Preparation and Characterization of *N,N*-Bridged and/or *S,S*-Bridged Sexidentate-N_2,O_2,S_2 Cobalt(III) Complexes. Crystal Structure of {(3*S*, 8*S*)-2,2,9,9-Tetramethyl-1,10-dithia-4,7-diazacyclotetradecane-3,8-dicarboxylato}cobalt(III) Bromide

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Four kinds of cobalt(III) complexes with *N,N*-bridged, *S,S*-bridged, or *N,N*- and *S,S*-bridged (cyclo type) sexidentate-N_2,O_2,S_2 ligand containing two D-penicillaminate moieties were newly synthesized. Of these complexes, the crystal structure of the title complex was determined by the X-ray diffraction method. The crystal was orthorhombic, space group $P2_12_12_1$, a=16.935(5), b=23.506(7), c=13.057(6) Å, V=5198(3) Å^3, Z=8, and the final R value was 0.0685. The ligand coordinates to the cobalt atom as the *N,N*- and *S,S*-bridged sexidentate-N_2,O_2,S_2. The absolute configurations of the nitrogen and sulfur donor atoms are *S*(N),*S*(N) and *R*(S),*R*(S) respectively. The *N,N*-bridged five-membered ring is the gauche form with the δ conformation and the *S,S*-bridged seven-membered ring is the twist-chair form with the λ conformation. The other three complexes were characterized by their electronic absorption, ^{13}C NMR, and circular dichroism (CD) spectra. The *N,N*- and/or *S,S*-bridged complexes showed the characteristic absorption and CD spectral behavior in the region of 16—24×10^3 cm^{-1}.

Cobalt(III) complexes with an *N,N*- or *S,S*-bridged sexidentate-N_2,O_2,S_2 thioether type ligand containing two *S*-methyl-L-cysteinate (L-smc) or L-cysteinate (L-cys) moieties have been investigated for the stereochemical and spectrochemical interests.[1,2] For example, the cobalt(III) complexes with *S,S'*-ethylenebis(L-cysteinate), *S,S'*-trimethylenebis(L-cysteinate), *N,N'*-ethylenebis(*S*-methyl-L-cysteinate), and *N,N'*-trimethylenebis(*S*-methyl-L-cysteinate) exhibited an extreme trans(O) selectivity concerning the formation of the geometrical isomers, where the expectant isomers are trans(O) and trans(N) for the *S,S*-bridged complexes, and trans(O) and trans(S) for the *N,N*-bridged ones.[1,2] This stereochemical characteristic seems to reveal that the cobalt(III) complexes with an *N,N*- and *S,S*-bridged (cyclo type) sexidentate-N_2,O_2,S_2 ligand are possibly formed.

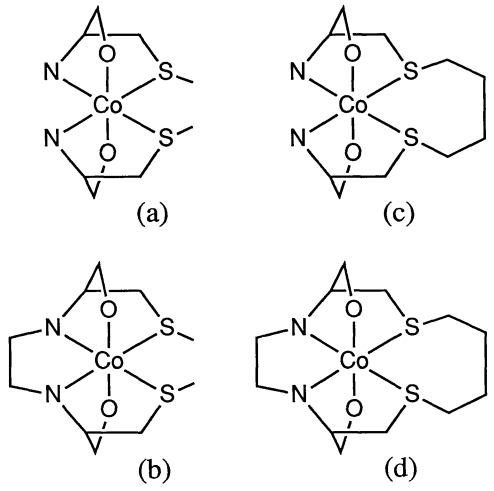

Fig. 1. Structure of (a) *trans*-(O)-[Co(D-smp)$_2$]$^+$, (b) *trans*-(O)-[Co(*N,N*-ebsmp)]$^+$, (*N,N*-bridged complex), (c) *trans*-(O)-[Co(*S,S*-tmbp)]$^+$, (*S,S*-bridged one), and (d) [Co(cyc-etmbp)]$^+$ (cyclo type one).[3]

The cyclo type complex is of interest not only in preparative work, but also in spectrochemistry. In the present work, D-penicillaminate (D-pen), which has the same framework as L-cysteinate, was used as the two terminals of the sexidentate-N_2,O_2,S_2 ligand. The trans(O) cobalt(III) complexes with the *N,N*-bridged, *S,S*-bridged, or cyclo type ligand[3] were synthesized by the alkylation reaction of the thiolato complex[4] containing two D-penicillaminate moieties with dimethyl sulfate, 1,2-dibromoethane, or 1,4-dibromobutane (Fig. 1). This paper reports the isolation of the four kinds of cobalt(III) complexes with the sexidentate-N_2,O_2,S_2 ligand, and their stereochemical and spectrochemical behavior. Of these complexes, the crystal structure of the cyclo type complex, [Co(*cyc*-etmbp)]$^+$ (Fig. 1), was determined by X-ray diffraction method.

Experimental

Materials. All reagents were purchased from the Wako Pure Chemical Ind. Co., Ltd., or Tokyo Chemical Ind. Co., Ltd. in Japan. All chemicals were of reagent grade and were used without further purification.

Preparation of Ligands. 1) *N,N'*-Ethylenebis(D-penicillamine): *N,N*-H_4ebp. This ligand was prepared by a procedure similar to that used for *N,N'*-ethylenebis(*S*-benzyl-L-cysteine).[5] The reaction solution was adjusted to pH 5 with hydrochloric acid and allowed to stand at 0 °C for 2 h. The deposited precipitate was collected by filtration, washed with deaerated cold water and methanol, and then dried in a vacuum desiccator. Found: C, 42.50; H, 7.31; N, 8.15%. Calcd for $H_4ebp\cdot 3/4H_2O=C_{12}H_{24}N_2O_4S_2\cdot 3/4H_2O$: C, 42.65; H, 7.60; N, 8.29%. ^{1}H NMR[100 MHz; solvent D_2O; standard DSS δ=2.99 (2H, S, CH), 2.65 (4H, broad, CH_2), 1.47 (6H, s, CH_3), 1.35 (6H, s, CH_3)]. ^{13}C NMR δ: see Table 4.

Preparation of Complexes. 2) *trans*(O)-Bis(*S*-methyl-D-penicillaminato)cobalt(III) Perchlorate: *trans*(O)-[Co(D-smp)$_2$]ClO_4. This complex was prepared by the procedure described in the literature,[4] and obtained as the perchlorate salt

by using a column of QAE-Sephadex A-25 (ClO_4^- form, 3 cm×35 cm). Found: C, 28.60; H, 5.37; N, 5.52%. Calcd for $[Co(D\text{-}smp)_2]ClO_4\cdot 3/2H_2O = C_{12}H_{24}N_2O_4S_2CoClO_4\cdot 3/2H_2O$: C, 28.27; H, 5.34; N, 5.49%.

