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Preparation and Characterization of Triethylenetetramine Cobalt(III) Complexes with 1,2-Ethanedithiolate or 1,2-Ethanedisulfinate

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Synopsis. Triethylenetetramine (trien) cobalt(III) complexes with 1,2-ethanedithiolate (edt) or 1,2-ethanedisulfinate (edsi) were prepared and characterized by absorption, CD, and ^{13}C NMR spectra. Each of the two complexes gave three possible geometrical isomers (cis-α, cis-β-*RR,SS*, and cis-β-*RS,SR*) which were separated and optically resolved by fractional crystallization and/or column chromatography.

In a previous paper[1] we reported the stereochemistry of triethylenetetramine (trien) cobalt(III) complexes with 1,3-propanedithiolate (pdt; $^-S(CH_2)_3S^-$) or 1,3-propanedisulfinate (pdsi; $^-O_2S(CH_2)_3SO_2^-$). Both complexes produced only the cis-α isomer, although three geometrical isomers (cis-α, cis-β-*RR,SS*, and cis-β-*RS,SR*)[2] are possible for the [Co(bidentate-*S,S*)(trien)]$^+$-type complexes. This note discusses the preparation and resolution of the trien cobalt(III) complexes with 1,2-ethanedithiolate (edt; $^-S(CH_2)_2S^-$) or 1,2-ethanedisulfinate (edsi; $^-O_2S(CH_2)_2SO_2^-$); three possible geometrical isomers were formed for each of the two complexes. These isomers were characterized on the basis of absorption, CD, and ^{13}C NMR spectra compared with those of the corresponding pdt and pdsi isomers.

Experimental

(1) Preparation and Resolution of Complexes. a) [Co(edt)(trien)]X (X=ClO$_4$ and I). To an ice-cold solution containing 3.1 g (0.01 mol) of *cis*-α- or *cis*-β-[CoCl$_2$(trien)]Cl[3] in 60 cm^3 of water was added an ice-cold solution containing 0.95 g (0.01 mol) of 1,3-propanedithiol in a mixture of a 1 mol dm^{-3} NaOH aqueous solution (20 cm^3) and methanol (20 cm^3). The mixture was stirred for 1 h in an ice bath. After removing the precipitate by filtration, to the filtrate was added 20 cm^3 of a saturated NaClO$_4$ solution; this mixture was kept in a refrigerator for 5 h. The precipitate which appeared was filtered off again. The filtrate was concentrated to one half its volume with a rotary evaporator below 25 °C and kept in a refrigerator overnight. The resulting black complex was collected by filtration and recrystallized from a small amount of water. It was found from absorption and ^{13}C NMR spectral measurements that this complex contained a mixture of *cis*-α-, *cis*-β-*RR,SS*-, and *cis*-β-*RS,SR*-[Co(edt)(trien)]$^+$. Attempts to separate the isomers using column chromatography were unsuccessful because of decomposition in the column. Yield: 64%. Found: C, 23.96; H, 5.63; N, 14.07%. Calcd for [Co(edt)(trien)]ClO$_4$=C$_8$H$_{22}$N$_4$O$_4$S$_2$ClCo: C, 24.22; H, 5.59; N, 14.12%.

The iodide salt was precipitated using 20 cm^3 of a saturated NaI solution instead of a saturated NaClO$_4$ solution. Black tetragonal crystals were obtained by recrystallization from a small amount of water. It was found from absorption and ^{13}C NMR spectral measurements that these crystals contained only the cis-α isomer. Yield: 20%. Found: C, 22.61; H, 5.27; N, 13.22%. Calcd for [Co(edt)(trien)] I=C$_8$H$_{22}$N$_4$S$_2$CoI: C, 22.64; H, 5.22; N, 13.20%

An excess amount (0.5 g) of Na$_2$[Sb$_2$(*d*-tart)$_2$]·5H$_2$O (*d*-tart=*d*-tartrate) was added with stirring to a solution containing 0.1 g of *cis*-α-[Co(edt)(trien)]I in 10 cm^3 of water. After the solution was stirred for 3 min at room temperature, 3 cm^3 of ethanol was added in an ice bath; the resulting black-brown precipitate of the $(-)^{\rm CD}_{580}$-cis-α isomer was collected by filtration. The H$_2$O$_2$ oxidation product of the $(-)^{\rm CD}_{580}$-cis-α showed identical absorption spectrum and CD patterns with $(-)^{\rm CD}_{460}$-*cis*-α-[Co(edsi)(trien)]$^+$ (A-2 isomer) described in b), though the CD intensity of the former complex was smaller than that of the latter. This indicates that *cis*-α-[Co(edt)(trien)]$^+$ was partially resolved; the CD intensity of the $(-)^{\rm CD}_{580}$-cis-α isomer is shown by an arbitrary scale in Fig. 1.

