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Preparation, Stereochemistry, and CD Spectra of Cobalt(III) Complexes with 1,3-Propanedithiolate and 1,3-Propanedisulfinate. Crystal Structure and Absolute Configuration of $(-)^{CD}_{460}$-(1,3-Propanedisulfinato)(3,6-diazaoctane-1,8-diamine)-cobalt(III) Perchlorate Monohydrate

Ken-ichi Okamoto,* Hideki Umehara, and Jinsai Hidaka
Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305
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The cis-α isomers of the 3,6-diazaoctane-1,8-diamine (trien) cobalt(III) complexes with 1,3-propanedithiolate (pdt) and 1,3-propanedisulfinate (pdsi) were selectively prepared and optically resolved. Of these isomers, the crystal structure and the absolute configuration of $(-)^{CD}_{460}$-[Co(pdsi)(trien)]$ClO_4 \cdot H_2O$ have been determined by X-ray diffraction method. The complex cation takes a Δ-cis-α configuration. The 1,3-propanedisulfinate coordinates to cobalt atom through two sulfur atoms and its chelate ring takes a skew boat form with the λ conformation. The CD spectral behaviors in the d-d transition and the sulfur-to-metal ($Co(\sigma^*) \leftarrow S(\sigma)$) charge-transfer band regions are discussed in relation to the absolute configurations of the cobalt(III) complexes with sulfinate type sulfur donor atoms and the corresponding thiolate ones.

Cobalt(III) complexes with the 3,6-diazaoctane-1,8-diamine (trien) and its derivatives have been extensively investigated for the relation between their CD spectra in the d-d transition region and the absolute configuration, which arises from the chirality due to the skew pair of the chelate rings.[1-6] Recently, it has been reported that the absolute configuration of the cobalt(III) complexes with two or three thiolate type sulfur donor atoms and the corresponding sulfinate ones can be estimated on the basis of the two CD bands with the opposite signs in the sulfur-to-metal ($Co(\sigma^*) \leftarrow S(\sigma)$) charge-transfer band region, taking the CD spectral pattern in the d-d transition band region into consideration.[7] For the trien cobalt(III) complexes with 1,3-propanedithiolate (pdt; $S(CH_2)_3S^{2-}$) and 1,3-propanedisulfinate (pdsi; $O_2S(CH_2)_3SO_2^{2-}$), which were employed in the present work, however, this empirical estimation based on the CD spectral behaviors in the sulfur-to-metal charge-transfer band region is inconsistent with that in the d-d transition band region.

This paper deals with the preparation and resolution of the trien cobalt(III) complexes with the pdt and pdsi, and with the X-ray crystal structure analysis of $(-)^{CD}_{460}$-[Co(pdsi)(trien)]$ClO_4 \cdot H_2O$. The CD spectra of the pdt and pdsi isomers obtained are discussed in relation to the absolute cofiguration of $(-)^{CD}_{460}$ pdsi isomer, which is determined by the X-ray crystal structure analysis.

Experimental

1) Preparation of Complexes. a) *cis*-α-(1,3-Propanedithiolato)(3,6-diazaoctane-1,8-diamine)cobalt(III) Perchlorate. *cis*-α-[Co(pdt)(trien)]ClO_4. To an ice-cold solution containing 3.1 g (0.01 mol) of *cis*-α-[$Co(Cl)_2$(trien)]Cl in 60 cm^3 of water was added an ice-cold solution containing 1.08 g (0.01 mol) of 1,3-propanedithiol in 40 cm^3 of an 1 mol dm^{-3} NaOH solution of an H_2O-methanol (1 : 1) mixture. The mixture was stirred for 1 h in an ice bath. After removing the precipitate by filtration, about 20 cm^3 of a saturated $NaClO_4$ solution was added to the filtrate and it was kept in a refrigerator for 5 h. The precipitate which appeared was filtered off. The filtrate was concentrated to a half volume and kept in a refrigerator overnight. After this procedure was repeated twice, the desired black complex was collected by filtration. The crude complex was recrystallized from a small amount of water, washed with ethanol and ether, and then dried in a vacuum desiccator. It was found from the absorption and ^{13}C NMR spectral measurements that the complex contained only *cis*-α-[Co(pdt)(trien)]$^+$. Yield: 21%. Found: C, 26.09; H, 5.94; N, 13.52%. Calcd for $C_9H_{24}N_4O_4S_2ClCo \cdot 0.25H_2O$: C, 26.03; H, 5.94; N, 13.49%.

