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Preparation and Characterization of Cobalt(III) Complexes with *S,S*-Bridge *R,S*-Sexidentate-N_2,S_2,O_2 Type Ligands. Crystal Structure of $(+)^{CD}_{560}$-((2*R*,9*S*)-Diamino-3,3,8,8-tetramethyl-4,7-dithia-1,10-decanedioato)cobalt(III) Ion

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[Co(*R,S*-sexidentate-N_2,S_2,O_2)] and [Co(*R*-terdentate-*N,S,O*)(*S-terdentate-N,S,O*)] type complexes, including the title complex cation, [Co(*R,S*-ebp)]$^+$, were prepared and resolved. The crystal structure and absolute configuration of the $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$ isomer were determined by X-ray diffraction. The complex cation has an [*S*] configuration. The *R,S*-ebp coordinates as a sexidentate, of which two sulfur donor atoms take selectively *R*(*S*). The absorption and CD spectra are discussed in comparison with those of the related complexes.

In a previous paper,[1] we reported the preparation, CD spectra, and stereochemistry of [Co(LL-sexidentate-N_2,S_2,O_2)] and [Co-(L-terdentate-*N,S,O*)$_2$] type complexes. Regarding the CD spectral analysis of these complexes, the CD contribution due to *S*(*C*) of the ligand was troublesome. This paper deals with the preparation and resolution of [Co(*R,S*-sexidentate-N_2,S_2,O_2)] type complex cations, [Co(OOCCH(NH$_2$)C(CH$_3$)$_2$S(CH$_2$)$_n$SC(CH$_3$)$_2$CH(NH$_2$)COO)]$^+$ (n=2, *R,S*-ebp; n=3, *R,S*-tbp; n=4, *R,S*-tetp),[2] and (*S*-methyl-*R*-penicillaminato)(*S*-methyl-*S*-penicillaminato)cobalt(III), [Co(*R*-smp)(*S*-smp)]$^+$, and with the X-ray crystal structure analysis of $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$. The reaction of *cis·cis·cis*-(*R*-penicillaminato)(*S*-penicillaminato)cobaltate(III),[3] [Co(*R*-pen)(*S*-pen)]$^-$, with Br(CH$_2$)$_n$Br (n=2, 3, and 4) spanned with ethylene, trimethylene, or tetramethylene the thiolato type sulfur donor atoms of the *R*- and *S*-pen to give an *R,S*-ebp, *R,S*-tbp, or *R,S*-tetp complex. The reaction of *cis·cis·cis*-[Co(*R*-pen)(*S*-pen)]$^-$ with dimethyl sulfate gave *cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$, and the oxidation reaction of a cobalt(II) ion with the *R*- and *S*-smp gave *cis·cis·cis*- and *trans·trans·trans*-[Co(*R*-smp)(*S*-smp)]$^+$. The *cis·cis·cis* isomers of the above complexes were resolved into their optical isomers, which can be designated as [*R*] and [*S*] based on the chiral arrangement of the coordinated atoms.[4]

Experimental

1) Preparation of the Ligand. *a) S*-Methylpenicillamine was prepared by a procedure similar to that used for *S*-benzylpenicillamine.[5] Found: C, 44.95; H, 8.20; N, 9.36%. Calcd for $C_6H_{13}NO_2S$: C, 44.14; H, 8.02; N, 8.58%.

2) Preparation and Resolution of Complexes. *b) [Co(*R,S*-ebp)]Br.* An excess (5 cm^3) of 1,2-dibromoethane was added to a solution containing 0.8 g of *cis·cis·cis*-K[Co(*R*-pen)(*S*-pen)]·2H$_2$O[3] in 14 cm^3 of dimethyl sulfoxide. The mixture was stirred at room temperature for a few minutes and allowed to stand for about 1 d. The color of the solution changed from green to dark-red, and then to a deep-red. Dimethyl sulfoxide and unreacted 1,2-dibromoethane were extracted with ether several times. To the remaining dark-red solution a small amount of water was added. This solution was then poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 4.0 cm×25 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} aqueous solution of NaBr. Only one red-violet band was eluted and fractionated. It was found, from the absorption spectral measurements, that all the eluates contained only [Co(*R,S*-ebp)]$^+$. The eluates were combined and concentrated to a small volume with a rotary evaporator at a temperature below 25 °C. The deposited NaBr was filtered off. The filtrate was poured onto a column of Sephadex G-10 (3.0 cm×85 cm) and eluted with water. The eluate was concentrated to a small volume again and an appropriate amount of ethanol was added to the solution. The resulting red-violet crystals were collected by filtration, recrystallized from water by adding ethanol, and washed with ethanol and ether. Found: C, 27.21; H, 5.65; N, 5.28%. Calcd for [Co(*R,S*-ebp)]Br·4H$_2$O=CoC$_{12}$H$_{22}$N$_2$O$_4$S$_2$Br·4H$_2$O: C, 27.02; H, 5.65; N, 5.25%.