b) [Co(edsi)(trien)]ClO$_4$. An excess amount (8 cm^3) of a 5% H$_2$O$_2$ solution was added to a solution containing 0.5 g of [Co(edt)(trien)]ClO$_4$ in 20 cm^3 of water, followed by 1 cm^3 of a 30% HClO$_4$ solution. The mixture was stirred for 1 h in an ice bath and then kept in a refrigerator overnight. The resulting yellow powder (A-1) was collected by filtration. The filtrate was concentrated to one half its volume with a rotary evaporator below 24 °C and kept in a refrigerator overnight. After the yellow powder (A-1) was again removed by filtration, the filtrate was concentrated to one half its volume and kept in a refrigerator overnight. The deep-yellow needle crystals (A-2) which appeared were collected by filtration. Each of the A-1 and A-2 complexes was recrystallized from a small amount of water. It was found from the absorption and ^{13}C NMR spectral measurements that the A-1 complex contained a mixture of *cis*-β-*RR,SS*- and *cis*-β-*RS,SR*-[Co(edsi)(trien)]$^+$ and the A-2 one contained the cis-α isomer. A-1 complex: Yield: 28%. A-2 complex: Yield: 13%. Found for A-2: C, 20.15; H, 5.03; N, 11.65%. Calcd for [Co(edsi)(trien)]ClO$_4$·H$_2$O=C$_8$H$_{22}$N$_4$O$_8$S$_2$ClCo·H$_2$O: C, 20.07; H, 5.05; N, 11.70%.

An aqueous solution of the A-1 complex (cis-β-*RR,SS* and cis-β-*RS,SR*) was poured onto a Dowex 50W-X8 column (Na$^+$ form, 200—400 mesh, 3 cm×20 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.075 mol dm^{-3} K$_2$[Sb$_2$(*d*-tart)$_2$] solution. Two pairs of yellow bands, B-1 and B-2, were eluted in this order. It was found from the ^{13}C NMR spectral measurements that the earlier moving pair (B-1) contained *cis*-β-*RR,SS*-[Co(edsi)(trien)]$^+$ and the later moving one (B-2) contained the cis-β-*RS,SR* isomer. The formation ratio of the two isomers, B-1 (cis-β-*RR,SS*): B-2 (cis-β-*RS,SR*), was about 4:1. For each of the two pairs, the earlier moving and the later moving bands contained the $(-)^{\rm CD}_{470}$ and $(+)^{\rm CD}_{470}$ isomers respectively. The $(-)^{\rm CD}_{470}$ isomer of B-1 (cis-β-*RR,SS*) was isolated as the perchlorate salt. The B-2 (cis-β-*RS,SR*) isomer was not isolated because of its poor yield, and the concentration of this isomer was evaluated by the method of plasma emission spectral analysis. Found for $(-)^{\rm CD}_{470}$ B-1 isomer: C, 20.12; H, 5.06; N, 11.68%. Calcd for [Co(edsi)(trien)]ClO$_4$·H$_2$O: C, 20.07; H, 5.07; N, 11.70%.

When the A-2 (cis-α) complex was chromatographed on a Dowex 50W-X8 column (Na$^+$ form, 200—400 mesh, 3.0 cm×20 cm) eluting with a 0.075 mol dm^{-3} K$_2$[Sb$_2$(*d*-tart)$_2$] solution, two deep yellow bands of the $(-)^{\rm CD}_{460}$ and $(+)^{\rm CD}_{460}$ isomers were eluted in this order. Each eluate was converted into the perchlorate salt using a QAE-Sephadex A-25 column (ClO$_4^-$

form, 2.5 cm×20 cm). The concentration of each isomer was evaluated on the basis of the absorption spectral datum of the racemic perchlorate salt.

(2) 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 measurements were carried out in aqueous solution at room temperature. The concentration of *cis-β-RS,SR*-[Co(edsi)(trien)]$^+$ (B-2 isomer) was determined with a Jarrel-Ash Model-975 Plasma Atom Comp ICP spectrometer. The ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate was used as an internal reference.