b) *cis*-α-(1,3-Propanedisulfinato)(3,6-diazaoctane-1,8-diamine)cobalt(III) Perchlorate. *cis*-α-[Co(pdsi)(trien)]ClO_4. An excess amount of 8 cm^3 of a 5% H_2O_2 solution was added to a solution containing 0.5 g of *cis*-α-[Co(pdt)(trien)]$ClO_4 \cdot 0.25H_2O$ in 20 cm^3 of water, followed by the addition of 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 thiolato complex reacts almost quantitatively with hydrogen peroxide to form the sulfinato complex. The orange crystals which appeared were collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Orange crystals were obtained more by concentrating the filtrate. Yield: 48%. Found: C, 22.76; H, 5.11; N, 11.82%. Calcd for $C_9H_{24}N_4O_8S_2ClCo$: C, 22.76; H, 5.10; N, 11.80%.

2) Resolution of Complexes. a) *cis*-α-[Co(pdt)(trien)]$^+$. An excess amount (0.5 g) of $Na_2[Sb_2(d\text{-}tart)_2] \cdot 5H_2O$ was added with stirring to a solution containing 0.1 g of *cis*-α-[Co(pdt)(trien)]$ClO_4 \cdot 0.25H_2O$ in 10 cm^3 of water. After the solution was stirred for 3 min, 3 cm^3 of ethanol was added to it and cooled in an ice bath. The precipitate which appeared was filtered. The aqueous solution of the precipitate showed an enantiomeric CD spectrum in the region of 260—650 nm for the filtrate, which contained $(+)^{CD}_{530}$-*cis*-α-[Co(pdt)(trien)]$^+$. This fact seems to indicate that the present complex was partially resolved, because of the small Δε values. However, the complete resolution of this complex was unsuccessful, since the optically active isomer was unstable in the aqueous

solution without the resolving agent.

The partially resolved $(+)^{CD}_{530}$-*cis*-α-[Co(pdt)(trien)]$^+$ isomer could be oxidized by a procedure similar to that used in (1b). This oxidation product showed the identical absorption and CD spectral patterns with $(+)^{CD}_{460}$-*cis*-α-[Co(pdsi)(trien)]$^+$ as in (2b) (vide infra).

b) *cis*-α-[Co(pdsi)(trien)]ClO_4. The solution containing 0.4 g of *cis*-α-[Co(pdsi)(trien)]ClO_4 in 30 cm^3 of water was poured onto a Dowex 50W-X8 column (Na^+ form, 200—400 mesh, 3.0 cm×20 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.075 mol dm^{-3} aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot H_2O$. Two deep yellow bands were separated completely and then fractionated. It was found from the CD spectral measurements for each of the fractions that the earlier moving band contained $(-)^{CD}_{460}$-*cis*-α-[Co(pdsi)(trien)]$^+$ and the later one contained the $(+)^{CD}_{460}$ isomer. The fractions were combined to two portions and they were concentrated to a small volume with a rotary evaporator below 25 °C. The deposited $K_2[Sb_2(d\text{-tart})_2]$ was filtered off. The filtrate was converted into the perchlorate salt using a QAE-Sephadex A-25 column (ClO_4^- form, 2.5 cm×20 cm) by eluting with water. The eluate was concentrated to a small volume again and kept in a refrigerator overnight. The resulting crystals were collected by filtration. Found: C, 21.82; H, 5.27; N, 11.24%. Calcd for $(-)^{CD}_{460}$-*cis*-α-[Co(pdsi)(trien)]$ClO_4\cdot H_2O$: C, 21.93; H, 5.31; N, 11.36%. A piece of the crystals of the $(-)^{CD}_{460}$ isomer was used for the X-ray crystal structure analysis.

