Preparation, Crystal Structure, and Stereochemical Properties of {*N,N'*-Ethylenebis(1,1,1-trifluoro-4-imino-2-pentanonato)} (L-methioninato)cobalt(III)

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The $(-)_{435}$ isomer of the {*N,N'*-ethylenebis(1,1,1-trifluoro-4-imino-2-pentanonato)}(L-methioninato)cobalt-(III) complex, $(-)_{435}$-[Co(tfac$_2$en)(L-met)], was preferentially crystallized from an equilibrium mixture of the $(-)_{435}$ and $(+)_{435}$ isomers in methanol. The crystal structure of the $(-)_{435}$ isomer was determined by X-ray diffraction. The $(-)_{435}$ isomer is of a Λ-cis-β_2 type in which the quadridentate tfac$_2$en takes a nonplanar configuration, and the L-methioninate is bound to the cobalt atom by nitrogen and oxygen atoms as a bidentate ligand. The electronic absorption, CD, and ^{1}H NMR spectral behaviors of both $(-)_{435}$ and $(+)_{435}$ isomers are discussed in relation to their geometrical and absolute configurations.

Mixed cobalt(III) complexes with quadridentate Schiff base and bidentate ligands (such as amino carboxylates and β-diketonates) have been investigated regarding their kinetic and thermodynamic stereoselectivities.[1-6] Some of these have been determined by X-ray crystal structure analyses.[7-10] Concerning these cobalt(III) complexes, it has been known that a quadridentate Schiff base, which usually contains salicylideneaminate moieties, selectively takes a nonplanar cis-β configuration[11a] by coordination.[1-10] Further, complexes with amino carboxylate as a bidentate ligand preferentially take a mer(N)[11b] configuration.[1-5] In order to elucidate the source of a regioselective effect due to the quadridentate Schiff base, we employed in this work *N,N'*-ethylenebis(1,1,1-trifluoro-4-imino-2-pentanonate), tfac$_2$en, which has flexible β-imino ketone moieties instead of salicylideneaminate ones. Also, its cobalt(III) complex with L-methioninate was prepared.

The present paper deals with the crystal structure of $(-)_{435}$-[Co(tfac$_2$en)(L-met)], which was preferentially crystallized from an equilibrium mixture of the $(-)_{435}$ and $(+)_{435}$ isomers in methanol. The absorption and CD spectra of the $(-)_{435}$ and $(+)_{435}$ isomers are discussed in comparison with those of corresponding cobalt(III) complexes with a quadridentate Schiff base, together with their stereochemical properties.

Experimental

1) Preparation of [Co(tfac$_2$en)(L-met)]. A warm solution (*ca.* 40 °C) containing 0.57 g of L-methionine in 15 cm^3 of water was added to a hot solution (*ca.* 40 °C) containing 1.5 g of [Co(tfac$_2$en)] (prepared by a procedure similar to that described in the literature[16,17]) in 80 cm^3 of methanol. The solution was vigorously stirred in the open for about 4 h at room temperature. The color of the solution changed from orange-brown to green. After filtration, the green filtrate was concentrated to about 10 cm^3 and appeared as a green crude product. The product (collected by filtration) was dissolved in a small amount of methanol and then slowly recrystallized by evaporating the solvent at room temperature to form the $(-)_{435}$ isomer as massive crystals in about 80% yield. A piece of crystal, thus obtained, was used for an X-ray diffraction study. Found: C, 37.84; H, 4.08; N, 7.83%. Calcd for [Co(tfac$_2$en)(L-met)]=$CoC_{17}H_{22}N_3O_4SF_6$: C, 38.00; H, 4.13; N, 7.82%. $[M]^{25}_{435}=-52900°$ / mol dm^{-3} m (mixed solvent of *N,N*-dimethylformamide (DMF)–$CHCl_3$ (1:4 in volume); concentration, 1.0×10^{-3} mol dm^{-3}).