To a solution containing 86 mg of the racemic [Co(*R,S*-ebp)]Br·4H$_2$O and 32.4 mg of $(+)_{546}$-K[Co(edta)]·2H$_2$O[6] (edta; ethylenediaminetetraacetate) in a small amount of water were added 14 mg of silver acetate and 17 mg of silver perchlorate. After the mixture was stirred for 10 min, the precipitated silver bromide and potassium perchlorate were filtered off. After the filtrate had been concentrated to a small volume, the concentrated solution, to which was added a small amount of ethanol, was kept in a refrigerator for 5 d. The less-soluble diastereomer (violet needle crystals) was recrystallized from water by adding ethanol. A piece of a crystal was used for an X-ray diffraction study. By use of the anion exchange column (Br$^-$ form), the diastereomer was converted into the bromide salt, $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]Br. The $\Delta\varepsilon$ values were evaluated from the absorption spectral data.

*c) [Co(*R,S*-tbp)]Br.* The $(-)^{CD}_{560}$-[Co(*R,S*-tbp)]$^+$ complex was prepared and resolved by a procedure similar to that used for [Co(*R,S*-ebp)]Br described in *b)*, using 1,3-dibromopropane instead of 1,2-dibromoethane. Found for the *R,S*-tbp complex: C, 30.79; H, 5.48; N, 5.50%. Calcd for [Co(*R,S*-tbp)]Br·2H$_2$O=CoC$_{13}$H$_{24}$N$_4$O$_4$S$_2$Br·2H$_2$O: C, 30.54; H, 5.52; N, 5.28%. Found for the less-soluble diastereomer: C, 35.05; H, 4.95; N, 6.91%. Calcd for [Co(*R,S*-tbp)][Co(edta)]·2.5H$_2$O=Co$_2$C$_{23}$H$_{36}$N$_6$O$_{12}$S$_2$·2.5H$_2$O: C, 35.07; H, 5.25; N, 7.11%.

The bromide salt was obtained by the same procedure as in *b)* and the $\Delta\varepsilon$ values were also evaluated from the absorption spectral data.

*d) [Co(*R,S*-tetp)]Br.* The $(+)^{CD}_{560}$-[Co(*R,S*-tetp)]$^+$ complex was prepared and resolved by a procedure similar to that used for [Co(*R,S*-ebp)]Br as in *b)*, using 1,4-dibromobutane instead of 1,2-dibromoethane, and $(-)_{546}$-K[Co(edta)]·2H$_2$O as resolving agent. Found for the *R,S*-tetp complex: C, 32.55; H, 5.41; N, 5.41%. Calcd for [Co(*R,S*-tetp)]Br·

$1.5H_2O=CoC_{14}H_{26}N_2O_4S_2Br \cdot 1.5H_2O$: C, 32.56; H, 5.65; N, 5.42%. The bromide salt and the $\Delta\varepsilon$ values were obtained by the same procedure as in *b)*.

Here, it is noted that for the *S,S*-bridge complex, the [*S*]-$(+)^{CD}_{560}$ *R,S*-ebp isomer forms the less-soluble diastereomer with $(+)_{546}$-[Co(edta)]$^-$, whereas the [*R*]-$(-)^{CD}_{560}$ *R,S*-tbp isomer forms the less-soluble diastereomer with $(+)_{546}$-[Co(edta)]$^-$ and the [*S*]-$(+)^{CD}_{560}$ *R,S*-tetp isomer with $(-)_{546}$-[Co(edta)]$^-$.

*e) [Co(*R*-smp)(*S*-smp)]NO$_3$.* *Method 1.* This complex was prepared by a procedure similar to that used for [Co(*R*-smp)(dien)]$^{+}$ 7) and [Co(*S*-smp)$_2$]$^+$,8) namely, *cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$ was obtained by the reaction of the coordinated thiolato type donor atoms of *cis·cis·cis*-[Co(*R*-pen)(*S*-pen)]$^-$ 3) with dimethyl sulfate. It was confirmed using a cation exchange column chromatography (Dowex 50W-X8, 200—400 mesh, Na$^+$ form, 3.5 cm×20 cm) that no isomerization had taken place. Found: C, 29.60; H, 5.77; N, 8.60%. Calcd for [Co(*R*-smp)(*S*-smp)]NO$_3 \cdot 2.5H_2O$ $=CoC_{12}H_{24}N_3O_7S_2 \cdot 2.5H_2O$: C, 29.39; H, 5.96; N, 8.57%.

Method 2. The [Co(*R*-smp)(*S*-smp)]$^+$ complex was also prepared by a procedure similar to that used for [Co(L-met)$_2$]$^+$,9) using *S*-methylpenicillamine instead of L-methionine. The reaction mixture was filtered to remove any insoluble material. The filtrate was allowed to stand at room temperature overnight and was then poured onto a column of Dowex 50W-X8 (200—400 mesh, Na$^+$ form, 3.5 cm×60 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of NaCl. Three colored bands, dark-violet (F-1), reddish violet (F-2), and violet (F-3), were eluted in this order and were in the ratio of about F-1:F-2:F-3=1:5:3. From their absorption spectral measurements, it was found that F-1 and F-2 eluates contained *trans·trans·trans*- and *cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$ isomers, respectively. The F-3 eluate showed the same spectrum as the *trans*(*S*)-[Co(*S*-smp)$_2$]$^+$ isomer,8) but did not exhibit the optical activity, indicating it was a mixture of *trans*(*S*)-[Co(*S*-smp)$_2$]$^+$ and *trans*(*S*)-[Co(*R*-smp)$_2$]$^+$. Each of the F-1 and F-2 eluates was concentrated to a small volume with a rotary evaporator at a temperature of about 20 °C. The deposited NaCl was filtered off. As the amount of the earlier eluate (F-1) was very small, it could not be obtained as in crystal form. The absorption spectrum of the *trans·trans·trans*-[Co(*R*-smp)(*S*-smp)]$^+$ was measured with the solution and it is illustrated with an arbitrary scale in Fig. 3.