3) General Data. 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 ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 or-FX-90Q NMR spectrometer at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference. The X-ray analysis calculations were carried out on a Facom M-382 computer in the Science Information Processing Center of the University of Tsukuba.

4) X-Ray Data Collection. Unit cell parameters and intensity data for the single crystal (ca. 0.16×0.20×0.35 mm^3) were measured on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo*Kα* radiation. The unit cell parameters were determined by a least-squares refinement based on 25 reflections. Systematic absences led to the space group $P3_1$ or $P3_2$. The final space group was determined to $P3_1$ by the anomalous scattering technique (vide infra). Crystal Data: $C_9H_{26}N_4O_9S_2ClCo$, M.W.=492.8, trigonal, space group $P3_1$, a=12.350(2), c=10.407(5) Å, V=1374.7(7) Å^3, d_m=1.77 g cm^{-3}, d_x=1.786 g cm^{-3}, Z=3, and μ(Mo*Kα*)=1.391 mm^{-1}.

The intensity data were collected by the ω—2θ scan technique up to 2θ=60° with scan rate of 3° min^{-1}. The intensity data were converted to the F_o data in the usual manner. Absorption corrections were not applied. A total of 2453 independent reflections with $|F_o|>3\sigma(|F_o|)$ of the measured 3056 reflections were considered as 'observed' and used for the structure analysis.

5) Determination of the Crystal Structure. The positions of the cobalt atom and the coordinated two sulfur and four nitrogen atoms were determined by the direct method (program MULTAN was used).[8] The difference-Fourier maps based on these atomic positions revealed the other non-hydrogen atoms. The structure was refined by a full-matrix least-squares refinement using the positional parameters, the anisotropic thermal parameters of the non-hydrogen atoms for the complex cation and chloride, and the isotropic thermal parameters for the oxygen atoms of the perchlorate and water molecule (program RFINE[9] was used). Since the positions of the hydrogen atoms of the complex cation were not determined exactly on the difference-Fourier map, we did not add their parameters to the calculation. The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literatures.[10] The final residual values were R=0.066 and R_w=0.082, respectively.

The absolute configuration was determined by the anomalous scattering technique. When the refinements were carried out by use of a set of the atomic parameters containing the Δ configuration of the complex cation, the residual values converged to R=0.064 and R_w=0.080, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Λ configuration) resulted in the residual values of R=0.074 and R_w=0.088, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the Δ configuration (Fig. 1). A similar relationship between the residual values and the absolute configuration was observed for the determination of the crystal structure of cobalt(III) complexes with 2-aminoethaneseleninate.[11,12] The final positional parameters for the Δ-cis-α isomer are listed in Table 1. A list of

Table 1. Positional and Thermal Parameters (with e.s.d.'s)