When the green crude product or the pure $(-)_{435}$ isomer obtained above was recrystallized from a methanol–water (4:1) mixture, the complex consisted of two kinds of crystalline forms, a large amount of massive crystals ($(-)_{435}$ isomer) and a small amount of needle-shaped crystals ($(+)_{435}$ isomer). The needle-shaped crystals could be sorted by hand. Yield; about 15%. Found: C, 38.04; H, 4.13; N, 8.08%. Calcd for [Co(tfac$_2$en)(L-met)]: C, 38.00; H. 4.13; N, 7.82%. $[M]^{25}_{435}=+50100°$ / mol dm^{-3} m (mixed solvent of DMF–$CHCl_3$ (1:4); concentration, 1.0×10^{-3} mol dm^{-3}).

2) General Data. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers and the CD spectra with a JASCO J-20 spectropolarimeter. All measurements were carried out at room temperature. Rotations at 435 nm were measured with a JASCO DIP-140 polarimeter at 25 °C. The ^{1}H NMR spectra were recorded with a Hitachi R-20 spectrometer at 35 °C, using tetramethylsilane (TMS) as an internal reference. X-Ray analysis calculations were carried out on a FACOM M-380 computer at the Uviversity of Tsukuba.

3) X-Ray Characterization. Unit cell parameters and intensity data for the single crystal (*ca.* $0.1\times0.12\times0.5$ mm^3) were measured on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares refinement based on 44 reflections. Systematic absences led to an assignment of the space group $P2_12_12_1$. The crystal data are summarized in Table 1.

Intensity data were collected by a ω—2θ scan technique up to $2\theta=60°$ with a scan rate of 3 °/min. The intensity data were converted to F_o data in the usual manner. Absorption corrections were not applied. A total of 2059 independent reflections with $F_o>3\sigma(|F_o|)$ were considered as 'observed' and used for the structure analysis.

4) Determination of the Crystal Structure. The position of the cobalt atom was obtained from a three-dimentional Patterson function. Difference Fourier maps, based on the cobalt position, revealed all the non-hydrogen atoms. The

TABLE 1. CRYSTAL DATA

Compound	$CoC_{17}H_{22}N_3O_4SF_6$
Formula weight	537.37
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	12.623(2)
b/Å	19.404(5)
c/Å	9.153(2)
Cell volume/Å^3	2241.9(8)
Z	4
D_x/g cm^{-3}	1.592
D_m/g cm^{-3}	1.59
μ(Mo $K\alpha$)/cm^{-1}	9.70

TABLE 2. POSITIONAL AND THERMAL PARAMETERS

Atom	X	Y	Z	B_{eq}/Å^3
Co	0.15075(13)	0.11730(8)	0.06267(16)	3.56
S1	0.4793(4)	0.1738(3)	−0.2118(5)	6.76
N1	0.2568(8)	0.1000(5)	−0.0905(9)	3.62
N2	0.0585(8)	0.1268(6)	0.2267(11)	4.61
N3	0.2359(9)	0.1838(6)	0.1675(11)	4.10
O1	0.2078(8)	0.0409(5)	0.1543(9)	4.73
O2	0.3156(8)	−0.0484(5)	0.1230(10)	5.32
O3	0.0615(8)	0.0550(5)	−0.0394(10)	5.00
O4	0.0894(7)	0.1891(4)	−0.0504(10)	4.40
C1	0.2844(11)	0.0059(6)	0.0859(12)	3.83
C2	0.3291(10)	0.0456(6)	−0.0468(12)	3.87
C3	0.4382(13)	0.0715(10)	−0.0038(16)	6.65
C4	0.5118(15)	0.0918(11)	−0.1280(21)	8.65
C5	0.4266(20)	0.1441(13)	−0.3869(21)	11.79
C6	−0.0364(13)	0.0487(9)	−0.0018(17)	5.47
C7	−0.0984(17)	0.0087(9)	−0.1179(23)	7.04
C8	−0.0887(12)	0.0689(8)	0.1185(17)	5.47
C9	−0.0381(13)	0.1039(7)	0.2356(15)	5.39
C10	−0.1014(13)	0.1176(10)	0.3783(16)	6.88
C11	0.1118(12)	0.1622(7)	0.3544(13)	4.64
C12	0.2293(12)	0.1616(8)	0.3244(15)	5.16
C13	0.2649(11)	0.2414(8)	0.1205(16)	4.75
C14	0.3192(15)	0.2938(9)	0.2181(25)	8.48
C15	0.2387(12)	0.2646(7)	−0.0229(17)	5.08
C16	0.1499(13)	0.2387(6)	−0.0906(13)	4.66
C17	0.1170(15)	0.2707(9)	−0.2360(20)	6.81
F1	−0.1954(11)	0.0000(13)	−0.0899(22)	21.33
F2	−0.0966(12)	0.0408(8)	−0.2481(15)	12.56
F3	−0.0586(15)	−0.0496(7)	−0.1501(17)	14.60
F4	0.1055(17)	0.2259(7)	−0.3354(11)	14.11
F5	0.0217(10)	0.2993(7)	−0.2238(13)	10.70
F6	0.1748(10)	0.3186(8)	−0.2830(18)	14.92

