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Molecular Structure of $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-(2-Aminoethanesulfenato)bis(1,3-propanediamine)cobalt(III) Perchlorate

Ken-ichi Okamoto,* Takumi Konno, Hisahiko Einaga,1) and Jinsai Hidaka
Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305

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Synopsis. The molecular structure of the title complex, $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$](ClO$_4$)$_2$, has been determined by the X-ray analysis. This isomer having the Λ configuration takes S configuration for the sulfur donor atom and one of the two 1,3-propanediamine chelate rings takes a chair form and the other an asymmetric skew-boat one.

In the previous papers,2,3) we reported the preparation and the spectro- and stereochemical properties of the [Co(aese)(diamine)$_2$]$^{2+}$-type complexes, where the aese denotes 2-aminoethanesulfenate and the diamine is 1,2-ethanediamine (en) and 1,3-propanediamine (tn). In Λ-[Co(aese)(en)$_2$]$^{2+}$ generated by the oxidation reaction of Λ-[Co(2-aminoethanethiolato)(en)$_2$]$^{2+}$ with hydrogen peroxide, the formation ratio of the two isomers, Λ-(*R*) and Λ-(*S*),4) is about 3:1.2) While, the formation ratio of the two isomers for Λ-[Co(aese)(tn)$_2$]$^{2+}$ obtained from a similar oxidation reaction is Λ-(*R*):Λ-(*S*)≈5:6.3) In order to elucidate the difference in these formatiom ratios between the en and tn complexes, we determined in this work the molecular structure of $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$](ClO$_4$)$_2$ by the X-ray diffraction method. The structure of the present tn complex is discussed in comparison with that of the corresponding [Co(aese)(en)$_2$]$^{2+}$ complex.5)

Experimental

X-Ray Data Collection. $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$](ClO$_4$)$_2$ was prepared by the method of the literature.3) The resultant precipitate of the $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$ isomer was collected by filtration. When the filtrate was kept in a refrigerator for 2 h, fairly large needle crystals, which showed the identical absorption and CD spectra with the $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$ isomer, were obtained. The unit cell parameters and intensity data for the single crystal (ca. 0.18×0.24×1.00 mm^3) were measured on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo *Kα* radiation. The systematic absence led to either the space groups $P6_1$ or $P6_5$, which could not be determined by using the anomalous scattering factors for the Mo *Kα* radiation. Taking the absolute configuration based on the CD spectral behavior into consideration,3) the space group is tentatively determined to be $P6_5$. The crystal data are as follows; $C_8H_{26}N_5O_9SCl_2Co$, a=9.367(1), c=37.878 (15) Å, V=2878.5(13) Å^3, hexagonal, $P6_5$, D_m=1.73 g cm^{-3}, D_x=1.724 g cm^{-3}, Z=6, and μ(Mo *Kα*)=13.6 cm^{-1}.

The intensity data were collected by a ω—2θ scan technique up to 2θ=60° with a scan rate of 3° min^{-1}. During the cource of the data collection, three reflections were monitored every 40 reflections. The intensity data were converted to F_o data in the usual manner. Absorption corrections were not applied. A total of 1020 indepedent reflections with $F_o>3\sigma(|F_o|)$ were considered as 'observed' and used for the structure analysis.