Atom	x	y	z	B_{eq}/Å^2[a]	Atom	x	y	z	B_{eq}/Å^2[a]
Co	0.1845(1)	0.3320(1)	0.7819[c]	1.54	C3	0.2649(11)	0.4385(11)	0.4881(10)	2.59
S1	0.1346(2)	0.1870(2)	0.6349(3)	1.89	C4	−0.0183(12)	0.3433(10)	0.9095(13)	3.47
S2	0.2183(2)	0.4754(2)	0.6372(3)	1.91	C5	0.0981(12)	0.4669(10)	0.9341(14)	3.40
N1	0.0074(7)	0.2864(7)	0.7945(9)	2.04	C6	0.2429(12)	0.4024(12)	1.0465(11)	3.16
N2	0.2132(9)	0.4510(7)	0.9263(8)	2.37	C7	0.1710(12)	0.2626(11)	1.0503(11)	3.17
N3	0.1732(8)	0.2133(8)	0.9175(9)	2.41	C8	0.2816(11)	0.1910(10)	0.9005(11)	2.62
N4	0.3636(7)	0.3817(8)	0.7733(9)	2.19	C9	0.4005(11)	0.3131(11)	0.8678(13)	3.34
O1	0.0347(8)	0.0652(6)	0.6853(8)	3.05	CL	0.4854(3)	0.2752(3)	0.2376(4)	4.49
O2	0.2457(7)	0.1850(7)	0.5873(8)	2.91	OA1	0.4712(17)	0.1779(19)	0.1485(20)	11.19[b]
O3	0.3259(7)	0.5950(7)	0.6776(8)	3.18	OA2	0.4740(14)	0.3626(14)	0.1718(14)	8.22[b]
O4	0.1053(7)	0.4833(7)	0.6093(7)	2.36	OA3	0.4712(39)	0.2492(38)	0.3525(40)	26.59[b]
C1	0.0665(13)	0.2163(11)	0.4971(12)	3.37	OA4	0.6207(19)	0.3487(17)	0.2658(22)	11.68[b]
C2	0.1615(15)	0.3271(13)	0.4160(14)	4.20	OW	0.8846(16)	0.4390(16)	0.2329(16)	9.69[b]

a) $B_{eq}=8\pi^2(U_{11}+U_{22}+U_{33})/3$. b) Isotropic temperature factor. c) The z coordinate is held constant.

structure factors (Table A), anisotropic thermal parameters (Table B), and bond lengths and angles of the perchlorate ion (Table C) is kept at the Chemical Society of Japan as Document No. 8747.

Results and Discussion

Description of the Structure. A perspective drawing of the complex cation, $(-)^{CD}_{460}$-[Co(pdsi)(trien)]$^+$, is given in Fig. 1,[13] together with a numbering scheme. The bond lengths and angles (with their standard deviations) in the complex cation are summarized in Table 2. The coordination geometry around cobalt atom is approximately octahedral. The trien, which coordinates as a quadridentate ligand, takes the cis-α configuration by coordination.[14] The pdsi ligand coordinates to the cobalt atom through two sulfur atoms to form the six-membered chelate ring. This indicates that the treatment of the thiolato complex with hydrogen peroxide proceeds without the linkage isomerization as in the case of the cobalt(III) complexes with the sulfinate ligands,[15] although the linkage isomerization was observed for the sulfinato complex[16] obtained by the photochemical preparation and the seleninato complex.[11]

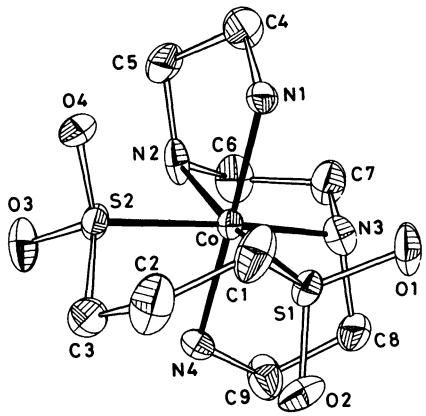

Fig. 1. Perspective view of $(-)^{CD}_{460}$-Δ-*cis*-α-[Co(pdsi)(trien)]$^+$ ion with the numbering scheme.

For *cis*-α-[Co(pdsi)(trien)]$^+$, the optical isomers, Δ and Λ, are possible.[17] The result of the X-ray crystal structure analysis indicates that the absolute configuration of the $(-)^{CD}_{460}$ isomer takes the Δ configuration and the two asymmetric nitrogen atoms in the trien have the absolute configuration S. In the trien ligand, the two outer chelate rings take the unsymmetrical skew form with the λ conformation. The central chelate ring takes nearly symmetrical skew form with the δ conformation. Similar conformational relationship of the chelate rings was also observed for the L-3,8-dimetrien (δλδ conformation) in $(-)_{589}$-*Λ-cis*-α-[Co$(NO_2)_2$(L-3,8-dimetrien)]$^+$,[4,5] where L-3,8-dimetrien denotes (2*S*,7*S*)-2,7-dimethyl-3,6-diazaoctane-1,8-diamine. The pdsi has the symmetrical skew boat form with the λ conformation. Thus, the complex cation of the $(-)^{CD}_{460}$-Δ-cis-α isomer has an approximately twofold axis.