$B_{eq}=8\pi^2\ (U_{12}+U_{22}+U_{33})/3$.

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 used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.[18] The final R and R_w values converged to 0.086 and 0.098, respectively. The absolute configuration was determined on the basis of the known configuration of L-methioninate.[19] The final atomic parameters are given in Table 2. A list of structure factors (Table A), anisotropic thermal parameters of non-hydrogen atoms (Table B), and the projected figure of the crystal structure (Fig. A) are kept at the Chemical Society of Japan as Document No. 8551.

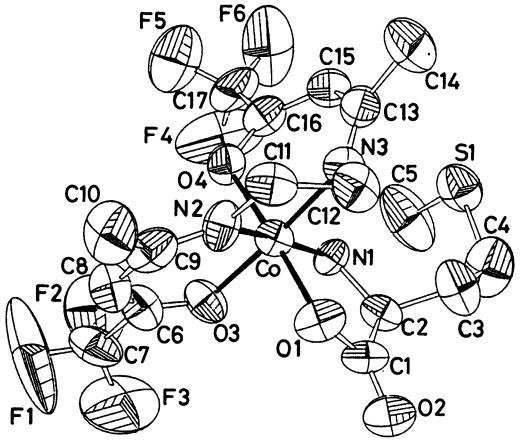

Fig. 1. A perspective drawing of (−)$_{435}$-Λ-*cis*-β_2-[Co(tfac$_2$en) (L-met)] with the numbering scheme of atoms.

Results and Discussion

Description of the Structure. A perspective drawing of (−)$_{435}$-[Co(tfac$_2$en)(L-met)] is given in Fig. 1, together with a numbering scheme. The bond lengths and angles (with their standard deviations) for the (−)$_{435}$ isomer are listed in Table 3. The L-methioninate ligand coordinates to a cobalt atom with nitrogen and oxygen atoms serving as a bidentate ligand. The tfac$_2$en Schiff base, which coordinates as a quadridentate ligand, takes the cis-β_2 configuration by coordination.[11] Namely, the cobalt atom is surrounded by a meridional N_3O_3 structure and the nitrogen atom in the L-met (N1) is located on the trans position of the nitrogen atom (N2) of the tfac(1) moiety (tfac; 1,1,1-trifluoro-4-imino-2-pentanonate). The absolute configuration of (−)$_{435}$-[Co(tfac$_2$en)(L-met)] was determined to be Λ on the basis of the known absolute configuration, $S(C)$, of the asymmetric carbon atom of the L-methioninate.[19] Thus, the structure of the (−)$_{435}$ isomer is denoted as the Λ-cis-β_2 type (Fig. 1). This has a similar structure to those of [Co(α-Me-sal$_2$en)(L-isoleu)][9] and [Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)][10] (α-Me-sal$_2$en; *N*,*N*′-ethylenebis(*o*-hydroxy-α-methylbenzylideneaminate, L-isoleu; L-isoleucine, and *N*-Bz-L-ala; *N*-benzyl-L-alanine). These results coincide with the fact that the cis-α structure of the cobalt(III) Schiff base complexes is unstable and such a complex has not been found yet.[1-5,9,10]