The F-2 eluate, which showed the same absorption spectrum as that in *Method 1*, was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3.0 cm×90 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.03 mol dm^{-3} aqueous solution of K$_2$[Sb$_2$(*d*-tart)$_2$]·3H$_2$O. After circulating the eluates in the same column two times, they separated into two reddish violet bands and fractionated. Each of the fractions was concentrated to a small volume with a rotary evaporator at a temperature of about 20 °C and the deposited K$_2$[Sb$_2$(*d*-tart)$_2$] was filtered off. The filtrate was converted into the bromide salt using a column of QAE-Sephadex A-25 (Br$^-$ form) and the CD spectra were measured with its solutions. The earlier eluate contained $(-)^{CD}_{560}$-*cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$ and the later contained $(+)^{CD}_{560}$ one. The $\Delta\varepsilon$ values were also evaluated from the absorption spectral data.

3) 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 in aqueous solutions at room temperature. The calculations were carried out on a FACOM M-200 computer at University of Tsukuba.

4) X-Ray Characterization. The unit cell parameters and intensity data for the single crystal (*ca.* 0.12×0.18×0.35 mm^3) were measured on a Rigaku-denki automated 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 38 reflections. The systematic absence led to the space group $P2_12_12_1$. Crystal data: $Co_2C_{22}H_{44}N_4O_{17}S_2$, *M.W.*=818.6, orthorhombic, space group $P2_12_12_1$, a=13.215(5), b=37.035(12), c=6.527(2) Å, V=3194.1(18) Å^3, D_m=1.72 g cm^{-3} (by the flotation), D_x= 1.70 g cm^{-3}, Z=4, and μ(Mo $K\alpha$)=12.9 cm^{-1}.

Intensity data up to $2\theta=60°$ were collected by the ω-2θ scan technique with a scan rate of 3° min^{-1}. During the course of the data collection, three reflections were monitored every 40 reflections. The intensity data were converted into F_o data in the usual manner. Absorption corrections were not applied. A total of 2322 independent reflections with $|F_o|>3\sigma(|F_o|)$ was observed and used for the structure analysis.

5) Determination of the Crystal Structure. The positions of two cobalt atoms were obtained from the three dimensional Patterson function. The difference Fourier maps, based on the cobalt positions, 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 used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.10) The final R value converged to 0.088. The absolute configuration could not be determined by the anomalous scattering technique, using Cu $K\alpha$ radiation, but it was determined on the basis of the known configuration of the $(+)_{546}$-[Co(edta)]$^-$.6) The final atomic parameters with their estimated standard deviations are given in Table 1. A list of structure factors, anisotropic thermal parameters of non-hydrogen atoms, and the projected figure of the crystal structure, which indicated distance in the range of 2.63—3.02 Å, are kept at the Chemical Society of Japan as Document No. 8446.

Results and Discussion

Description of the Structure. The perspective drawings of the complex cation and anion are given in Figs. 1 and 2, respectively, together with their numbering scheme. The bond lengths and angles with their estimated standard deviations in the complex ions are listed in Table 2. The cobalt atom in the complex cation is surrounded by two *cis* sulfur, two *cis* oxygen, and two *cis* nitrogen atoms, and the *R,S*-ebp coordinates to cobalt atom as a sexidentate. The [Co(*R,S*-ebp)]$^+$ complex, was resolved into the optical isomers, which are designated as [*R*] and [*S*] configurations based on the chiral arrangement of the coordinated atoms.4) The absolute configuration of the $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$ isomer was determined to be the [*S*] configuration (Fig. 1) on the basis of the known configuration, Δ, of the $(+)_{546}$-[Co(edta)]$^-$ (Fig. 2).6) Both of the chiral sulfur donor atoms take selectively the *R*(*S*)4) configuration and the *S,S*-bridged five-membered chelate ring has a gauche form with the λ conformation (Fig. 1 and Table 3). The remaining chelate rings of the $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$ isomer show similar conformations to those of the cobalt(III) complexes having the same framework as the penicillamine moiety.3,11—13) The bond lengths and angles for the $(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$ isomer are quite similar to those of the parent complex, *cis·cis·cis*-[Co(R-pen)(S-pen)]$^-$.[3] These facts suggest that the two sulfur atoms of the parent complex anion react with 1,2-dibromoethane to give an S,S-bridged five-membered ring without any strain. It is noted that the Co–S bond lengths of 2.199(7) and 2.221(8) Å for the $(+)^{\rm CD}_{560}$ R,S-ebp isomer are significantly shorter than those of the thioether type complexes such as *trans*(S)-bis(S-methyl-L-cysteinato)cobalt(III)[11] and *trans*(O)-N,N'-ethylenebis(S-methyl-L-cysteinato)cobalt(III),[12] which have a similar framework to the penicillamine moiety of the R,S-ebp.