3) *trans*(O)-*N*,*N*′-Ethylenebis(*S*-methyl-D-penicillaminato)cobalt(III) Hexafluorophosphate: *trans*(O)-[Co(*N*,*N*-ebsmp)]PF_6. To a solution containing 1 g of $[Co(NH_3)_6]Cl_3$[6] in 30 cm^3 of hot water (ca. 60 °C) were added 2 g of *N*,*N*′-ethylenebis(D-penicillamine) described in (1) and 0.5 g of activated charcoal. The mixture was stirred at 60 °C for 15 min, cooled to room temperature, and then filtered to remove insoluble materials. From the absorption spectral measurements and the column chromatographic behavior, it was found that the reaction mixture contained only *trans*(O)-[Co(*N*,*N*-ebp)]$^-$.[3] To the filtrate was added ca. 10 cm^3 of a 2.0 mol dm^{-3} aqueous solution of $NaClO_4$. This solution was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. To the filtrate was added an appropriate amount of acetone and it was kept in a refrigerator for 6 h. The resulting brown precipitate was collected by filtration, washed with acetone, and then dried in a vacuum desiccator. Found: C, 29.81; H, 5.48; N, 5.82%. Calcd for $Na[Co(N,N\text{-ebp})]\cdot 3H_2O\cdot 1/2NaCl = C_{12}H_{20}N_2O_4S_2CoNa\cdot 3H_2O\cdot 1/2NaCl$: C, 29.68; H, 5.40; N, 5.77 %.

About 10 cm^3 of dimethyl sulfate was added to the reaction solution containing *trans*(O)-[Co(*N*,*N*-ebp)]$^-$ and the mixture was stirred for a few minutes. After being allowed to stand at room temperature overnight, the solution separated into two layers. The upper reddish layer was poured onto a column of SP-Sephadex C-25 (Na^+ form, 4.5 cm×45 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.02 mol dm^{-3} aqueous solution of Na_2SO_4. Only deep red band was eluted and fractionated. From the absorption spectral measurements, it was found that each eluate contained only *trans*(O)-[Co(*N*,*N*-ebsmp)]$^+$. The eluates were combined and concentrated to a small volume with a rotary evaporator. The deposited Na_2SO_4 was filtered off. To the filtrate was added an appropriate amount of saturated NH_4PF_6 aqueous solution. The solution was concentrated to a small volume again and kept in a refrigerator overnight. The resulting deep red crystals were collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 28.38; H, 5.26; N, 4.77 %. Calcd for $[Co(N,N\text{-ebsmp})]PF_6\cdot 2H_2O = C_{14}H_{26}N_2O_4S_2PF_6Co\cdot 2H_2O$: C, 28.48; H, 5.12; N, 4.74 %.

4) *trans*(O)-*S*,*S*′-Tetramethylenebis(D-penicillaminato)cobalt(III) Perchlorate: *trans*(O)-[Co(*S*,*S*-tmbp)]ClO_4. *trans*(O)-$[Co(D\text{-}pen)_2]^-$ was prepared by the same procedure as that used for *trans*(O)-[Co(*N*,*N*-ebp)]$^-$ described in (3), using D-penicillamine (2 g) instead of *N*,*N*-H_4ebp. The greenish brown filtrate was concentrated to a small volume with a rotary evaporator, and to this was added to 10 cm^3 of 1,4-dibromobutane in 50 cm^3 of dimethyl sulfoxide. After being allowed to stand at room temperature for 1 d, unreacted 1,4-dibromobutane and dimethyl sulfoxide were extracted into diethyl ether. The leaving deep purple solution was poured onto a column of SP-Sephadex C-25 (Na^+ form, 4.5 cm×45 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} aqueous solution of NaCl. The five bands, dark red, reddish purple, purple, dark purple, and purple, were eluted in this order. The faster moving dark red band was transferred to another column of SP-Sephadex C-25 (Na^+ form, 4 cm×90 cm) and eluted with a 0.05 mol dm^{-3} aqueous solution of NaCl, because the other four bands were decomposed or disappeared during elution. The dark red band was separated into the three bands, dark red, reddish purple, and purple, in this order. From the absorption and ^{13}C NMR spectral measurements, it was found that the faster moving band contained the desired complex but the other two eluates were by-products whose sulfur atoms were not spanned by tetramethylene bridge. Then, the first moving dark red band was concentrated to a small volume with a rotary evaporator. The deposited NaCl was filtered off. The filtrate was passed through a column of QAE-Sephadex A-25 (ClO_4^- form, 3 cm×35 cm) eluting with water. After the eluate had been concentrated again, an appropriate amount of ethanol was added to it. The resulting red precipitate was collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 31.46; H, 5.61; N, 5.06%. Calcd for $[Co(S,S\text{-tmbp})]ClO_4\cdot 3/2H_2O = C_{14}H_{26}N_2O_4S_2CoClO_4\cdot 3/2H_2O$: C, 31.38; H, 5.45; N, 5.22%.

5) *trans*(O)-*S*,*S*′-Ethylenebis(D-penicillaminato)cobalt(III) Chloride: *trans*(O)-[Co(*S*,*S*-ebp)]Cl. This complex was prepared and chromatographed by a procedure similar to that used in (4), using 1,2-dibromoethane instead of 1,4-dibromobutane. The only purple band was eluted. From the absorption spectral measurements, it was found that the eluate contained only *trans*(O)-[Co(*S*,*S*-ebp)]$^+$. The eluate was concentrated to a small volume with a rotary evaporator. The deposited NaCl was filtered off. The filtrate was poured onto a column of Sephadex G-10 (3 cm×70 cm) eluting with water. After the eluate had been concentrated to a small volume again, an appropriate amount of ethanol was added to it. The solution was kept in a refrigerator for 5 h. The resulting purple crystals were collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 32.97; H, 5.53; N, 6.42 %. Calcd for $[Co(S,S\text{-ebp})]Cl\cdot H_2O = C_{12}H_{22}N_2S_2O_4ClCo\cdot H_2O$: C, 33.15; H, 5.56; N, 6.44 %.