The bond lengths and angles of (−)$_{435}$-[Co(tfac$_2$en)(L-met)] are similar to those of cobalt(III) complexes with amino carboxylate and quadridentate Schiff bases such as salen and α-Me-sal$_2$en (Table 3).[9,10] The Co–O and Co–N bond lengths of the tfac$_2$en ligand are somewhat longer than those of [Co(α-Me-sal$_2$en)(L-isoleu)][9] and [Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)],[10] while the distances of the L-methioninate, Co–O1 1.849(9) Å and Co–N1 1.968(9) Å, are significantly shorter than those of the *N*-Bz-L-ala and L-isoleu in the α-Me-sal$_2$en complexes.[9,10] On the contrary, the chelate angles for the L-met,

Table 3. Intermolecular distances and bond angles (with e.s.d.'s)

(a) Bond distances (l/Å)			
Co-N1	1.968(9)	Co-N2	1.909(10)
Co-N3	1.933(11)	Co-O1	1.849(9)
Co-O3	1.898(9)	Co-O4	1.900(9)
S1-C4	1.814(22)	S1-C5	1.829(21)
N1-C2	1.451(15)	N2-C9	1.300(19)
N2-C11	1.513(17)	N3-C12	1.501(17)
N3-C13	1.253(18)	O1-C1	1.337(15)
O2-C1	1.175(15)	O3-C6	1.289(19)
O4-C16	1.282(16)	C1-C2	1.546(16)
C2-C3	1.517(21)	C3-C4	1.520(25)
C6-C7	1.532(26)	C6-C8	1.342(22)
C8-C9	1.421(21)	C9-C10	1.554(21)
C11-C12	1.509(22)	C13-C14	1.517(25)
C13-C15	1.427(21)	C15-C16	1.377(21)
C16-C17	1.526(22)	C7-F1	1.263(26)
C7-F2	1.345(25)	C7-F3	1.273(23)
C17-F4	1.265(21)	C17-F5	1.329(23)
C17-F6	1.259(23)		
(b) Bond angles (ϕ/°)			
N1-Co-N2	172.7(4)	N1-Co-N3	95.1(4)
N1-Co-O1	85.5(4)	N1-Co-O3	86.8(4)
N1-Co-O4	90.8(4)	N2-Co-N3	83.4(5)
N2-Co-O1	87.6(4)	N2-Co-O3	95.0(4)
N2-Co-O4	96.3(4)	N3-Co-O1	95.3(4)
N3-Co-O3	177.2(5)	N3-Co-O4	90.4(4)
O1-Co-O3	86.8(4)	O1-Co-O4	173.4(4)
O3-Co-O4	87.5(4)	C4-S1-C5	100.2(10)
Co-N1-C2	110.9(7)	Co-N2-C9	126.0(9)
Co-N2-C11	112.3(8)	C9-N2-C11	121.6(11)
Co-N3-C12	104.7(8)	Co-N3-C13	126.0(10)
C12-N3-C13	126.8(12)	Co-O1-C1	118.5(7)
Co-O3-C6	119.9(9)	Co-O4-C16	117.7(9)
O1-C1-O2	124.3(11)	O1-C1-C2	112.3(10)
O2-C1-C2	123.4(11)	N1-C2-C1	110.4(10)
N1-C2-C3	113.6(11)	C1-C2-C3	107.0(10)
C2-C3-C4	116.5(13)	S1-C4-C3	113.9(13)
O3-C6-C7	110.6(14)	O3-C6-C8	131.6(15)
C7-C6-C8	117.8(15)	C6-C8-C9	122.5(14)
N2-C9-C8	122.5(13)	N2-C9-C10	118.4(13)
C8-C9-C10	119.0(14)	N2-C11-C12	107.0(10)
N3-C12-C11	103.1(11)	N3-C13-C14	121.9(14)
N3-C13-C15	122.0(13)	C14-C13-C15	115.7(14)
C13-C15-C16	119.2(13)	O4-C16-C15	129.0(12)
O4-C16-C17	113.2(13)	C15-C16-C17	117.7(13)
C6-C7-F1	115.0(19)	C6-C7-F2	111.8(15)
C6-C7-F3	114.2(18)	F1-C7-F2	105.0(19)
F1-C7-F3	108.2(19)	F2-C7-F3	101.5(17)
C16-C17-F4	112.2(14)	C16-C17-F5	110.0(15)
C16-C17-F6	116.2(16)	F4-C17-F5	104.1(17)
F4-C17-F6	109.2(17)	F5-C17-F6	104.1(15)