In $(-)^{CD}_{460}$-*Λ-cis*-α-[Co(pdsi)(trien)]$^+$, the bond lengths and angles around the sulfinato group are almost equal to those in [Co(aesi-*N*,*S*)$(en)_2$]$^{2+}$,[15] except for the angles of Co-S-C (111.2(5) and 110.1(5)° for the pdsi complex and 100.1(2)° for the aesi one) which seem to depend on the difference between the pdsi and aesi chelate rings, where aesi denotes 2-aminoethanesulfinate. The bond lengths and angles for the trien are similar to those for $(-)_{589}$-*cis*-α-[Co$(NO_2)_2$(L-3,8-dimetrien)]ClO_4,[4] except for the Co-N distances. The mean value of the Co-N distance in the pdsi complex, 1.987(9) Å, is significantly longer than the corresponding distance (1.952(7)) Å in $(-)_{589}$-*cis*-α-[Co$(NO_2)_2$(L-3,8-dimetrien)]ClO_4[4] and those (1.95(2) and 1.955(9) Å) in *cis*-β-[Co(*S*-pro)(trien)]$^+$.[18] Lange et al. reported the structural trans effect that the Co-N distance for the group trans to the sulfur atom in the sulfinato group

Table 2. Intermolecular Distances and Bond Angles (with e.s.d.'s)

	(a) Bond distances (l/Å)						
Co-S1	2.196(3)	Co-S2	2.200(3)	S2-Co-N4	89.2(3)	N1-Co-N2	85.6(4)
Co-N1	1.971(9)	Co-N2	2.007(9)	N1-Co-N3	94.8(4)	N1-Co-N4	178.3(4)
Co-N3	1.988(10)	Co-N4	1.980(9)	N2-Co-N3	86.0(4)	N2-Co-N4	92.6(4)
S1-O1	1.484(7)	S1-O2	1.471(10)	N3-Co-N4	85.2(4)	Co-S1-O1	109.4(4)
S1-C1	1.788(15)	S2-O3	1.470(7)	Co-S1-O2	111.4(3)	Co-S1-C1	111.2(5)
S2-O4	1.475(10)	S2-C3	1.791(12)	O1-S1-O2	114.3(6)	O1-S1-C1	104.6(5)
N1-C4	1.50(2)	N2-C5	1.53(2)	O2-S1-C1	105.7(6)	Co-S2-O3	109.0(4)
N2-C6	1.51(2)	N3-C7	1.52(2)	Co-S2-O4	112.5(3)	Co-S2-C3	110.1(5)
N3-C8	1.51(2)	N4-C9	1.51(2)	O3-S2-O4	113.6(5)	O3-S2-C3	105.0(5)
C1-C2	1.53(2)	C2-C3	1.53(2)	O4-S2-C3	106.3(6)	Co-N1-C4	112.6(7)
C4-C5	1.51(1)	C6-C7	1.50(2)	Co-N2-C5	107.3(7)	Co-N2-C6	108.5(8)
C8-C9	1.53(1)			C5-N2-C6	115.7(10)	Co-N3-C7	111.1(8)
				Co-N3-C8	108.1(6)	C7-N3-C8	112.1(10)
				Co-N4-C9	113.6(6)	S1-C1-C2	113.2(10)
	(b) Bond angles (ϕ/°)			C1-C2-C3	117.1(11)	S2-C3-C2	115.1(9)
S1-Co-S2	92.4(1)	S1-Co-N1	89.7(3)	N1-C4-C5	107.0(10)	N2-C5-C4	109.8(11)
S1-Co-N2	173.8(2)	S1-Co-N3	90.3(3)	N2-C6-C7	111.1(9)	N3-C7-C6	108.6(9)
S1-Co-N4	92.1(3)	S2-Co-N1	90.7(3)	N3-C8-C9	110.5(11)	N4-C9-C8	106.7(10)
S2-Co-N2	91.7(3)	S2-Co-N3	173.9(2)				