6) {(3*S*,8*S*)-2,2,9,9-tetramethyl-1,10-dithia-4,7-diazacyclotetradecane-3,8-dicarboxylato}cobalt(III) Nitrate: [Co(*cyc*-etmbp)]NO_3. To a solution containing 1.5 g of *trans*(O)-$Na[Co(N,N\text{-ebp})]\cdot 3H_2O\cdot 1/2NaCl$ (described in (3)) in 30 cm^3 of dimethyl sulfoxide was added about 10 cm^3 of 1,4-dibromobutane. After being allowed to stand at room temperature for 18 h, the reaction mixture turned to deep red. Dimethyl sulfoxide and unreacted 1,4-dibromobutane were extracted into diethyl ether. The leaving dark red oil was poured onto a column of SP-Sephadex C-25 (Na^+ form, 4 cm×65 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} aqueous solution of NaCl. Two bands, orange red and red, were eluted in this order. Since the faster moving band seemed to contain two isomers, it was transferred to another column of SP-Sephadex C-25 (Na^+ form, 4.5 cm×45 cm). By developing the band with a 0.05 mol dm^{-3} aqueous solution of NaCl, two bands, orange red and red, were eluted in this order. From the absorption and CD spectral measurements, it was found that the orange red band contained the desired complex and the two red bands were by-products whose sulfur atoms were not spanned by tetramethylene bridge. The faster moving band was concentrated to a small volume with a rotary evaporator. The deposited NaCl was filtered off. The filtrate was passed through a column of QAE-Sephadex A-25 (NO_3^- form,

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2$) for the Non-H Atoms

Atom	*x*	*y*	*z*	B_{eq}[a)]
Co(A)	0.9417(1)	0.0649(0)	0.9180(1)	2.09(4)
S(1A)	1.0689(1)	0.0637(1)	0.9620(2)	2.64(8)
S(2A)	0.9548(1)	0.0596(1)	0.7484(2)	2.67(8)
O(1A)	0.9370(4)	−0.0157(2)	0.9255(5)	3.23(27)
O(2A)	0.9461(7)	−0.0851(3)	1.0411(6)	6.33(46)
O(3A)	0.9442(3)	0.1455(2)	0.9149(4)	2.40(22)
O(4A)	0.8740(4)	0.2182(3)	0.8530(5)	3.62(29)
N(1A)	0.9184(4)	0.0614(3)	1.0618(5)	2.61(28)
N(2A)	0.8291(4)	0.0749(3)	0.8935(5)	2.63(29)
C(1A)	0.9495(7)	−0.0348(4)	1.0190(8)	3.80(44)
C(2A)	0.9671(6)	0.0116(4)	1.0971(7)	3.45(41)
C(3A)	1.0556(7)	0.0288(4)	1.0912(7)	3.61(42)
C(4A)	1.1109(8)	−0.0214(5)	1.1063(10)	5.48(59)
C(5A)	1.0761(7)	0.0755(5)	1.1697(7)	4.05(47)
C(6A)	0.8843(5)	0.1672(4)	0.8655(7)	2.63(34)
C(7A)	0.8299(5)	0.1224(4)	0.8194(6)	2.63(34)
C(8A)	0.8636(5)	0.1006(4)	0.7146(7)	2.93(37)
C(9A)	0.8063(6)	0.0574(5)	0.6651(7)	4.08(46)
C(10A)	0.8786(7)	0.1515(4)	0.6439(8)	4.10(48)
C(11A)	0.8313(5)	0.0521(4)	1.0742(7)	3.25(40)
C(12A)	0.7926(5)	0.0895(4)	0.9929(7)	3.19(38)
C(13A)	1.1217(7)	0.0144(4)	0.8761(8)	4.05(47)
C(14A)	1.1622(6)	0.0467(5)	0.7930(8)	4.12(47)
C(15A)	1.1128(6)	0.0621(5)	0.6984(8)	4.41(50)
C(16A)	1.0394(5)	0.1018(4)	0.7121(7)	3.56(43)
Co(B)	0.2211(1)	0.2733(0)	0.7672(1)	1.98(4)
S(1B)	0.1319(1)	0.3100(1)	0.8733(2)	2.48(8)
S(2B)	0.2556(1)	0.1988(1)	0.8607(2)	2.24(7)
O(1B)	0.1417(4)	0.2303(3)	0.7009(5)	2.99(26)
O(2B)	0.0319(4)	0.2425(3)	0.6068(7)	4.91(37)
O(3B)	0.3006(3)	0.3194(2)	0.8270(4)	2.36(22)
O(4B)	0.4312(4)	0.3281(3)	0.8310(6)	1.61(26)
N(1B)	0.1916(4)	0.3310(3)	0.6689(5)	2.42(27)
N(2B)	0.3048(4)	0.2504(3)	0.6749(5)	2.35(27)
C(1B)	0.0890(6)	0.2619(4)	0.6572(8)	3.36(41)
C(2B)	0.1047(5)	0.3256(4)	0.6703(7)	3.01(37)
C(3B)	0.0729(5)	0.3454(4)	0.7723(7)	3.14(38)
C(4B)	−0.0170(6)	0.3342(6)	0.7866(10)	4.85(55)
C(5B)	0.0922(7)	0.4104(4)	0.7877(9)	4.44(49)
C(6B)	0.3734(5)	0.3024(3)	0.8055(6)	2.52(33)
C(7B)	0.3743(5)	0.2477(4)	0.7461(7)	2.78(35)
C(8B)	0.3621(5)	0.1963(4)	0.8171(7)	2.69(34)
C(9B)	0.3684(6)	0.1391(4)	0.7596(9)	3.64(42)
C(10B)	0.4189(5)	0.1963(5)	0.9056(8)	3.64(43)
C(11B)	0.2289(6)	0.3150(4)	0.5709(7)	3.55(42)
C(12B)	0.3121(6)	0.2951(4)	0.5957(7)	3.35(40)
C(13B)	0.0755(6)	0.2511(4)	0.9238(7)	3.59(42)
C(14B)	0.1044(6)	0.2372(4)	1.0347(7)	3.66(43)
C(15B)	0.1768(6)	0.1995(4)	1.0440(7)	3.42(41)
C(16B)	0.2550(5)	0.2181(4)	0.9965(6)	3.01(37)
Br(1)	0.7132(1)	−0.0431(0)	0.8618(1)	3.90(4)
Br(2)	0.1983(1)	−0.0624(1)	0.5274(1)	5.76(6)
O(W1)	0.2972(6)	0.1006(4)	0.2735(8)	7.0(5)
O(W2)	0.7779(8)	0.3400(5)	0.4714(8)	8.9(7)
O(W3)	0.1880(6)	0.0717(5)	0.4265(9)	7.9(6)
O(W4)	0.9712(7)	0.0671(5)	0.4374(12)	10.7(9)
O(W5)	0.0619(10)	0.1626(6)	0.4382(10)	13.1(11)
O(W6)	0.2947(6)	0.2156(5)	0.2979(9)	7.7(6)
O(W7)	0.1076(8)	0.4206(5)	0.1358(11)	10.4(8)
O(W8)	0.9380(8)	0.3166(5)	0.4856(12)	11.6(9)
O(W9)	0.1075(12)	0.3532(5)	0.2944(12)	13.2(11)
O(W10)	0.4832(10)	0.0387(8)	−0.0341(25)	22.8(19)
O(W11)	0.1343(10)	0.2397(6)	0.3084(14)	12.5(11)