Table 4. Displacements of atoms from the least-squares plane (d/Å) and dihedral angles between the planes

Least-square planes:

plane(1); $0.4109X-0.7637Y+0.4979Z+0.6449=0$

Co −0.0258 N1 0.0833 N2 0.1031 N3 −0.0913 O3 −0.0310

plane(2); $-0.7088X+0.0866Y+0.7001Z+0.7608=0$

Co 0.0110 N3 0.0326 O1 −0.0410 O3 0.0504 O4 −0.0442

plane(3); $-0.6434X-0.6255Y-0.4423Z+2.8790=0$

Co −0.0222 N1 −0.0544 N2 −0.0507 O1 0.0711 O4 0.0609

tfac(1); $0.2575X-0.8507Y+0.4582Z+0.9085=0$

N2 −0.0431 O3 0.0349 C6 −0.0220 C8 −0.0201 C9 0.0574

tfac(2); $0.5818X-0.6342Y-0.5092Z+1.4335=0$

N3 0.1242 O4 −0.0017 C13 −0.1535 C15 0.0365 C16 0.0198

met; $-0.6759X-0.5172Y-0.5251Z+2.8872=0$

N1 0.1280 O1 −0.0383 O2 0.0895 C1 −0.0110 C2 −0.1528

Dihedral angles between the planes:

plane(1)-tfac(1)	10.4°	plane(2)-plane(3)	84.7°
plane(1)-plane(2)	89.5°	plane(2)-tfac(1)	86.3°
plane(1)-plane(3)	89.6°	plane(2)-met	86.2°
plane(1)-tfac(2)	62.0°	plane(3)-met	8.1°
plane(1)-met	81.7°	plane(3)-tfac(1)	80.6°
plane(2)-tfac(2)	34.5°	plane(3)-tfac(2)	75.7°

N1-Co-O1 85.5(4)°, and for the tfac$_2$en, N2-Co-N3 83.4(5)° and N3-Co-O4 90.4(4)°, are approximately in agreement with those of the cobalt(III) complexes with α-Me-sal$_2$en and amino carboxylate.[9,10]

The angles among the planes of the three equatorial planes, plane(1)-plane(3), of the octahedron around the cobalt atom and the planes passing through tfac(1), tfac(2), and the L-met moieties are summarized in Table 4. These dihedral angles are affected by the highly strained conformational state about the coordinated ethylene ring, N2-C11-C12-N3, and the coordination geometry around the azomethine nitrogens, N2 and N3, as in the case of the cobalt(III) complexes with a quadridentate Schiff base.[7-10] In the present complex, however, the dihedral angle between plane(1) and tfac(1) is 10.4° and is smaller than the corresponding angles of [Co(salen)(acac)] (17.9°)[7] and [Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)](29.3°).[10] This seems to reflect the difference in the rigidity between the 1,1,1-trifluoro-4-imino-2-pentanonate and salicylideneaminate moieties.

Absorption and CD Spectra. The electronic absorption and CD spectra of $(-)_{435}$-Λ-cis-β_2-and $(+)_{435}$-[Co(tfac$_2$en)(L-met)] are shown in Fig. 2 and their data are summarized in Table 5. The absorption spectral behaviors of the $(-)_{435}$-Λ-cis-β_2 and $(+)_{435}$ isomers closely resemble each other, showing identical peaks at 17.24, 29.76, and 38.17×10^3 cm^{-1}. The $(-)_{435}$-Λ-cis-β_2 isomer exhibits four CD bands in the region of 14—35×10^3 cm^{-1}, corresponding to absorption peaks and shoulders as shown in Fig. 2. The $(+)_{435}$ isomer exhibits CD patterns that are almost enantiomeric relative to that of the $(-)_{435}$-Λ-cis-β_2 one. These facts indicate that the $(+)_{435}$ isomer can safely be assigned a Δ-cis-β_2 structure.