Table 1. Positional and thermal parameters ($\times 10^4$)

Atom	x	y	z	$B_{\rm eq}$/Å^2 a)
Co1	2083(2)	2248(1)	439(5)	1.65
Co2	1272(2)	4203(1)	1689(5)	1.94
N1	1433(12)	1893(5)	2190(29)	1.90
N2	3126(14)	2325(5)	2469(28)	2.24
N3	2072(14)	3765(5)	1429(29)	2.12
N4	−43(15)	4003(5)	2558(32)	2.50
S1	1933(4)	4191(2)	4781(9)	2.13
S2	573(5)	4740(2)	2224(11)	2.70
O1	1206(11)	2599(4)	1551(24)	2.44
O2	−64(12)	2679(5)	3767(30)	4.11
O3	1047(10)	2086(4)	−1461(25)	2.05
O4	469(12)	1545(5)	−2461(28)	3.97
O5	2717(11)	2643(4)	−994(22)	2.57
O6	3569(12)	3152(5)	−277(31)	3.78
O7	2952(12)	1889(4)	−724(24)	2.28
O8	4510(13)	1649(4)	−368(30)	3.69
O9	2434(12)	4450(4)	506(27)	2.80
O10	4009(14)	4326(5)	−418(30)	3.93
O11	662(12)	4176(5)	−997(25)	2.87
O12	−850(14)	4127(6)	−2496(28)	4.58
C1	521(16)	2477(6)	2857(36)	1.81
C2	550(16)	2061(6)	3170(42)	2.07
C3	886(16)	1741(8)	−1179(43)	2.97
C4	1158(21)	1584(6)	898(36)	2.93
C5	3200(17)	2858(6)	218(39)	2.29
C6	3290(18)	2738(7)	2417(36)	2.81
C7	3818(20)	1872(6)	89(38)	2.68
C8	4093(17)	2155(6)	1725(41)	2.65
C9	2257(19)	1803(7)	3811(34)	3.03
C10	2726(17)	2162(7)	4444(35)	2.69
C11	1954(19)	4673(6)	5300(41)	3.07
C12	831(19)	4783(7)	4999(37)	3.21
C13	3219(18)	4254(7)	400(41)	2.46
C14	3127(17)	3920(7)	1752(41)	2.67
C15	3250(16)	4026(7)	4112(37)	2.73
C16	3416(17)	3679(6)	5379(44)	2.71
C17	4080(21)	4317(9)	4419(43)	4.63
C18	4639(17)	846(7)	930(45)	2.90
C19	−754(16)	4202(8)	1264(32)	2.33
C20	−813(17)	4620(8)	1791(49)	3.52
C21	−1400(20)	4667(7)	3800(41)	3.80
C22	−1165(19)	4851(7)	30(39)	3.38
O21	940(13)	3340(5)	4176(27)	3.85
O22	2080(17)	813(7)	3022(39)	8.07
O23	1052(15)	533(7)	−98(44)	8.28
O24	6738(16)	4048(6)	3036(40)	6.67
O25	6306(13)	1727(5)	1707(27)	3.46

a) $B_{\rm eq}$ is the equivalent isotropic temperature factors defined by Hamilton.[16]

The bond lengths and angles in the $(+)_{546}$-[Co(edta)]$^-$ isomer agree well with the data for [Co(sarmp)(NH$_3$)$_3$]·$(+)_{546}$-[Co(edta)] (sarmp; N-(2-carboxyethyl)-sarcosinate) (Table 2).[6] The crystal structure consists of the complex cations and anions, and water molecules. The several hydrogen bonds are recognized between the complex ions and/or water molecules (Fig. A).

Absorption and CD Spectra. The electronic absorption and CD spectra of the non-bridge complex, [Co(R-smp)(S-smp)]$^+$, and the S,S-bridge complexes, [Co(R,S-ebp)]$^+$, [Co(R,S-tbp)]$^+$, and [Co(R,S-tetp)]$^+$, are shown in Figs. 3 and 4, and their spectral data are summarized in Table 4. Two geometrical isomers, *cis·cis·cis* and *trans·trans·trans*, are possible for the non-bridge complex, [Co(R-smp)(S-smp)]$^+$. In the first absorption band region, the F-1 isomer exhibits well separated two absorption components, while the F-2 isomer exhibits a sharp band (Fig. 3 and Table 4). These absorption spectral patterns indicate that the F-1 isomer takes the *trans·trans·trans* configuration and the F-2 isomer takes the *cis·cis·cis* configuration.

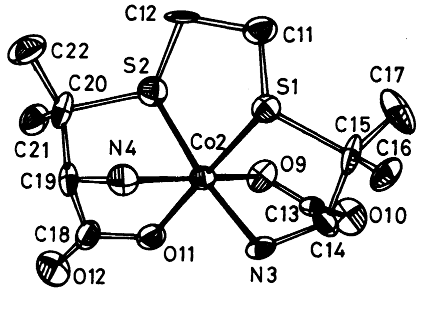

Fig. 1. A perspective drawing of [S]-$(+)^{\rm CD}_{560}$-[Co(R,S-ebp)]$^+$ with the numbering scheme of atoms.