Results and Discussion

Three geometrical isomers (cis-*α*, cis-*β-RR,SS*, and cis-*β-RS,SR*)[2] are possible for each of [Co(edt)(trien)]$^+$ and [Co(edsi)(trien)]$^+$. The absorption spectrum of [Co(edt)(trien)]$^+$ isolated as the perchlorate or iodide salt is similar to that of *cis-α*-[Co(pdt)(trien)]$^{+}$[1] in the whole region (Fig. 1). The edt complex exhibits the sulfur-to-metal charge transfer (SMCT) band at ca. 35×10^3 cm^{-1}, which is composed of two components. This absorption spectral behavior is characteristic for the cis(*S*)-type cobalt(III) complexes with two thiolato donor atoms.[4—7] For the three isomers of [Co(edsi)(trien)]$^+$, which were derived from the perchlorate salt of [Co(edt)(trien)]$^+$ by the H_2O_2 oxidation reaction, the absorption spectral behavior agrees well with that of *cis-α*-[Co(pdsi)(trien)]$^{+}$[1] in the whole region (Fig. 2). It has been established by X-ray structural analysis that the pdsi in *cis-α*-[Co(pdsi)(trien)]$^+$ coordinates through two sulfur atoms.[1] Accordingly, the present edsi complex can be assigned to the *S,S*-bonded isomer having the cis(*S*) geometry. The absorption spectrum of the edsi complex also shows an intense SMCT band consisting of two components at ca. 34×10^3 cm^{-1}.

The iodide salt of [Co(edt)(trien)]$^+$ exhibits four ^{13}C NMR signals at δ 36.84, 46.54, 57.86, and 58.83 due to the eight methylene carbon atoms in the complex, indicating the C_2 symmetry. Further, the H_2O_2 oxidation of the iodide salt gave *cis-α*-[Co(edsi)(trien)]$^+$ (A-2 complex, vide infra). A similar oxidation reaction of the thiolato cobalt(III) complexes has proceeded with retention of the geometrical configuration to form the sulfinato complexes.[1,8] These facts suggest that the iodide salt of [Co(edt) trien)]$^+$ is the cis-*α* isomer. The perchlorate salt of [Co(edt)(trien)]$^+$ shows twenty ^{13}C NMR signals in the region of δ 35—60, of which four signals are the same as those of the iodide salt. The H_2O_2 oxidation of the perchlorate salt produced *cis-α-*, *cis-β-RR,SS-*, and *cis-β-RS,SR*-[Co(edsi)(trien)]$^+$ (vide infra). Therefore, it is probable that the perchlorate salt of [Co(edt)(trien)]$^+$ is a mixture of the cis-*α*, cis-*β-RR,SS*, and cis-*β-RS,SR* isomers. In the ^{13}C NMR spectra of [Co(edsi)(trien)]$^+$ containing eight methylene carbon atoms, the A-1 and A-2 complexes exhibit fifteen and four (δ 45.61, 45.72, 58.78, and 59.65) signals respectively. The A-1 complex was separated into two isomers, B-1 and B-2, which show eight ^{13}C NMR signals (δ 43.83, 50.44, 51.68, 52.33, 56.12, 57.53, 58.40, and 60.68 for B-1, and δ 45.13, 47.84, 53.09, 53.20, 57.26, 59.43, 59.70, and 60.68 for B-2). These results indicate that the A-1 complex is a mixture of the cis-*β-RR,SS* and cis-*β-RS,SR* isomers (C_1 symmetry), while the A-2 complex is the cis-*α* isomer (C_2 symmetry). The ^{13}C NMR signals of the B-1 isomer appear at higher magnetic fields than those of the B-2 isomer. For [Co(NH$_3$)$_2$(trien)]$^{3+}$[9] and [Co(CN)$_2$(trien)]$^+$,[10] the cis-*β-RR,SS* isomer commonly shows ^{13}C NMR signals at higher magnetic fields than those of the cis-*β-RS,SR* isomer. Therefore, it is tentatively assigned that the B-1 and B-2 isomers take

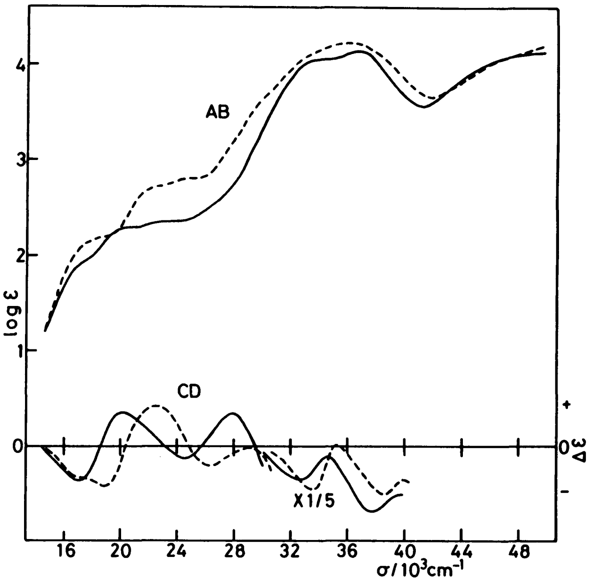

Fig. 1. Absorption and CD spectra of Δ-(−)$^{\mathrm{CD}}_{580}$-*cis-α*-[Co(edt)(trien)]$^+$ (——) and Δ-*cis-α*-[Co(pdt)(trien)]$^+$ (-----). CD scale is arbitrary.

