spectrum of each complex exhibits two or three signals due to the six carbon atoms of the trien ligand. Moreover, one signal due to the two CH_3 groups and two signals due to the two C_2H_5 groups are observed for $[Co(CH_3S$ or $CH_3SO_2\text{-}S)(trien)]^+$ and $[Co(C_2H_5S$ or $C_2H_5SO_2\text{-}S)(trien)]^+$, respectively. These ^{13}C NMR spectral behavior imply that the trien complexes obtained in this work are *cis*-α isomers with C_2 symmetry.

Two optical isomers, Δ and Λ, are possible for the *cis*-(en)$_2$ and *cis*-α-trien complexes. As shown in Fig. 3 and Table 3, the CD spectra of $(-)^{CD}_{480}$-*cis*-$[Co(CH_3SO_2\text{-}S)_2(en)_2]^+$, $(-)^{CD}_{480}$-*cis*-α-$[Co(CH_3SO_2\text{-}S)_2(trien)]^+$, $(-)^{CD}_{480}$-*cis*-α-$[Co(C_2H_5SO_2\text{-}S)_2(trien)]^+$ are quite similar to one another, giving negative and positive CD bands from lower energy in the d–d absorption band region (ca. 18—26×10^3 cm^{-1}) and positive and negative CD bands in the SMCT band region (ca. 28—38×10^3 cm^{-1}). For the *cis(S)*-$[Co(sulfinato\text{-}S)_2(amine)_4]^+$-type complexes, the (−)(+) CD pattern from lower energy has commonly been observed for the Δ isomers in the d–d region.[14,17,18)] Thus, the $(-)^{CD}_{480}$ sulfinato isomers are assignable to have the Δ configuration. The CD spectral behavior of the partially resolved $(-)^{CD}_{500}$ isomers of *cis*-$[Co(CH_3S)_2(en)_2]^+$ and *cis*-α-$[Co(CH_3S)_2(trien)]^+$ is quite similar to that of Δ-$(-)^{CD}_{480}$-*cis*-$[Co(CH_3SO_2\text{-}S)_2(en)_2]^+$ and Δ-$(-)^{CD}_{480}$-*cis*-α-$[Co(CH_3SO_2\text{-}S)_2(trien)]^+$, showing a major (−)(+) CD pattern from lower energy in the d–d region

Table 2. ^{13}C NMR spectral Data (ppm from DSS) of trien Complexes

Complex	trien	RS
cis-α-[Co(CH$_3$S)$_2$(trien)]$^+$	45.16, 57.15, 57.42	10.67
cis-α-[Co(C$_2$H$_5$S)$_2$(trien)]$^+$	46.27, 57.05, 57.37	19.61, 23.02
cis-α-[Co(CH$_3$SO$_2$-*S*)$_2$(trien)]$^+$	46.92, 58.62	50.54
cis-α-[Co(C$_2$H$_5$SO$_2$-*S*)$_2$(trien)]$^+$	46.92, 58.51	6.61, 56.34

Table 3. CD Spectral Data of Complexes[a)]

Complex	d–d region	SMCT region
$(-)^{\mathrm{CD}}_{500}$-*cis*-[Co(CH$_3$S)$_2$(en)$_2$]$^+$	14.12 (−)	32.68 (+)
	16.31 (+)	36.63 (−)
	19.46 (−)	
	23.58 (+)	
	26.60 (−)	
$(-)^{\mathrm{CD}}_{500}$-*cis*-α-[Co(CH$_3$S)$_2$(trien)]$^+$	15.15 (−)	33.11 (+)
	17.51 (+)	37.04 (−)
	19.80 (−)	
	23.81 (+)	
	27.17 (−)	
$(-)^{\mathrm{CD}}_{480}$-*cis*-[Co(CH$_3$SO$_2$-*S*)$_2$(en)$_2$]$^+$	21.10 (−0.97)	31.45 (+5.74)
	23.87 (+0.67)	35.03 (−8.36)
$(-)^{\mathrm{CD}}_{480}$*cis*-α-[Co(CH$_3$SO$_2$-*S*)$_2$(trien)]$^+$	21.03 (−0.51)	30.86 (+8.68)
	23.47 (+0.39)	34.36 (−13.31)
$(-)^{\mathrm{CD}}_{480}$-*cis*-α-[Co(C$_2$H$_5$SO$_2$-*S*)$_2$(trien)]$^+$	20.79 (−0.73)	30.03 (+7.20)
	23.45 (+1.22)	33.78 (−11.81)

a) Wave numbers and Δε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.