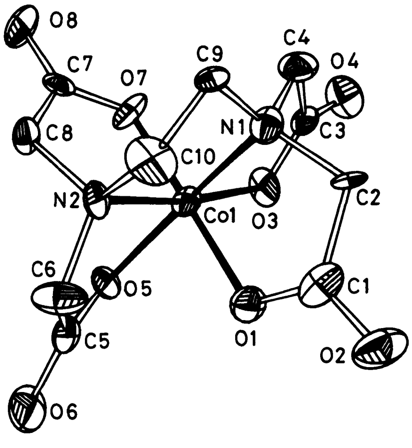

Fig. 2. A perspective drawing of Δ-$(+)_{546}$-[Co(edta)]$^-$ with the numbering scheme of atoms.

Furthermore, the maximum positions of their thioether charge transfer bands ($29.59\times10^3\,cm^{-1}$ for F-1 and $32.95\times10^3\,cm^{-1}$ for F-2) also support the geometries which *trans(S)* is for F-1 isomer and *cis(S)* for F-2 one. These absorption spectra agree well with those of $[Co(aeta)_2]^+$ and $[Co(aetp)_2]^+$ (aeta; (2-aminoethylthio)acetate and aetp; 3-(2-aminoethylthio)propionate).[14] All the *S,S*-bridge complexes exhibit similar absorption spectral patterns over the whole region to that of the *cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$ isomer, indicating the same geometrical arrangements with respect to the coordinated atoms. The *R,S*-ebp, *R,S*-tbp, and *R,S*-tetp complexes exhibit a sharp first absorption band at *ca.* $19\times10^3\,cm^{-1}$, regardless of their *S,S*-bridged backborn rings (five-, six-, and seven-membered ones, respectively). On the contrary, the absorption maxima of the sulfur-to-metal charge tansfer bands are shifted to lower energy in the order of *R,S*-ebp>*R,S*-tbp>*R,S*-tetp≈non-bridge complex, as shown in Figs. 3 and 4, and Table 4. This order seems to run parallel to the rigidity of the *S,S*-bridged backborn rings.

The $(+)^{CD}_{560}$-[Co(*R,S*-tbp)]$^+$ and $(+)^{CD}_{560}$-[Co(*R,S*-tetp)]$^+$ isomers exhibit quite similar CD spectral patterns over the whole region to that of [*S*]-$(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$, accordingly, it is assigned that the $(+)^{CD}_{560}$ *R,S*-tbp and $(+)^{CD}_{560}$ *R,S*-tetp isomers also take an [*S*] configuration, respectively. Similarly, the $(+)^{CD}_{560}$-*cis·cis·cis*-[Co(*R*-smp)(*S*-smp)]$^+$ isomer can be tentatively assigned to an [*S*] configuration by comparing its CD spectrum with that of the [*S*]-$(+)^{CD}_{560}$-[Co(*R,S*-ebp)]$^+$ isomer, though a little difference from that of the *R,S*-ebp isomer is observed (Fig. 3).

In order to estimate the absolute configuration of

TABLE 2. INTERMOLECULAR DISTANCES AND BOND ANGLES (WITH e.s.d.'s)