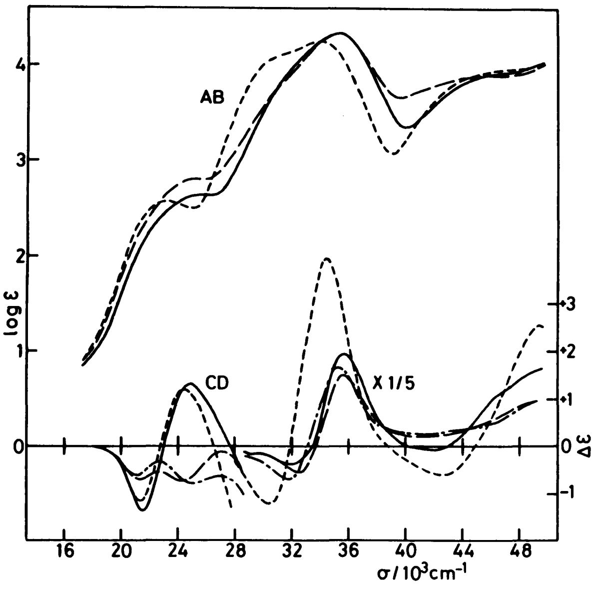

Fig. 2. Absorption and CD spectra of Δ-(−)$^{\mathrm{CD}}_{460}$-*cis-α*-(——), Δ-(−)$^{\mathrm{CD}}_{470}$-*cis-β-RR-* (– – –), Δ-(−)$^{\mathrm{CD}}_{470}$-*cis-β-RS*-[Co(edsi)(trien)]$^+$ (-----), and Δ-*cis-α*-[Co(pdsi)(trien)]$^+$ (-----).

the cis-*β*-*RR,SS* and cis-*β*-*RS,SR* configurations respectively. The assignment for the two cis-*β* isomers is supported from a 4:1 formation ratio of the *RR,SS* (B-1) isomer to the *RS,SR* (B-2) isomer, which is an usual trend observed for $[\mathrm{CoX_2(trien)}]^{n+}$ ($\mathrm{X_2{=}NH_2CH_2CO_2^-}$,[11] $2\mathrm{NH_3}$,[9] $2\mathrm{CN^-}$,[10] and $2\mathrm{NCS^-}$ [12]).

As shown in Fig. 2, the CD spectrum of $(-)^{\mathrm{CD}}_{460}$-*cis*-*α*-$[\mathrm{Co(edsi)(trien)}]^+$ is similar to that of *Δ*-*cis*-*α*-$[\mathrm{Co(pdsi)(trien)}]^+$ over the whole region, whose absolute configuration has been determined by X-ray structural analysis.[1] Therefore, the $(-)^{\mathrm{CD}}_{460}$-cis-*α* edsi isomer is assignable to the *Δ* configuration. The CD spectra of $(-)^{\mathrm{CD}}_{470}$-*cis*-*β*-*RR,SS*- and $(-)^{\mathrm{CD}}_{470}$-*cis*-*β*-*RS,SR*-$[\mathrm{Co(edsi)(trien)}]^+$ quite resemble each other, showing the two negative CD bands in the first absorption band region (18—$28\times10^3\ \mathrm{cm^{-1}}$) and a negative and a positive band from lower energy in the SMCT band region (28—$38\times10^3\ \mathrm{cm^{-1}}$) (Fig. 2). This CD spectral pattern is the same as that of *Δ*-$(-)^{\mathrm{CD}}_{460}$-*cis*-*α*-$[\mathrm{Co(edsi)(trien)}]^+$, except for some deviation at the higher-energy side in the first absorption band region, suggesting that the two $(-)^{\mathrm{CD}}_{470}$-cis-*β* edsi isomers also take the *Δ* configuration (*Δ*-cis-*β*-*RR* and *Δ*-cis-*β*-*RS*). The CD spectrum of $(-)^{\mathrm{CD}}_{580}$-*cis*-*α*-$[\mathrm{Co(edt)(trien)}]^+$ is similar to that of *Δ*-*cis*-*α*-$[\mathrm{Co(pdt)(trien)}]^+$ [1] in the SMCT band regions (30—$40\times10^3\ \mathrm{cm^{-1}}$), although the intensities are shown by an arbitrary scale (Fig. 1). Furthermore, the oxidation product of $(-)^{\mathrm{CD}}_{580}$-*cis*-*α*-$[\mathrm{Co(edt)(trien)}]^+$ showed an identical CD pattern with that of *Δ*-*cis*-*α*-$[\mathrm{Co(edsi)(trien)}]^+$. Accordingly, it is reasonable to assign that the $(-)^{\mathrm{CD}}_{580}$-cis-*α* edt isomer takes the *Δ* configuration.

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