Table 1. Positional and Thermal Parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2 a)
Co	0.3504(4)	0.1852(3)	0.1500	2.36
S	0.1968(8)	0.1124(8)	0.1978(2)	3.77
N1	0.139(3)	0.068(3)	0.1213(6)	4.99
N2	0.342(3)	0.396(3)	0.1461(8)	5.25
N3	0.554(3)	0.299(2)	0.1777(7)	4.12
N4	0.367(3)	−0.018(2)	0.1537(6)	4.22
N5	0.482(3)	0.259(3)	0.1031(8)	5.32
C1	0.010(4)	−0.045(3)	0.1769(10)	5.54
C2	−0.006(3)	0.026(4)	0.1438(8)	5.34
C3	0.383(5)	0.506(4)	0.1738(10)	6.88
C4	0.573(4)	0.570(4)	0.1824(12)	7.64
C5	0.579(4)	0.425(4)	0.2036(12)	6.69
C6	0.480(4)	−0.042(4)	0.1314(8)	6.26
C7	0.489(7)	−0.001(5)	0.0950(12)	9.78
C8	0.564(6)	0.171(5)	0.0875(18)	15.34
O3	0.252(2)	0.025(3)	0.2243(6)	5.31
CL1	0.0040(9)	0.5450(9)	0.1351(2)	4.93
CL2	0.6550(9)	0.6907(8)	0.0671(3)	5.29
O11	0.057(6)	0.584(6)	0.1689(14)	17.15b)
O12	0.089(4)	0.689(4)	0.1141(9)	8.92b)
O13	−0.160(4)	0.504(5)	0.1351(12)	13.94b)
O14	0.017(4)	0.414(4)	0.1218(9)	9.64b)
O21	0.542(4)	0.646(4)	0.0947(9)	10.65b)
O22	0.839(6)	0.793(5)	0.0752(14)	15.87b)
O23	0.612(4)	0.779(4)	0.0373(11)	12.17b)
O24	0.635(4)	0.543(4)	0.0500(10)	10.49b)

a) B_{eq} is the equivalent isotropic temperature factors defined by Hamilton.15) b) Isotropic temperature factor.

Determination of Crystal Structure. The position of the cobalt atom was obtained from a three-dimensional Patterson function. Difference Fourier maps, based on the cobalt position, revealed all the non-hydrogen atoms. The structure was refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE by L. W. Finger was used6)). The neutral atomic scattering factors for the non-hydrogen atoms were taken from the literature.7) The final R and R_w values are 0.089 and 0.079, respectively. The final positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table 1. Tables of structure factors, anisotropic temperature factors, and bond lengths and angles are kept at the Chemical Society of Japan (Document No. 8714).

Results and Discussion

The perspective drawing of $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$ is shown in Fig. 1. The coordination geometry

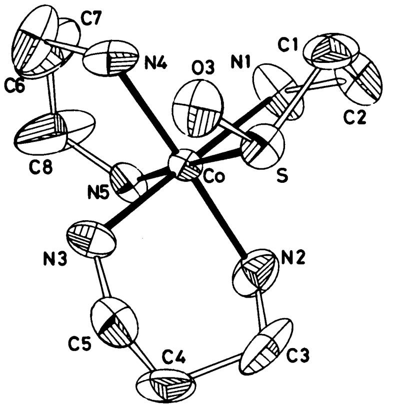

Fig. 1. A perspective drawing of $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$ with the numbering scheme of the atoms.

around the cobalt atom is approximately octahedral. The 2-aminoethanesulfenate coordinates to the cobalt atom with the nitrogen and sulfur atoms. The asymmetric sulfur donor atom in $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$ takes the (*S*) configuration for the Λ configuration which was suggested from the CD spectral behavior.[3] The five-membered chelate ring of the coordinated aese ligand, S-C1-C2-N1, takes the reasonable gauche form with a δ conformation (Fig. 1).[8] The six-membered 1,3-propanediamine chelate ring N2-C3-C4-C5-N3, takes the chair conformation, as in the case of the tn ligand in [Co(tn)$_3$]$^{3+}$,[9] [Co(X)$_2$(tn)$_2$]$^{n+}$ ((X)$_2$=(NCS)$_2$[10,11] and 2,4-pentanedionato (acac)[12]), and [Co(en)$_2$(tn)]$^{3+}$.[13] The other tn chelate ring, N4-C6-C7-C8-N5, however, has the asymmetric skew-boat form (Fig. 1). This irregular conformation seems to be caused by the intramolecular hydrogen bond between the sulfenato oxygen atom, O3, and the nitrogen atom, N4, of the amino group, because the distance between the oxygen atom and nitrogen one is 2.986 Å.