(a) Bond distances (l/Å)			
[Co(edta)]$^-$:			
Co1–N1	1.942(18)	Co1–N2	1.932(18)
Co1–O1	1.886(15)	Co1–O3	1.943(15)
Co1–O5	1.928(15)	Co1–O7	1.915(15)
N1–C2	1.47(3)	N1–C4	1.47(3)
N1–C9	1.55(3)	N2–C6	1.54(3)
N2–C8	1.51(3)	N2–C10	1.52(3)
O1–C1	1.32(3)	O2–C1	1.23(3)
O3–C3	1.31(3)	O4–C3	1.24(3)
O5–C5	1.29(3)	O6–C5	1.24(3)
O7–C7	1.26(3)	O8–C7	1.27(3)
C1–C2	1.56(3)	C3–C4	1.52(4)
C5–C6	1.51(4)	C7–C8	1.54(4)
C9–C10	1.52(4)		
[Co(*R,S*-ebp)]$^+$:			
Co2–S1	2.199(7)	Co2–S2	2.221(8)
Co2–N3	1.944(18)	Co2–N4	1.972(20)
Co2–O9	1.945(16)	Co2–O11	1.933(16)
S1–C11	1.82(2)	S1–C15	1.89(2)
S2–C12	1.85(3)	S2–C20	1.91(2)
N3–C14	1.52(3)	N4–C19	1.46(3)
O9–C13	1.27(3)	O10–C13	1.20(3)
O11–C18	1.36(3)	O12–C18	1.21(3)
C11–C12	1.55(4)	C13–C14	1.52(4)
C14–C15	1.60(4)	C15–C16	1·54(4)
C15–C17	1.55(4)	C18–C19	1.53(4)
C19–C20	1.59(4)	C20–C21	1.53(4)
C20–C22	1.51(4)		
(b) Bond angles (ϕ/°)			
[Co(edta)]$^-$:			
N1–Co1–N2	90.7(8)	N1–Co1–O1	88.2(7)
N1–Co1–O3	81.6(7)	N1–Co1–O5	172.5(7)
N1–Co1–O7	91.6(7)	N2–Co1–O1	94.2(7)
N2–Co1–O3	170.3(7)	N2–Co1–O5	84.9(7)
N2–Co1–O7	86.9(7)	O1–Co1–O3	91.5(7)
O1–Co1–O5	86.1(7)	O1–Co1–O7	178.8(7)
O3–Co1–O5	103.4(7)	O3–Co1–O7	87.4(7)
O5–Co1–O7	94.3(6)	Co1–N1–C2	108.8(13)
Co1–N1–C4	107.4(14)	Co1–N1–C9	103.6(13)
Co1–N2–C6	103.4(13)	Co1–N2–C8	108.8(14)
Co1–N2–C10	106.0(13)	Co1–O1–C1	115.7(14)
Co1–O3–C3	109.1(14)	Co1–O5–C5	112.6(14)
Co1–O7–C7	114.2(15)	O1–C1–C2	113.9(19)
O1–C1–O2	122.2(21)	O2–C1–C2	123.8(21)
N1–C2–C1	112.4(18)	O3–C3–O4	123.3(24)
O3–C3–C4	117.4(22)	O4–C3–C4	119.1(24)
N1–C4–C3	105.9(19)	O5–C5–O6	125.2(23)
O5–C5–C6	116.2(20)	O6–C5–C6	118.6(22)
N2–C6–C5	107.6(19)	O7–C7–O8	125.8(22)
O7–C7–C8	118.2(20)	O8–C7–C8	115.9(21)
N2–C8–C7	107.9(18)	N1–C9–C10	106.5(18)
N2–C10–C9	105.0(18)		
[Co(*R,S*-ebp)]$^+$:			
S1–Co2–S2	92.2(3)	S1–Co2–N3	81.2(6)
S1–Co2–N4	94.5(6)	S1–Co2–O9	93.5(6)
S1–Co2–O11	175.7(6)	S2–Co2–N3	170.9(6)
S2–Co2–N4	85.6(6)	S2–Co2–O9	88.3(5)
S2–Co2–O11	90.9(5)	N3–Co2–N4	101.0(7)
N3–Co2–O9	85.9(7)	N3–Co2–O11	96.0(8)
N4–Co2–O9	170.2(8)	N4–Co2–O11	82.7(8)
O9–Co2–O11	89.6(7)	Co2–S1–C11	99.0(9)
Co2–S1–C15	99.2(8)	Co2–S2–C12	98.9(8)
Co2–S2–C20	99.7(9)	Co2–N3–C14	99.9(13)
Co2–N4–C19	102.2(14)	Co2–O9–C13	113.5(15)
Co2–O11–C18	113.0(16)	S1–C11–C12	102.7(16)
S2–C12–C11	106.1(17)	O9–C13–O10	127.5(24)
O9–C13–C14	111.5(21)	O10–C13–C14	120.4(22)
N3–C14–C13	107.4(19)	C13–C14–C15	110.5(21)
N3–C14–C15	108.6(18)	S1–C15–C14	102.0(14)
S1–C15–C16	106.0(15)	S1–C15–C17	113.3(18)
C14–C15–C16	109.0(21)	C14–C15–C17	111.5(20)
C16–C15–C17	114.1(20)	O11–C18–O12	120.6(24)
O11–C18–C19	111.1(21)	O21–C18–C19	128.0(21)
N4–C19–C18	105.3(19)	N4–C19–C20	113.4(19)
C18–C19–C20	109.4(22)	S2–C20–C19	102.2(15)
S2–C20–C21	109.4(19)	S2–C20–C22	106.1(18)
C19–C20–C21	108.7(21)	C19–C20–C22	113.8(23)
C21–C20–C22	115.6(21)		

the sulfur donor atom in the present complexes, the ^{1}H and ^{13}C NMR spectra of the S,S-bridge complexes and *cis·cis·cis*-[Co(R-smp)(S-smp)]$^+$ isomer were measured. The ^{13}C NMR spectrum of the [S]-$(+)^{CD}_{560}$-[Co(R,S-ebp)]$^+$ isomer, which takes selectively $R(S)_D$,R-$(S)_L$ configuration,[15] exhibits the eleven resonance lines for the twelve carbon atoms (Fig. 5). Similar ^{13}C NMR spectral behavior is observed for the [R]-

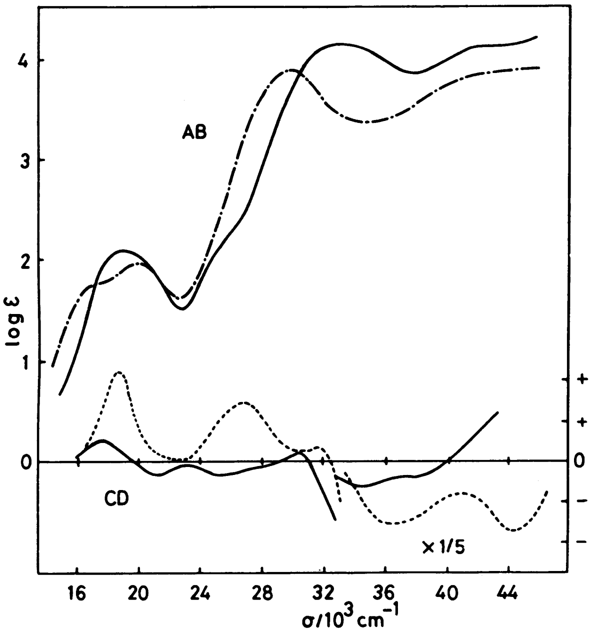

Fig. 3. Absorption and CD spectra of [Co(R-smp)(S-smp)]$^+$: *trans·trans·trans* (—·—) and $(+)^{CD}_{560}$-*cis·cis·cis* (——), together with CD spectrum of $(+)^{CD}_{560}$-[Co(R,S-ebp)]$^+$ (----).