The configurational CD curve (Λ) and the vicinal CD curve (L) due to a coordinated L-met of the $(-)_{435}$-Λ-cis-β_2 isomer are shown in Fig. 2. These were calculated using the following equations:

$$(\mathrm{L}) = 1/2 \times \{\Delta\varepsilon(-) + \Delta\varepsilon(+)\}$$

$$(\Lambda) = 1/2 \times \{\Delta\varepsilon(-) - \Delta\varepsilon(+)\}$$

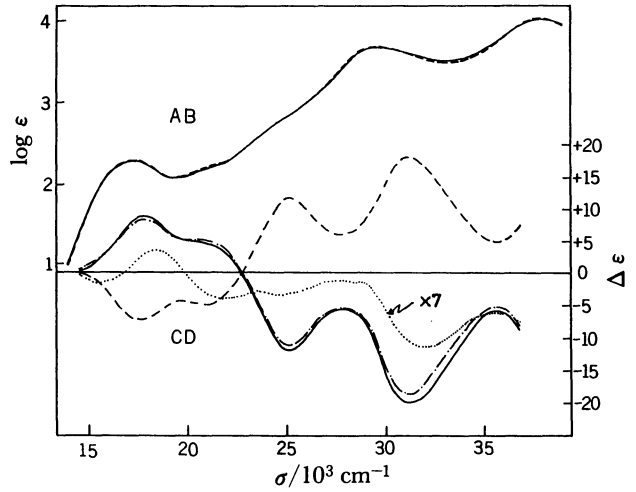

Fig. 2. Absorption and CD spectra of *cis*-β_2-[Co(tfac$_2$en)(L-met)] in DMF-$CHCl_3$ (1:4) mixture: $(-)_{435}$-*Λ*-*cis*-β_2 (——) and $(+)_{435}$-Δ-*cis*-β_2 (------). Two calculated CD curves of the vicinal (·····) and configurational (—·—·—·—) effects are also shown.

TABLE 5. ABSORPTION AND CD SPECTRAL DATA OF [Co(tfac$_2$en)(L-met)][a]

Isomer	Absorption maxima $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
	17.24 (2.31)	17.54 (+8.43)
$(-)_{435}$-Λ-cis-β_2	21.28 (2.21 sh[b])	20.83 (+4.15)
	24.50 (2.75 sh)	24.69 (−12.25)
	29.76 (3.69)	30.86 (−20.54)
	38.17 (4.08)	
	17.24 (2.33)	17.24 (−7.68)
$(+)_{435}$-Δ-cis-β_2	21.28 (2.23 sh)	20.83 (−5.26)
	24.50 (2.75 sh)	24.69 (+11.28)
	29.76 (3.71)	30.67 (+17.62)
	38.17 (4.10)	

a) Solvent; DMF-$CHCl_3$ (1:4) mixture. b) sh; shoulder.

where $\Delta\varepsilon(-)$ and $\Delta\varepsilon(+)$ denote the CD curves of the $(-)_{435}$ and $(+)_{435}$ isomers, respectively. The calculated configurational curve (Λ) shows almost the same pattern as the $(-)_{435}$-Λ-cis-β_2 isomer over the whole region and the positive CD sign in the first d-d absorption band region (Fig. 2). A similar configurational CD behavior has also been observed for the Λ-cis-β_2 isomers of cobalt(III) complexes with a sal$_2$en-type Schiff base and amino carboxylate.[5] The vicinal CD contribution (L) in the first d-d absorption band region is quite similar to those of sal$_2$en and α-Me-sal$_2$en cobalt(III) complexes with L-amino carboxylates chelated by their nitrogen and oxygen atoms (Fig. 2).[5] *This fact coincides with the results of the present* X-ray crystal analysis: (1) the coordinated atoms of L-met in [Co(tfac$_2$en)(L-met)] are nitrogen and oxygen and (2) the conformation of the N–O chelate ring of the coordinated L-met is quite similar to those of the L-amino carboxylates in α-Me-sal$_2$en complexes.[9,10]