was longer than the other Co-N distances in [Co(aesi-*N*,*S*)(en)$_2$]$^{2+}$.[15] Therefore, the lengthening of the Co-N distances in the present pdsi complex seems to depend on the trans effect for the two sulfinato groups.

^{13}C NMR Spectra. The ^{13}C NMR spectrum of $(-)^{CD}_{460}$-*Δ-cis-α*-[Co(pdsi)(trien)]$^+$ exhibits five resonance lines (20.37, 46.21, 55.20, 58.08, and 58.35 ppm) due to the nine methylene carbon atoms. This indicates that the $(-)^{CD}_{460}$-Δ-cis-α isomer has C_2 symmetry in an aqueous solution as well as in the crystalline state. The spectrum of [Co(pdt)(trien)]$^+$ exhibits also five resonance lines (24.05, 35.11, 46.43, 57.05, and 57.43 ppm) due to the nine methylene carbon atoms, indicating the C_2 symmetry. Further, [Co(pdt)(trien)]$^+$ reacts with hydrogen peroxide to give selectively *cis-α*-[Co(pdsi)(trien)]$^+$. Similar oxidation reaction has proceeded with retention of the geometrical configuration in the reaction of the thiolato cobalt(III) complexes with hydrogen peroxide.[11,19] These facts indicate that [Co(pdt)-(trien)]$^+$ takes the cis-α configuration.

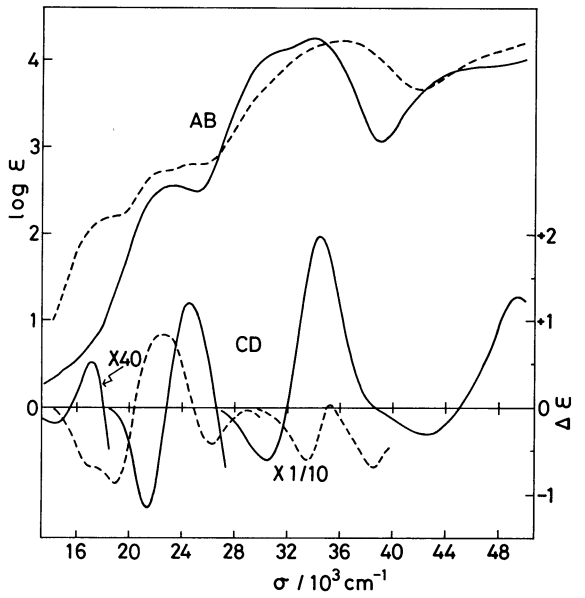

Fig. 2. Absorption and CD spectra of $(-)^{CD}_{460}$-Δ-*cis-α*-[Co(pdsi)(trien)]$^+$ (——) and $(-)^{CD}_{530}$-*cis-α*-[Co(pdt)(trien)]$^+$ (----).

Electronic Absorption and CD Spectra. The electronic absorption and CD spectra of $(-)^{CD}_{460}$-*Δ-cis-α*-[Co(pdsi)(trien)]$^+$ are shown in Fig. 2, together with the corresponding thiolato complex, $(-)^{CD}_{530}$-*cis-α*-[Co(pdt)(trien)]$^+$, and their data are summarized in Table 3. The absorption spectrum of $(-)^{CD}_{460}$-Δ-*cis-α*-[Co(pdsi)(trien)]$^+$ exhibits a broad band at 23.26×10^3 cm^{-1}, similar to those of the cobalt(III) complexes including the sulfinate group.[11] The CD bands of the $(-)^{CD}_{460}$-Δ-cis-α pdsi isomer in this region exhibit a negative and a positive signs from the lower energy (Fig. 2). This CD spectral behavior of the Δ-sulfinato complex is consistent with those of the trien type cobalt(III) complexes.[1-6] which have been successfully assigned to the Δ configuration.