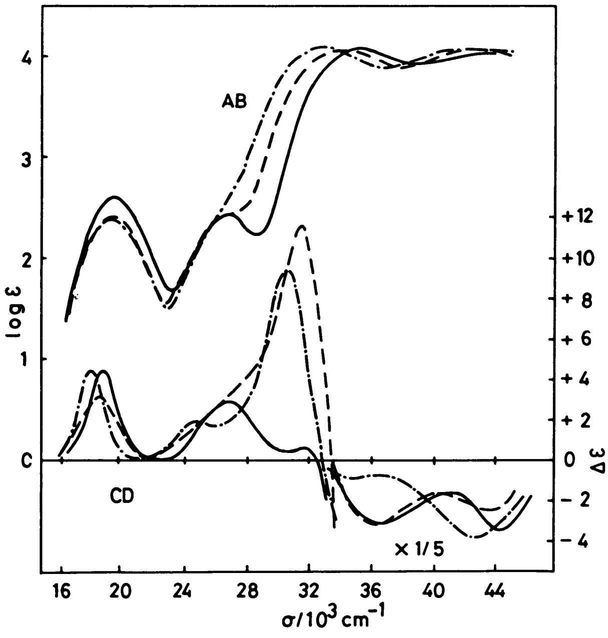

Fig. 4. Absorption and CD spectra of $(+)^{CD}_{560}$-[Co(R,S-ebp)]$^+$ (——), $(+)^{CD}_{560}$-[Co(R,S-tbp)]$^+$ (----), and $(+)^{CD}_{560}$-[Co(R,S-tetp)]$^+$ (—·—).

TABLE 3. DISPLACEMENTS OF ATOMS FROM THE LEAST-SQUARES PLANE (d/Å) FOR [Co(R,S-ebp)]$^+$ ION

Plane 1. *S–S* chelate ring (five-membered ring)					
$-0.8256X-0.4444Y+0.3477Z+7.9228=0$					
Co2	0.000	S 1	0.000	S 2	0.000
C 11	−0.698	C 12	0.278		
Plane 2. *N–S* chelate ring					
$-0.7766X-0.5401Y+0.3244Z+9.3553=0$					
Co2	0.000	S 1	0.000	N 3	0.000
C 14	−1.324	C 15	−1.162	C 16	−0.371
C 17	−2.531				
Plane 3. *N–S* chelate ring					
$-0.3174X+0.0190Y-0.9481Z+1.2833=0$					
Co2	0.000	S 2	0.000	N 4	0.000
C 19	1.113	C 20	0.842	C 21	−0.152
C 22	2.095				
Plane 4. *N–O* chelate ring					
$-0.3732X--0.1475Y-0.9159Z+3.9343=0$					
Co2	0.001	N 3	0.001	O9	0.000
O10	−0.157	C 13	−0.217	C 14	−0.797
Plane 5. *N–O* chelate ring					
$0.3581X-0.9270Y-0.1116Z+13.9501=0$					
Co2	0.000	N 4	0.000	O 11	0.000
O12	−0.440	C 18	−0.415	C 19	−0.925

TABLE 4. ABSORPTION AND CD SPECTRAL DATA OF [Co(R,S-sexidentate-N_2,S_2,O_2)] AND [Co(R-smp)(S-smp)]$^+$ COMPLEXES

Complex ion	Absorption maxima σ/10³ cm⁻¹ (log ε/ mol⁻¹ dm³ cm⁻¹)	CD extrema σ/10³ cm⁻¹ (Δε/ mol⁻¹ dm³ cm⁻¹)
$(+)^{CD}_{560}$-[Co(R,S-ebp)]$^+$	19.23 (2.63)	18.52 (+4.51)
	26.67 (2.45)	26.67 (+3.06)
	35.09 (4.09)	31.75 (+0.68)
	44.44 (4.08)	36.36 (−16.2)
		44.44 (−18.0)
$(-)^{CD}_{560}$-[Co(R,S-tbp)]$^+$	19.31 (2.43)	18.35 (−3.17)
	26.7 (2.44 sh)	31.45 (−11.7)
	33.90 (4.08)	35.97 (+16.1)
	42.55 (4.08)	43.86 (+13.1)
$(+)^{CD}_{560}$-[Co(R,S-tetp)]$^+$	19.12 (2.39)	17.89 (+4.45)
	24.7 (1.96 sh)	24.69 (+1.95)
	32.79 (4.08)	30.53 (+9.60)
	42.02 (4.05)	34.97 (−4.71)
		42.74 (−19.2)
$(+)^{CD}_{560}$-*cis·cis·cis*-	18.94 (2.09)	17.92 (+1.00)
[Co(R-smp)(S-smp)]$^+$	25.4 (2.14 sh)	20.96 (−0.60)
	32.95 (4.14)	25.32 (−0.75)
	42.74 (4.18)	30.30 (+0.47)
		34.36 (−6.82)
		38.17 (−3.88)
		45.45 (+15.8)
trans·trans·trans-	16.7 (—— sh)	
[Co(R-smp)(S-smp)]	19.80 (——)	
	29.59 (——)	
	42.92 (——)	

Sh denotes a shoulder.