$B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Bond Distances (Å) and Angles(°)

Co(A)–S(1A)	2.230(2)	Co(B)–S(1B)	2.223(2)
Co(A)–S(2A)	2.229(2)	Co(B)–S(2B)	2.214(2)
Co(A)–O(1A)	1.899(6)	Co(B)–O(1B)	1.892(6)
Co(A)–O(3A)	1.895(5)	Co(B)–O(3B)	1.896(6)
Co(A)–N(1A)	1.919(7)	Co(B)–N(1B)	1.933(7)
Co(A)–N(2A)	1.948(7)	Co(B)–N(2B)	1.937(7)
S(1A)–C(3A)	1.890(10)	S(1B)–C(3B)	1.852(10)
S(1A)–C(13A)	1.844(11)	S(1B)–C(13B)	1.807(10)
S(2A)–C(8A)	1.874(9)	S(2B)–C(8B)	1.892(8)
S(2A)–C(16A)	1.806(10)	S(2B)–C(16B)	1.830(9)
O(1A)–C(1A)	1.318(12)	O(1B)–C(1B)	1.294(11)
O(2A)–C(1A)	1.218(11)	O(2B)–C(1B)	1.254(12)
O(3A)–C(6A)	1.306(10)	O(3B)–C(6B)	1.324(10)
O(4A)–C(6A)	1.224(10)	O(4B)–C(6B)	1.198(11)
N(1A)–C(2A)	1.505(12)	N(1B)–C(2B)	1.477(11)
N(1A)–C(11A)	1.501(12)	N(1B)–C(11B)	1.476(12)
N(2A)–C(7A)	1.478(11)	N(2B)–C(7B)	1.502(11)
N(2A)–C(12A)	1.478(11)	N(2B)–C(12B)	1.478(11)
C(1A)–C(2A)	1.523(13)	C(1B)–C(2B)	1.530(13)
C(2A)–C(3A)	1.553(15)	C(2B)–C(3B)	1.510(13)
C(3A)–C(4A)	1.519(16)	C(3B)–C(4B)	1.556(13)
C(3A)–C(5A)	1.541(14)	C(3B)–C(5B)	1.575(14)
C(6A)–C(7A)	1.522(12)	C(6B)–C(7B)	1.502(12)
C(7A)–C(8A)	1.568(12)	C(7B)–C(8B)	1.536(12)
C(8A)–C(9A)	1.546(14)	C(8B)–C(9B)	1.545(12)
C(8A)–C(10A)	1.534(14)	C(8B)–C(10B)	1.504(13)
C(11A)–C(12A)	1.526(13)	C(11B)–C(12B)	1.521(14)
C(13A)–C(14A)	1.493(15)	C(13B)–C(14B)	1.563(14)
C(14A)–C(15A)	1.535(15)	C(14B)–C(15B)	1.518(14)
C(15A)–C(16A)	1.565(15)	C(15B)–C(16B)	1.525(13)
S(1A)–Co(A)–S(2A)	99.1(1)	S(1B)–Co(B)–S(2B)	98.2(1)
S(1A)–Co(A)–O(1A)	90.8(2)	S(1B)–Co(B)–O(1B)	90.6(2)
S(2A)–Co(A)–O(1A)	90.0(2)	S(2B)–Co(B)–O(1B)	91.0(2)
S(1A)–Co(A)–O(3A)	89.8(2)	S(1B)–Co(B)–O(3B)	90.3(2)
S(2A)–Co(A)–O(3A)	91.9(2)	S(2B)–Co(B)–O(3B)	92.1(2)
O(1A)–Co(A)–O(3A)	178.0(3)	O(1B)–Co(B)–O(3B)	176.7(3)
S(1A)–Co(A)–N(1A)	86.9(2)	S(1B)–Co(B)–N(1B)	88.1(2)
S(2A)–Co(A)–N(1A)	171.6(2)	S(2B)–Co(B)–N(1B)	171.7(2)
O(1A)–Co(A)–N(1A)	84.1(3)	O(1B)–Co(B)–N(1B)	83.5(3)
O(3A)–Co(A)–N(1A)	94.0(3)	O(3B)–Co(B)–N(1B)	93.3(3)
S(1A)–Co(A)–N(2A)	171.8(2)	S(1B)–Co(B)–N(2B)	173.0(2)
S(2A)–Co(A)–N(2A)	86.6(2)	S(2B)–Co(B)–N(2B)	86.0(2)
O(1A)–Co(A)–N(2A)	95.0(3)	O(1B)–Co(B)–N(2B)	95.0(3)
O(3A)–Co(A)–N(2A)	84.2(3)	O(3B)–Co(B)–N(2B)	84.0(3)
N(1A)–Co(A)–N(2A)	88.0(3)	N(1B)–Co(B)–N(2B)	88.3(3)
Co(A)–S(1A)–C(3A)	96.9(4)	Co(B)–S(1B)–C(3B)	95.6(3)
Co(A)–S(1A)–C(13A)	108.7(4)	Co(B)–S(1B)–C(13B)	106.8(3)
C(3A)–S(1A)–C(13A)	109.1(4)	C(3B)–S(1B)–C(13B)	108.5(4)
Co(A)–S(2A)–C(8A)	97.1(3)	Co(B)–S(2B)–C(8B)	96.3(3)
Co(A)–S(2A)–C(16A)	108.0(3)	Co(B)–S(2B)–C(16B)	109.7(3)
C(8A)–S(2A)–C(16A)	108.0(4)	C(8B)–S(2B)–C(16B)	107.7(4)
Co(A)–O(1A)–C(1A)	112.4(5)	Co(B)–O(1B)–C(1B)	112.6(6)
Co(A)–O(3A)–C(6A)	112.5(5)	Co(B)–O(3B)–C(6B)	113.7(5)
Co(A)–N(1A)–C(2A)	102.8(5)	Co(B)–N(1B)–C(2B)	100.9(5)
Co(A)–N(1A)–C(11A)	108.3(5)	Co(B)–N(1B)–C(11B)	106.6(5)
C(2A)–N(1A)–C(11A)	113.1(7)	C(2B)–N(1B)–C(11B)	114.5(7)
Co(A)–N(2A)–C(7A)	100.9(5)	Co(B)–N(2B)–C(7B)	101.5(5)
Co(A)–N(2A)–C(12A)	107.0(5)	Co(B)–N(2B)–C(12B)	107.4(5)
C(7A)–N(2A)–C(12A)	113.8(7)	C(7B)–N(2B)–C(12B)	113.4(7)
O(1A)–C(1A)–O(2A)	122.9(9)	O(1B)–C(1B)–O(2B)	123.7(9)
O(1A)–C(1A)–C(2A)	114.1(7)	O(1B)–C(1B)–C(2B)	113.1(8)
O(2A)–C(1A)–C(2A)	123.0(9)	O(2B)–C(1B)–C(2B)	123.1(9)
N(1A)–C(2A)–C(1A)	104.1(7)	N(1B)–C(2B)–C(1B)	104.9(7)
N(1A)–C(2A)–C(3A)	108.1(7)	N(1B)–C(2B)–C(3B)	109.9(7)
C(1A)–C(2A)–C(3A)	110.0(8)	C(1B)–C(2B)–C(3B)	109.8(8)