(ca. 18—26×10^3 cm^{-1}) and a (+)(−) CD pattern in the SMCT region (ca. 30—38×10^3 cm^{-1}) (Fig. 2 and Table 3). Furthermore, the H$_2$O$_2$ oxidation reactions of these partially resolved $(-)^{\mathrm{CD}}_{500}$-CH$_3$S isomers produced the partially resolved Δ-$(-)^{\mathrm{CD}}_{480}$-CH$_3$SO$_2$ isomers. These facts suggest that the $(-)^{\mathrm{CD}}_{500}$ thiolato isomers have the Δ configuration.

Formation and Properties. Syntheses of [Co(RS)$_2$(amine)$_4$]$^+$ (R = CH$_3$ or C$_2$H$_5$ and (amine)$_4$ = (en)$_2$, trien, or tren) were achieved by the treatment of [CoCl$_2$(amine)$_4$]$^+$ with RS$^-$ at low temperature (ca. 0 °C). The yield of [Co(CH$_3$S)$_2$(trien)]$^+$ (65%) is reasonable and higher than that of [Co(CH$_3$S)$_2$(en)$_2$]$^+$ (35%), which is expected from the so-called chelate effect. However, [Co(CH$_3$S)$_2$(tren)]$^+$ was obtained in poor yield (30%), although the tren ligand occupies the four coordination sites as tightly as the trien ligand. Molecular model examinations reveal that there exist significant non-bonding interactions between one of the two CH$_3$ groups and the rigid methylene groups attached to the tertiary nitrogen atom of the tren ligand, which seems to be responsible for the poor yield. The yield of [Co(C$_2$H$_5$S)$_2$(trien)]$^+$ (26%) is much lower than that of [Co(CH$_3$S)$_2$(trien)]$^+$ and attempts to prepare the corresponding (CH$_3$)$_3$CS complex were unsuccessful. These indicate that the efficiency of the preparative reaction decreases with increasing bulk of the alkyl R group.

The *cis(S)*-type isomers were selectively formed, even when *trans*-[CoCl$_2$(en)$_2$]$^+$ or *trans*-[CoCl$_2$(trien)]$^+$ was used as the starting complex instead of *cis*-[CoCl$_2$(en)$_2$]$^+$ or *cis*-α-[CoCl$_2$(trien)]$^+$. This result obviously supports the *cis(S)* preference of the cobalt(III) complexes with two or three thiolato groups, which has been ascribed to the strong structural trans effect of the thiolato sulfur atoms.[11,12,14)] Of the two possible isomers, *cis*-α and *cis*-β, for [Co(CH$_3$S or C$_2$H$_5$S)$_2$(trien)]$^+$ having a *cis(S)* geometry, only the *cis*-α isomers were formed. Furthermore, none of desired bis(thiolato) complexes were obtained when *cis*-β-[CoCl$_2$(trien)]$^+$ was used as the starting complex. Model examinations have shown that non-bonding interactions between the two R groups on the sulfur atoms and the trien ligand are significant in the *cis*-β structure. The selective formation of the *cis*-α isomer has been observed for [Co{S(CH$_2$)$_3$S}(trien)]$^+$,[17)] while the *cis*-β isomer has been formed besides the *cis*-α one for [Co{S(CH$_2$)$_2$S}(trien)]$^+$.[18)]