The coordination angles in the tn chelate rings, N2-Co-N3 and N4-Co-N5, are 90.6° and 93.4°, respectively, which are slightly smaller than those found in $(-)_{589}$-[Co(tn)$_3$]$^{3+}$ (mean 94.5°)[9] and $(-)_{589}$-[Co(acac)(tn)$_2$]$^{2+}$ (mean 96°).[12] The average bond lengths of Co-N2, Co-N3, and Co-N4, where the nitrogen atoms are cis position to the sulfur donor atom, is 1.991 Å, and this value is in consistent with that of Co-N in other (1,3-propanediamine)cobalt(III) complexes.[9-13] On the other hand, the trans Co-N5 bond length (2.074 Å) is longer than the average cis Co-N one. A similar trans effect has been observed in the bis(1,2-ethanediamine)cobalt(III) complexes with a coordinated sulfenato sulfur atom; [Co(aese)(en)$_2$]$^{2+}$[5] and [Co(L-cysteinesulfenato-*N,S*)(en)$_2$]$^{2+}$.[14] The bond lengths and angles associated with the aese ligand are similar to those of the corresponding bis(1,2-ethanediamine) complex,[5] although the Co-S bond length (2.199 Å) is somewhat shorter and Co-N1 one (2.033 Å) somewhat longer than those in [Co(aese)(en)$_2$]$^{2+}$ (Co-S=2.253 Å and Co-N=1.987 Å).

In *Λ*-(*S*)-[Co(aese)(tn)$_2$]$^{2+}$ (Fig. 1), the tn chelate ring, of which amine proton may participate in an intramolecular hydrogen bond with the oxygen atom of the aese ligand, takes the asymmetric skew-boat form, although the other tn chelate ring takes a chair form, as in the case of the tn chelate rings in [Co(tn)$_3$]$^{3+}$,[9] [Co(X)$_2$(tn)$_2$]$^{n+}$ ((X)$_2$=(NCS)$_2$[10,11] and acac[12]), and [Co(en)$_2$(tn)]$^{3+}$.[13] The Λ-(*R*) tn isomer can also be expected to take a similar intramolecular hydrogen bond to the Λ-(*S*) isomer because of the flexibility of the tn chelate ring. This stereochemical similarity of the Λ-(*R*) and Λ-(*S*) tn isomers is probably related to the fact that the two isomers are formed in roughly equal amounts. In crystal of *Λ*-(*R*)-[Co(aese)(en)$_2$]$^{2+}$,[5] both of the aese and en chelate rings, which take a lel conformation (δ conformation), form a similar intramolecular hydrogen bond to the Λ-(*S*) tn isomer. While, molecular model constructions reveal that the Λ-(*S*) en isomer can not be expected to have such interaction as the Λ-(*R*) en isomer because of the rigidity of the five-membered chelate rings. The stereochemical difference between the two Λ-[Co(aese)(en)$_2$]$^{2+}$ isomers suggests that the Λ-(*R*) isomer is more abundantly formed by the intramolecular hydrogen bond than the Λ-(*S*) isomer. In other words, the difference in the formation ratio between the isomers, (*R*) and (*S*), of *Λ*-[Co(aese)(en)$_2$]$^{2+}$ and those of *Λ*-[Co(aese)(tn)$_2$]$^{2+}$ is considered to be associated with that in the flexibility of the tn or en chelate ring and simultaneously with that in the formation of the intramolecular hydrogen bond.

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1) Present address: Institute of Materials Science, University of Tsukuba, Sakura, Ibaraki 305.

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4) Λ and Δ denote the absolute configuration due to the skew pair of the chelate rings, and (*R*) and (*S*) denote the absolute configuration of the sulfur donor atom in the aese.

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