Table 2. (Continued)

S(1A)–C(3A)–C(2A)	105.8(6)	S(1B)–C(3B)–C(2B)	107.3(6)
S(1A)–C(3A)–C(4A)	112.3(8)	S(1B)–C(3B)–C(4B)	111.6(7)
C(2A)–C(3A)–C(4A)	112.7(8)	C(2B)–C(3B)–C(4B)	113.8(8)
S(1A)–C(3A)–C(5A)	104.9(6)	S(1B)–C(3B)–C(5B)	103.4(7)
C(2A)–C(3A)–C(5A)	111.7(8)	C(2B)–C(3B)–C(5B)	109.8(8)
C(4A)–C(3A)–C(5A)	109.1(9)	C(4B)–C(3B)–C(5B)	110.6(9)
O(3A)–C(6A)–O(4A)	124.0(8)	O(3B)–C(6B)–O(4B)	123.4(8)
O(3A)–C(6A)–C(7A)	113.4(7)	O(3B)–C(6B)–C(7B)	112.1(7)
O(4A)–C(6A)–C(7A)	122.6(8)	O(4B)–C(6B)–C(7B)	124.6(8)
N(2A)–C(7A)–C(6A)	105.6(6)	N(2B)–C(7B)–C(6B)	106.0(7)
N(2A)–C(7A)–C(8A)	109.1(7)	N(2B)–C(7B)–C(8B)	107.6(6)
C(6A)–C(7A)–C(8A)	110.6(7)	C(6B)–C(7B)–C(8B)	111.1(7)
S(2A)–C(8A)–C(7A)	105.2(6)	S(2B)–C(8B)–C(7B)	106.6(5)
S(2A)–C(8A)–C(9A)	106.2(6)	S(2B)–C(8B)–C(9B)	103.8(6)
C(7A)–C(8A)–C(9A)	110.6(7)	C(7B)–C(8B)–C(9B)	112.5(8)
S(2A)–C(8A)–C(10A)	114.0(7)	S(2B)–C(8B)–C(10B)	112.2(6)
C(7A)–C(8A)–C(10A)	109.3(7)	C(7B)–C(8B)–C(10B)	112.2(7)
C(9A)–C(8A)–C(10A)	111.4(8)	C(9B)–C(8B)–C(10B)	109.2(8)
N(1A)–C(11A)–C(12A)	105.3(7)	N(1B)–C(11B)–C(12B)	106.9(7)
N(2A)–C(12A)–C(11A)	107.3(7)	N(2B)–C(12B)–C(11B)	106.9(8)
S(1A)–C(13A)–C(14A)	110.2(7)	S(1B)–C(13B)–C(14B)	109.4(7)
C(13A)–C(14A)–C(15A)	117.0(9)	C(13B)–C(14B)-C(15B)	116.7(8)
C(14A)–C(15A)–C(16A)	118.8(9)	C(14B)–C(15B)–C(16B)	120.1(8)
S(2A)–C(16A)–C(15A)	109.4(7)	S(2B)–C(16B)–C(15B)	109.2(6)

3 cm×35 cm) eluting with water. The eluate was concentrated to a small volume again and kept in a refrigerator for 6 h. The resulting dark red crystals were collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 36.63; H, 5.96; N, 7.97%. [Co(*cyc*-etmbp)]NO_3·3/2H_2O=$C_{16}H_{28}N_3O_7S_2Co$·3/2H_2O: C, 36.64; H, 5.95; N, 7.97%.

The nitrate salt of the complex was dissolved with the appropriate amount of water and it was passed through a column of QAE-Sephadex A-25 (Br^- form) eluting with water. The eluate was concentrated to a small volume and kept in a refrigerator. The resulting crystals, [Co(*cyc*-etmbp)]Br·5.5H_2O, were suitable for X-ray structure analysis and could be collected by filtration.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-610C or UVIDEC-505 spectrophotometer, and the CD spectra with a JASCO J-20 or J-600 spectropolarimeter. All the measurements were carried out in aqueous solutions at room temperature. The ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-FX-100 or -FX-90Q NMR spectrometer in a deuterium oxide (D_2O) or acetonitrile-d_3 (CD_3CN) solvent at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or tetramethylsilane (TMS) was employed as the internal reference.

Crystallography. X-Ray Data Collection. Unit cell parameters and intensity data for the single orange-red crystal (ca. 0.55×0.55×0.35 mm^3) were measured on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ 0.71069 Å, 50 kV and 26 mA). Unit cell parameters were determined by least-squares refinement from 25 reflections with $20°<2\theta<24°$. Crystal data: [$CoC_{16}H_{28}N_2O_4S_2$]Br·5.5H_2O, M=614.47, orthorhombic, space group $P2_12_12_1$, a=16.935(5), b=23.506(7), c=13.057(6) Å, U=5198(3) $Å^3$, Z=8, D_C=1.57 g cm^{-3}, $F(000)$=2536, μ=23.2 cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan mode up to $2<2\theta<56°$ ($0\leqslant h\leqslant 23$, $0\leqslant k\leqslant 33$, $0\leqslant l\leqslant 18$) with scan width $(0.8+0.350\tan\theta)°$ and scan rate varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization, and not for absorption. A total of 5929 independent reflections with $|F_o|>3\sigma(|F_o|)$ of the measured 8286 reflection were considered as "observed" and used for structure determination.