It is interesting to note that the CD intensities in the d-d absorption band regions of Λ- or Δ-cis-β_2-[Co(tfac$_2$en)(L-met)](Fig. 2 and Table 5) are stronger than those of optically active cobalt(III) complexes with the linear quadridentate ligands such as ethylenediamine-*N*,*N*′-diacetate (edda) and its derivatives.[20] The absorption shoulder at 24.50×10^3 cm^{-1} and the CD band at 24.69×10^3 cm^{-1} seem to correspond to the second d-d absorption band due to their position and the absorption intensity (log ε=2.75). Also, the CD intensity is quite strong compared with that of cobalt(III) complexes with an edda-type ligand.[20] This intense CD band in the second d-d absorption band region seems to arise from a coordination of the alcoholic oxygen atoms of the Schiff base ligand to the cobalt(III) ion.[21] Such an increase of CD intensity has also been observed in the case of sal$_2$en-type complexes.[1,2,4,5]

The Λ- or Δ-cis-β_2 isomer of [Co(tfac$_2$en)(L-met)] exhibit an absorption band at 29.76×10^3 cm^{-1} and the CD band at *ca.* 30×10^3 cm^{-1} (Fig. 2). It has been known that the sal$_2$en-type complexes of Cu(II), Ni(II), Co(II), Co(III), and so on exhibit broad absorption bands and CD bands at *ca.* 30×10^3 cm^{-1} due to ligand π-π* transitions. This is mostly associated with an azomethine chromophore.[12–15] This suggests that the absorption and CD bands at *ca.* 30×10^3 cm^{-1} are assignable to the ligand π-π* transition due to azomethine moieties in the tfac$_2$en ligand. In the simple sal$_2$en-type complexes of Cu(II), Ni(II), Co(II), and Co(III), π-π* transitions split into two CD components with different signs due to the exciton interaction.[12–15] However, *Λ*- or *Δ*-*cis*-β_2-[Co(tfac$_2$en)(L-met)] exhibits only one CD band for this transition region and no exciton couplet was observed (Fig. 2). A similar trend was also observed for cis-β_2 type cobalt(III) complexes with a sal$_2$en-type Schiff base and bidentate ligands.[1–5] These facts suggest that the two azomethine moieties in *Λ*- or *Δ*-*cis*-β_2-[Co(tfac$_2$en)(L-met)] form a negligible dihedral angle which gives rise to non-zero components regarding the exciton interaction between them.

Properties. The $(-)_{435}$-Λ- and $(+)_{435}$-Δ-cis-β_2 isomers of [Co(tfac$_2$en)(L-met)] showed no mutarotation in *N*,*N*-dimethylformamide, dimethyl sulfoxide, and chloroform. However, they did exhibit mutarotation in methanol and showed the same optical rotation under equilibrium conditions (Fig. 3). The absorption spectral change during mutarotation was very small for each of the $(-)_{435}$-Λ- and $(+)_{435}$-Δ-cis-β_2 isomers and plots of ln $\alpha_\infty-\alpha_t$ *vs.* time for each mutarotation gave a straight line with the same slope ($k_{obsd}=9.50\times10^{-5}$ s^{-1}) up to at least 90% completion,[22] *where* α_t *and* α_∞ *denote the optical rotation at 435 nm* at time t and at equilibrium, respectively. Accordingly, it is obvious that the two isomers of *cis*-β_2-[Co(tfac$_2$en)(L-met)] isomerize in methanol to give a mixture of both isomers under equilibrium conditions. As shown in Fig. 4, the ^{1}H NMR spectra of the $(-)_{435}$

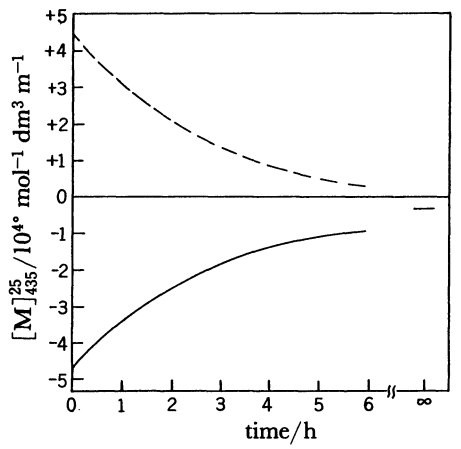

Fig. 3. Mutarotation of *cis*-β_2-[Co(tfac$_2$en)(L-met)] in CH_3OH at 25°C: $(-)_{435}$-*Λ-cis*-β_2 (——) and $(+)_{435}$-Δ-*cis*-β_2 (------).