The oxidation reactions of *cis*-[Co(CH$_3$S)$_2$(en)$_2$]$^+$ and *cis*-α-[Co(CH$_3$S or C$_2$H$_5$S)$_2$(trien)]$^+$ using an excess amount of H$_2$O$_2$ in the presence of acid produced the S-bonded sulfinato complexes, *cis*-[Co(CH$_3$SO$_2$-*S*)$_2$(en)$_2$]$^+$ and *cis*-α-[Co(CH$_3$SO$_2$-*S* or C$_2$H$_5$SO$_2$-*S*)$_2$(trien)]$^+$, in reasonable yields. This is consistent with the fact that similar H$_2$O$_2$ oxidation reactions of [Co{S(CH$_2$)$_n$S}(trien)]$^+$ (n=2 or 3) gave S,S-bonded disulfinato complexes [Co{O$_2$S(CH$_2$)$_n$SO$_2$-*S*,*S*}(trien)]$^+$ with a retention of the geometrical configuration.[17,18)] On the other hand, the formation

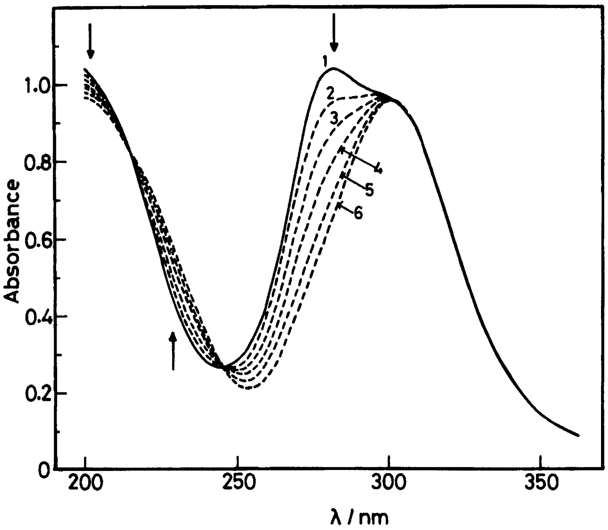

Fig. 4. Absorption spectral change with time for *cis*-α-$[Co(CH_3S)_2(trien)]^+$ in water at 22 °C. The curves 1—6 were measured at 0, 10, 30, 50, 70, and 90 min, respectively.

of $[Co(CH_3SO_2\text{-}S)_2(tren)]^+$ was not recognized for the same H_2O_2 oxidation reaction of $[Co(CH_3S)_2(tren)]^+$. That is, the absorption spectrum of the H_2O_2 reaction solution exhibited one sharp SMCT band at 310 nm, which has been observed characteristically for cobalt(III) complexes containing one sulfur donor atom.[1—7] Thus, it is considered that the present oxidation reaction of $[Co(CH_3S)_2(tren)]^+$ involves the cleavage of one of the two Co–S bonds. This is compatible with the molecular model examinations which indicate significant steric interactions between one of the two CH_3 groups on the sulfur atoms and the tren ligand.

The present sulfinato complexes are fairly stable in water at room temperature; no significant absorption spectral changes were recognized for at least several hours. On the other hand, the absorption spectra of the thiolato complexes drastically changed with time in water at room temperature. Figure 4 shows the absorption spectral change in water (pH=7) for the representative *cis*-α-$[Co(CH_3S)_2(trien)]^+$. The higher energy component of the SMCT band at 280 nm decreased in intensity with time for 90 min, during which time the lower energy component at ca. 300 nm remained almost unchanged. The absorption spectrum after 90 min corresponds well with that of $[Co(SCH_2COO\text{-}S,O)(tren)]^+$ which gives one sharp SMCT band at 289 nm.[4] It is, therefore, likely that one of the two CH_3S^- ligands is replaced by H_2O in aqueous solution. The well-defined isosbestic points are observed at 215 and 245 nm, and standard first-order kinetic plots of $\ln(A_t - A_\infty)$ vs. t (at 280 nm) are linear for more than three half-lives. From these plots the first-order rate constant (K_{obsd}) governing the replacement of one CH_3S^- ligand by H_2O was evaluated to be $2.01\times10^{-4}\ s^{-1}$. In acidic aqueous solution (pH=3 with HCl), this complex exhibited a sharp SMCT band at 302 nm, which gradually decreased in intensity with time ($K_{obsd}=1.27\times10^{-5}\ s^{-1}$). This implies that one CH_3S^- ligand in *cis*-α-$[Co(CH_3S)_2(trien)]^+$ is immediately replaced by H_2O in an acidic solution, followed by a relatively slow replacement of the remaining CH_3S^- ligand.

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