For $(-)^{CD}_{460}$-*Δ-cis-α*-[Co(pdsi)(trien)]$^+$, the intense and broad absorption band in the region of $27-37\times10^3$ cm^{-1}, which is assigned to the sulfur-to-metal charge-transfer transition,[7,19-21] is composed of two components at ca. 31.50 and 33.94×10^3 cm^{-1} (Fig. 2). This absorption spectral behavior is characteristically observed for the cis(S) geometry of the cobalt(III) complexes with the thiolate and sulfinate ligands.[7,20,21] In this absorption band region, $(-)^{CD}_{460}$-*Δ-cis-α*-[Co(pdsi)-(trien)]$^+$ exhibits the two CD bands with the opposite signs ((−) and (+) from the lower energy). According to the empirical estimation,[7] which a negative and a positive CD bands from the lower energy are favorable

Table 3. Absorption and CD Spectral Data of $(-)^{CD}_{460}$-*cis-α*-[Co(pdsi)(trien)]$^+$ and $(-)^{CD}_{530}$-*cis-α*-[Co(pdt)(trien)]$^+$

Complex	Absorption maxima σ/10^3 cm^{-1}	CD extrema σ/10^3 cm^{-1}
	log ε/mol^{-1} dm^3 cm^{-1}	$\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1}
$(-)^{CD}_{460}$-*cis-α*-[Co(pdsi)(trien)]$^+$	23.26 (2.55)	14.43 (−0.005)
	31.50 (4.12 sh)	17.12 (+0.013)
	33.94 (4.25)	21.36 (−1.154)
	46.51 (3.93 sh)	24.51 (+1.206)
		30.40 (−6.076)
		34.36 (+19.982)
		42.37 (−2.953)
		49.26 (+12.830)
$(-)^{CD}_{530}$-*cis-α*-[Co(pdt)(trien)]$^+$	18.69 (2.19 sh)	17.15 (− sh)
	22.42 (2.72 sh)	18.80 (−)
	25.00 (2.80)	22.47 (+)
	33.33 (4.11 sh)	26.32 (−)
	36.10 (4.22)	33.56 (−)
		35.09 (+)
		38.46 (−)

sh denotes a shoulder.

for the Λ configuration, the present $(-)^{CD}_{460}$-Δ-cis-α pdsi isomer may be assigned to the Λ configuration.

The absorption spectrum of $(-)^{CD}_{530}$-*cis*-α-[Co(pdt)(trien)]$^+$ coincides with the cis(S) cobalt(III) complexes with L-penicillaminate[20] and the [Co(amine)$_4$(thiolato)$_2$]-type complexes.[7,21] In the first absorption and sulfur-to-metal charge-transfer band regions, the $(-)^{CD}_{530}$-*cis*-α pdt isomer exhibits a similar CD spectral pattern to $(-)^{CD}_{460}$-*Δ*-*cis*-α-[Co(pdsi)(trien)]$^+$, although the intensities are shown by an arbitrary scale (Fig. 2). Further, the absorption and CD spectra of the oxidation product, which was obtained by the reaction of $(+)^{CD}_{530}$-*cis*-α-[Co(pdt)(trien)]$^+$ with hydrogen peroxide, exhibit the identical patterns with those of the $(+)^{CD}_{460}$-*Λ*-*cis*-α-[Co(pdsi)(trien)]$^+$ (Fig. 2). Accordingly, these facts suggest that $(-)^{CD}_{530}$-*cis*-α-[Co(pdt)(trien)]$^+$ takes the Δ configuration.

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