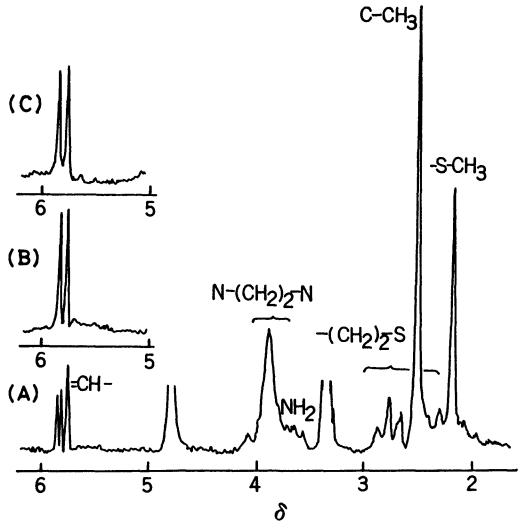

Fig. 4. ^{1}H NMR spectrum of *cis*-β_2-[Co(tfac$_2$en)(L-met)] in CD_3OD under equilibrium condition (A), and the C=CH signals of the $(-)_{435}$ (B) and $(+)_{435}$ (C) isomers soon after dissolution.

and $(+)_{435}$ isomers closely resemble each other except for the C=CH signal, supporting a similar geometrical structure to each other. From the intensity of the ^{1}H NMR signal for C=CH, the isomeric ratio in the equilibrium mixture, Λ-cis-β_2: Δ-cis-β_2, was estimated to be about 1:1. This ratio differs significantly from those in *cis*-β_2-[Co(sal$_2$en)(L-met)] (1.5:1) and *cis*-β_2-[Co(α-Me-sal$_2$en)(L-met)](2:1). This difference of diastereomeric stereoselectivity may be partly due to the flexibility of the β-imino ketone moieties as compared with those of salicylideneaminate. The $(-)_{435}$-Λ-cis-β_2 isomer was crystallized in high yield (*ca.* 80% for the total complex) from the solution, regardless of a 1:1 formation of the $(-)_{435}$-Λ- and $(+)_{435}$-Δ-cis-β_2 isomers under equilibrium conditions. Since the complex was labile in isomerization, the preferential crystallization of the $(-)_{435}$-Λ-cis-β_2 isomer could be safely ascribed to a thermodynamic origin. That is, a second-order asymmetric transformation from the Δ-cis-β_2 isomer to the Λ-cis-β_2 isomer due to the lower solubility of the latter. This kind of preferential crystallization is quite rare in cobalt(III) complexes.

In the case of [Co(tfac$_2$en)(L-met)], a cis-β_2 isomer was formed in the 100% regioselectivity as observed for the sal$_2$en-type Schiff base complexes.[1-5,9,10] Therefore, the regioselective behavior seems to be common in mixed cobalt(III) complexes with various kinds of quadridentate Schiff bases and amino carboxylate. It is fairly difficult, however, to explain the stereochemical reason for the high regioselectivity toward the cis-β_2 structure, *mer*(N_3O_3), as the corresponding cis-β_1 isomer, *fac*(N_3O_3), has not been found yet. It is probable that an electrostatic repulsion among three negatively charged oxygen atoms is much weaker in the *mer*(N_3O_3) configuration than in the *fac*(N_3O_3) configuration. Thus, the cis-β_2 isomer is thermodynamically more stable than the cis-β_1 isomer.[10]

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11) a) The cis-α and cis-β denote the trans(O) and cis(O) configurations of the coordinated quadridentate Schiff base ligand, respectively, when the remaining two coordination sites occupy the cis position. b) β_1 and β_2 refer to the two configurational isomers, *fac(N)* and mer(N), for the $[Co(N)_3(O)_3]$-type complex, as shown in Ref. 1—5, 8, and 9.

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