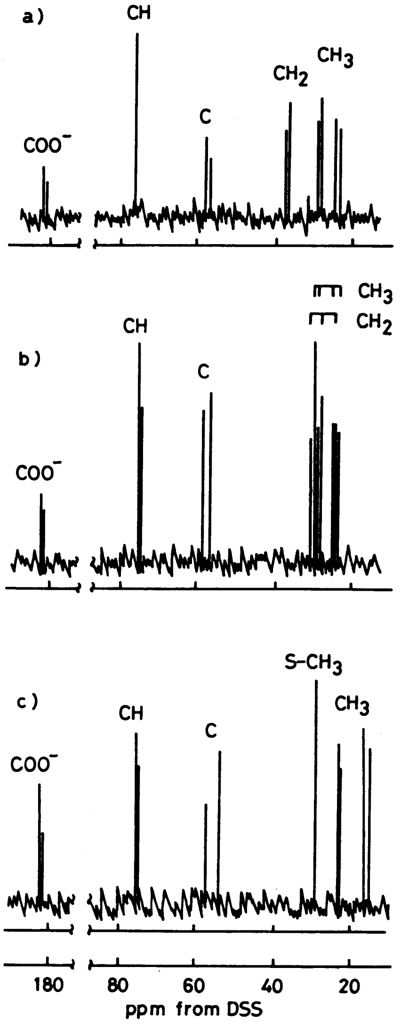

Fig. 5. ^{13}C NMR spectra of the complexes: (a) $(+)^{CD}_{560}$-$[Co(R,S\text{-ebp})]^+$, (b) $(-)^{CD}_{560}$-$[Co(R,S\text{-tbp})]^+$, and (c) $(-)^{CD}_{560}$-*cis*·*cis*·*cis*-$[Co(R\text{-smp})(S\text{-smp})]^+$.

$(-)^{CD}_{560}$-$[Co(R,S\text{-tbp})]^+$ (thirteen lines for thirteen carbons) and $[R]$-$(-)^{CD}_{560}$-*cis*·*cis*·*cis*-$[Co(R\text{-smp})(S\text{-smp})]^+$ (eleven lines for twelve carbons) isomers, as shown in Fig. 5. Further, the ^{1}H NMR spectrum of the $(-)^{CD}_{560}$-*cis*·*cis*·*cis*-$[Co(R\text{-smp})(S\text{-smp})]^+$ isomer shows two sharp signals (2.27 and 2.03 ppm) due to the *S*-methyl protons. Stereomodel examination elucidates these results as follow; namely, the $S(S)_D,S(S)_L$ configuration is assigned for $[R]$-$(-)^{CD}_{560}$-$[Co(R,S\text{-tbp})]^+$. The $R(S)_D$, $S(S)_L$ configuration is probable for the $[R]$-$(-)^{CD}_{560}$-*cis*·*cis*·*cis*-$[Co(R\text{-smp})(S\text{-smp})]^+$ isomer because of the steric interaction between the two *S*-methyl groups, though an $S(S)_D,S(S)_L$ configuration is also possible for the isomer. The CD spectrum of the $(+)^{CD}_{560}$-*cis*·*cis*·*cis*-$[Co(R\text{-smp})(S\text{-smp})]^+$ isomer, which was assigned to the same $[S]$ configuration as the $(+)^{CD}_{560}$ *R,S*-ebp isomer, differs partially from that of the latter, as mentioned above. A similar difference was observed between the CD spectra of the *trans(O)*-$[Co(\text{L-smp})_2]^+$ and *trans(O)* *S,S*-bridge isomers, *trans(O)*-$[Co(\text{LL-sexidentate-}N_2,S_2,O_2)]$.$^{1)}$ Taking the results from the ^{1}H and ^{13}C NMR spectral behavior of the present isomers into consideration, it is possible to consider that the difference is related to the additional CD contribution due to the fixation of two sulfur donor atoms located in the *cis* position.

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2) The abbreviations of the ligands are as follows: *R,S*-ebp=(2*R*,9*S*)-diamino-3,3,8,8-tetramethyl-4,7-dithia-1,10-decanedioate, *R,S*-tbp=(2*R*,10*S*)-diamino-3,3,9,9-tetramethyl-4,8-dithia-1,11-undecanedioate, and *R,S*-tetp=(2*R*,11*S*)-diamino-3,3,10,10-tetramethyl-4,9-dithia-1,12-dodecanedioate.

3) H. M. Helis, P. de Meester, and D. J. Hodgson, *J. Am. Chem., Soc.*, **99**, 3309 (1977). In this paper, the symbols, D and L, were used instead of *S* and *R*, respectively.

4) The symbols, [*R*] and [*S*], are denoted by the method of Chan *et al.*, (R. S. Chan, C. K. Ingold, and V. Prelog, *Angew, Chem, Int. Ed. Engl.*, **5**, 385 (1966)). The symbols, *R*(*S*) and *S*(*S*), are denoted the absolute configuration of the chiral sulfur atom.

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15) The subscripts, D and L, correspond to the absolute configurations, *S*(*C*) and *R*(*C*), of the penicillaminate moiety, respectively.

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