Determination of Crystal Structure. The cobalt and four coordinated atoms were located by the direct methods of the crystallographic program package SDP/VAN.[7] The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the full-matrix least-squares technique using SHELX76[8] on the FACOM M780/20 computer at the Computer Center of the University of Tsukuba. Anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were fixed by geometrical constrains (C–H=0.95 Å) and isotropic thermal parameters (U=0.05 $Å^2$). The water hydrogen atoms were not included in the calculation. The final refinement gave R=0.0685 and R_w=0.0708 with the weighting scheme $w=1.5254/\{\sigma^2(F_o)+0.002334F_o^2\}$. The final difference Fourier synthesis indicated no significant peaks larger than 1.0 eA^{-3}. Atomic positional parameters are given in Table 1 and selected bond distances and angles within the cations are summarized in Table 2.[9]

Results and Discussion

Crystal Structure of [Co(*cyc*-etmbp)]$^+$. A perspective drawing of the typical complex cation (A species) is shown in Fig. 2, together with its atomic numbering scheme. There are two crystallographically independent complex cations in an asymmetric unit, through their shapes and sizes remarkably resemble each other. In the both complex cations, the cobalt atom is octahedrally surrounded by two cis N, two trans O, and two cis S atoms, that is, the ligand coordinates to cobalt

atom as a sexidentate to take the trans(O) configuration. Two D-penicillaminate moieties are spanned by ethylene and tetramethylene to form the *N,N*-bridged five-membered and *S,S*-bridged seven-membered rings. As the result of bridging, the complex cations acquire two kinds of additionally optically active sources with regard to the chiral configuration of nitrogen donor atom (*R*(N) and *S*(N)) and sulfur donor one (*R*(S) and *S*(S)). The absolute configurations of these donor atoms and the chelate ring conformations in the complex cations can be confirmed on the basis of the asymmetric carbon atoms, *S*(C), in the two D-penicillaminate moieties.[10] Both of the chiral nitrogen donor atoms take selectively the *S*(N) configuration and the *N,N*-bridged five-membered ring has a gauche form with a δ conformation (Fig. 3(b)). Further, the two sulfur donor atoms take the *R*(S) configuration and the *S,S*-bridged seven-membered ring has a twist-chair form with a λ conformation (Fig. 3(a)), which is quite similar to those of the *N;N*-bridged seven-membered ring in *cis*-$[Co(NO_2)_2(tmd)_2]^+$ (tmd=1,4-butanediamine).[11]

The bond distances and angles are similar to those for the cobalt(III) complexes with thioether or thiolate ligands containing the cys, pen, or their derivatives (Table 3).[1,10,12-14] Especially, [Co(*cyc*-etmbp)]$^+$ shows quite similar bond distances and angles to *trans*(O)-[Co(*N,N*-ebsmc)]$^+$, except for the Co–S and S–C distances. The Co–S (2.214—2.230(2) Å; av. 2.224 Å) and S–C (1.852—1.892(10) Å; av. 1.877 Å) distances of the cyc-etmbp complex coincide with those of the *S,S*-bridged complex, $(+)^{CD}_{560}$-[Co{(2*R*,9*S*)-2,9-diamino-3,3,8,8-tetramethyl-4,7-dithia-1,10-decanedioato}]$^+$ (Co–S: 2.199(7) and 2.221(8) Å; S–C: 1.89(2) and 1.91(2) Å),[13] but differ from those of *trans*(O)-[Co(*N,N*-ebsmc)]$^+$ (Co–S: av. 2.261(4) Å; S–C; av. 1.843(14) Å)[1,3] and *trans*(S)-[Co(L-smc)$_2$]$^+$ (Co–S: 2.270(2) and 2.273(2) Å; S–C: 1.835(10) and 1.838(10) Å).[3,12] It is noteworthy that the bond angles of S–Co–S (98.2(1) and 99.1(1)°) are larger than those of N–Co–N of the *N,N*-bridged chelate rings, *cis*-$[Co(NO_2)_2(tmd)_2]^+$ (92.0—93.4(1)°; av. 92.4°).[11]

Characterization. The absorption and CD spectra of the present [Co(sexidentate-N_2,O_2,S_2)]$^+$ type complexes are shown in Figs. 4 and 5, and their data are summarized in Table 3. For the thioether type complexes such as [Co(L-smc)$_2$]$^+$, [Co(D-smp)$_2$]$^+$, and [Co(L-met)$_2$]$^+$, it has been known that the cis(S) isomer exhibits the intense broad absorption band at ca. 34×10^3 cm^{-1} and the trans(S) isomer the intense sharp one at ca. 28×10^3 cm^{-1}, arising from the sulfur-to-metal charge-transfer (SMCT) transition.[1,2,4,15] Taking these facts into consideration,

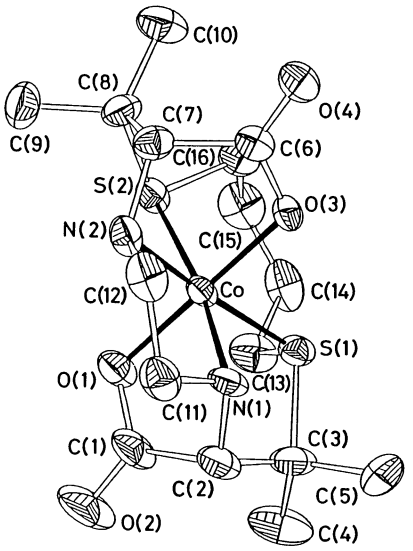

Fig. 2. A perspective drawing of [Co(*cyc*-etmbp)]$^+$ (A species) cation (50% probability thermal ellipsoids). The hydrogen atoms are omitted for clarity.

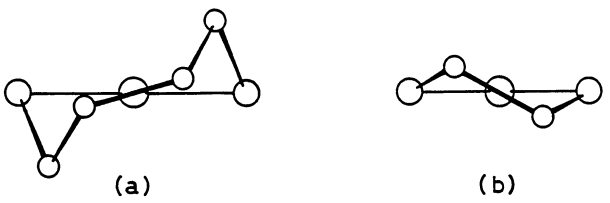

Fig. 3. Conformation of *S,S*-bridged seven-membered ring (a) and *N,N*-bridged five-membered ring (b) in [Co(*cyc*-etmbp)]$^+$.

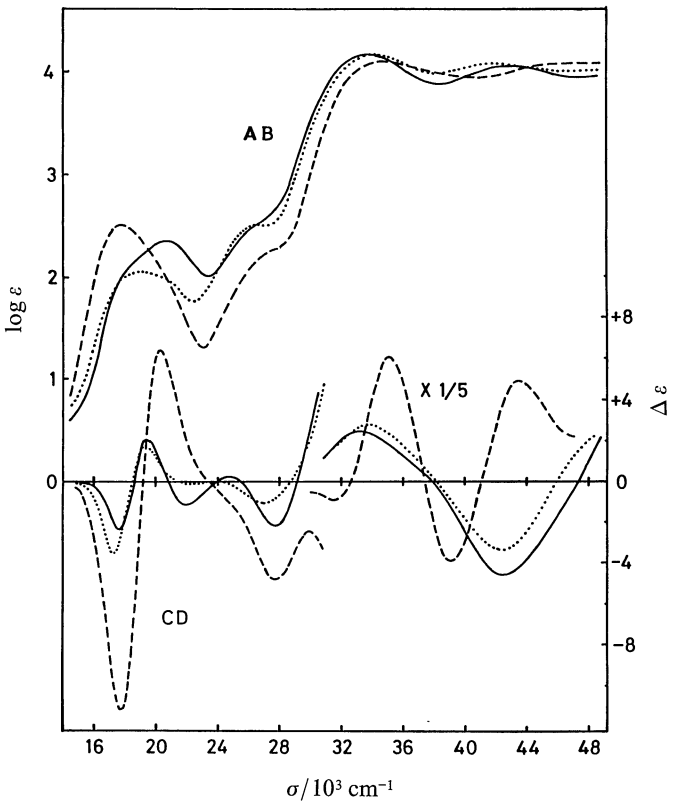

Fig. 4. Absorption and CD spectra of *trans*-(O)-[Co(*N,N*-ebsmp)]$^+$ (——), *trans*-(O)-[Co(*S,S*-ebp)]$^+$ (-----), and *trans*-(O)-[Co(D-smp)$_2$]$^+$ (·····).

Table 3. Absorption and CD Spectral Data of [Co(sexidentate-N_2,O_2,S_2)] Type Complexes

Complex ion	Absorption $\sigma/10^3$ cm^{-1} ($\log \varepsilon$/mol^{-1} dm^3 cm^{-1})	CD $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
[Co(*cyc*-etmbp)]$^+$	18.87 (1.86)	18.73 (+3.40)
	21.83 (1.99)	22.03 (−2.82)
	33.11 (4.18)	25.08 (+0.53)
	43.5 (4.07 sh)[a]	27.69 (−0.90)
		32.55 (+26.1)
		42.74 (−38.3)
trans(O)-[Co(*S,S*-tmbp)]$^+$	18.79 (1.82)	18.19 (+1.92)
	20.92 (1.85)	21.85 (−0.06)
	33.22 (4.13)	23.90 (+0.37)
	42.55 (4.10)	26.10 (−0.24)
		31.91 (+18.6)
		42.12 (−31.1)
trans-(O)-[Co(*S,S*-ebp)]$^+$	17.86 (2.52)	17.70 (−11.4)
	27.4 (2.25 sh)	20.28 (+6.48)
	34.97 (4.11)	27.78 (−4.81)
	47.62 (4.09)	31.55 (−4.05)
		35.21 (+30.6)
		39.22 (−19.0)
		43.48 (+24.8)
trans(O)-[Co(*S,S*-ebc)]$^+$[b]	17.61 (2.48)	17.76 (+10.3)
	27.9 (2.27 sh)	20.45 (−6.59)
	35.21 (4.06)	27.93 (+6.80)
		32.00 (+6.90)
		35.71 (−29.3)
		40.32 (+21.3)
trans(O)-[Co(*N,N*-ebsmp)]$^+$	18.5 (2.13 sh)	17.70 (−2.29)
	20.83 (2.35)	19.60 (+2.05)
	26.7 (2.52 sh)	22.08 (−1.07)
	33.78 (4.16)	24.81 (+0.26)
	43.10 (4.05)	27.70 (−2.15)
		33.33 (+12.2)
		42.74 (−23.1)
trans(O)-[Co(*N,N*-ebsmc)]$^+$[c]	18.5 (2.13 sh)	17.33 (+2.82)
	20.83 (2.35)	19.27 (−2.68)
	26.7 (2.52 sh)	21.93 (+1.38)
	33.78 (4.16)	24.57 (−0.17)
	43.10 (4.05)	27.47 (+2.64)
		33.67 (−10.8)
		43.48 (+19.2)
trans(O)-[Co(D-smp)$_2$]$^+$[d]	19.20 (1.99)	17.40 (−3.61)
	26.47 (2.46)	19.40 (+1.71)
	34.27 (4.00)	22.27 (−0.12)
		26.86 (−1.07)
		33.87 (+14.6)
		42.33 (−19.1)

a) sh denotes a shoulder. b) Ref. 2. c) Ref. 1 d) Ref. 4.

all the present complexes, which exhibit the intense broad SMCT band at ca. 34×10^3 cm^{-1}, are assigned to take the cis(S) configuration, that is, the trans(O) or trans(N) isomer. Of the present three complexes except for the cyc-etmbp complex, the *N,N*-ebsmp complex is assignable to *trans*(O)-[Co(*N,N*-ebsmp)]$^+$ (Fig. 1), because the two cis nitrogen donor atoms are spanned by ethylene to form the five-membered ring. This assignment is supported by the fact that the *N,N*-ebsmp complex exhibits quite similar absorption and CD spectral patterns to *trans*(O)-[Co(*N,N*-ebsmc)]$^+$ over the whole region (Fig. 4 and Table 3), which has a quite similar framework to the *N,N*-ebsmp complex and its configuration has been determined by the X-ray structure analysis.[1] The absorption and CD spectral patterns of the *S,S*-tmbp complex, which was prepared by the reaction of *trans*(O)-[Co(D-pen)$_2$]$^-$ with 1,4-dibromobutane, coincides well with those of [Co(*cyc*-etmbp)]$^+$ over the whole region (Fig. 5 and Table 3). Accordingly, the *S,S*-tmbp complex is probably assigned to *trans*(O)-[Co(*S,S*-tmbp)]$^+$ (Fig. 1). The *S,S*-ebp complex, which was prepared by a similar reaction to the *S,S*-tmbp complex using *trans*(O)-[Co(D-pen)$_2$]$^-$ and 1,2-dibromoethane, exhibits quite similar absorption spectrum

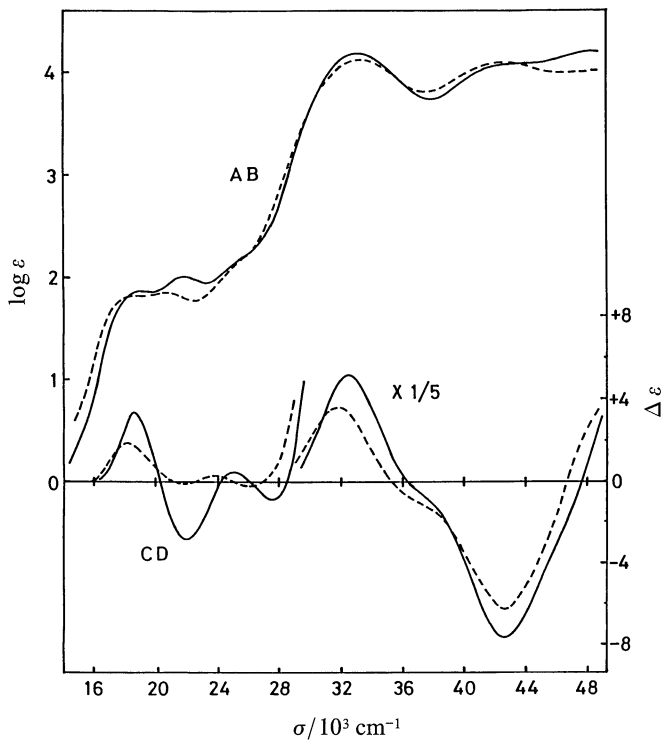

Fig. 5. Absorption and CD spectra of [Co(*cyc*-etmbp)]$^+$ (——) and *trans*-(O)-[Co(*S*,*S*-tmbp)]$^+$ (-----).

and CD pattern to those of *trans*(O)-[Co(*S*,*S*-ebc)]$^+$ over the whole region (Table 3).[2] These similarities suggest that the *S*,*S*-ebp complex takes a trans(O) configuration, *trans*(O)-[Co(*S*,*S*-ebp)]$^+$. These assignments based on their absorption and CD spectra are supported by their ^{13}C NMR spectral measurements.

The ^{13}C NMR chemical shift data for the four cobalt(III) complexes and *S*,*S*-H$_4$ebp are summarized in Table 4. Each signal was assigned on the basis of the insensitive nuclei enhanced by polarization transfer (INEPT) method and of the comparison with the chemical shift data for the related complexes.[1,2] [Co(*cyc*-etmbp)]$^+$ exhibits the eight resonance lines for the sixteen carbon atoms, indicating a C_2 symmetry of the complex. This reveals that the *cyc*-etmbp complex in solution retains the same conformation as in crystal. *trans*(O)-[Co(*S*,*S*-tmbp)]$^+$ exhibits a similar ^{13}C NMR spectral behavior to the *cyc*-etmbp complex, except that the resonance line (δ=75.47) due to the methine carbon atom appears significantly higher field than that (δ=81.42) of [Co(*cyc*-etmbp)]$^+$ whose two nitrogen donor atoms were spanned by ethylene. This suggests that the *S*,*S*-bridged seven-membered ring of the *S*,*S*-tmbp complex takes the twist-chair form with the λ conformation as in the *cyc*-etmbp complex. The ^{13}C NMR spectrum of *trans*(O)-[Co(*S*,*S*-ebp)]$^+$ exhibits six resonance lines due to the twelve carbon atoms, suggesting that the complex also has a C_2 symmetry, that is, the *S*,*S*-bridged five-membered ring takes a gauche form with a λ conformation and the chiral sulfur donor atoms takes the *S*(S), *S*(S) configuration. These regulations are probably ascribed to the rigid framework of the two D-terdentate terminal moieties.

In contrast with the three *S*,*S*-bridged complexes, the ^{13}C NMR spectrum of *trans*(O)-[Co(*N*,*N*-ebsmp)]$^+$ exhibits three resonance lines for each carbon atom of the two D-terdentate terminal moieties and of the *N*,*N*-bridged five-membered ring (Table 4). This suggests that the*N*,*N*-ebsmp complex is a mixture of the isomers (*R*(S),*R*(S), *R*(S),*S*(S) and/or *S*(S),*S*(S)) with regard to the chiral sulfur donor atoms. The *R*(S),*S*(S) isomer of *trans*(O)-[Co(*N*,*N*-ebsmp)]$^+$ being a C_1 symmetry is expected to show two sets of the resonance lines for each carbon atom, while one set of resonance lines is expected for the *R*(S),*R*(S) or *S*(S),*S*(S) isomer because of a C_2 symmetry of the complex cation. Accordingly, the *N*,*N*-ebsmp complex is assumed to be a mixture of either the *R*(S),*R*(S) and *R*(S),*S*(S) isomers or the *S*(S),*S*(S) and *R*(S),*S*(S) ones. *trans*(O)-[Co(*N*,*N*-ebsmc)]$^+$, which has the same framework as the present *N*,*N*-ebsmp complex, consists of the two isomers, *S*(S),*S*(S) and *R*(S),*S*(S), in crystal, although the *N*,*N*-ebsmc complex was proportionated to three isomers, *R*(S),*R*(S), *R*(S),*S*(S), and *S*(S),*S*(S), in solution.[1] Taking the structure of the *N*,*N*-ebsmc complex in crystal into consideration, it is probable that *trans*(O)-[Co(*N*,*N*-ebsmp)]$^+$ consists of the *R*(S),*R*(S) and *R*(S),*S*(S) isomers even in solution.

In the region of 16—24×10^3 cm^{-1}, the present trans(O) complexes with the *N*,*N*-bridged, *S*,*S*-bridged, or cyclo type sexidentate-N$_2$,O$_2$,S$_2$ ligand show the characteristic absorption spectral behavior in connection with the bridging type of the ligands. In comparison with the

Table 4. ^{13}C NMR Chemical Shifts[a]

Compound	COO	N–CH	S–C	N–CH$_2$	S–CH$_2$–CH$_2$	CH$_3$(pen)	S–CH$_3$
N,*N*-H$_4$ebp	183.87	80.88	50.98	46.54		37.38 32.29	
trans(O)-[Co(*N*,*N*-ebp)]$^+$	185.33	82.13	50.54	54.77		35.43 33.91	
trans(O)-[Co(*S*,*S*-ebp)]$^+$	182.51	74.11	61.05		38.30	29.58 26.22	
trans(O)-[Co(*S*,*S*-tmbp)]$^+$	182.71	75.47	58.08		36.84 30.77	30.77 24.38	
[Co(*cyc*-etmbp)]$^+$[b]	181.65	81.42	60.24	55.80	36.84 30.61	30.88 24.97	
trans(O)-[Co(*N*,*N*-ebsmp)]$^+$[b]	177.26	79.42	57.05	54.28		28.93 24.11	15.33
	176.23	78.88	56.88	54.01		28.50 23.67	15.01
	176.07	78.66	55.69			28.28 22.43	

a) ppm from DSS in D_2O. b) ppm from TMS in CD_3CN.

broad absorption band of *trans*(O)-[Co(D-smp)$_2$]$^+$ in this region, *trans*(O)-[Co(*S,S*-ebp)]$^+$ intensifies markedly the lower energy absorption component of the corresponding band, while *trans*(O)-[Co(*N,N*-ebsmp)]$^+$ intensifies the higher energy component (Fig. 4 and Table 3). On the other hand, *trans*(O)-[Co(*S,S*-tmbp)]$^+$ shows a similar absorption spectral pattern to [Co(*cyc*-etmbp)]$^+$, and furthermore, their intensities are similar to that of *trans*(O)-[Co(D-smp)$_2$]$^+$ (Figs. 4 and 5, and Table 3). These facts suggest that the strain due to the *S,S*-bridging contributes more dominantly to the absorption spectral behavior in the d-d transition region than that due to the *N,N*-bridging.

The CD spectral behavior of *trans*(O)-[Co(*S,S*-ebp)]$^+$ differs significantly from that of *trans*(O)-[Co(D-smp)$_2$]$^+$. This is attributed to the difference in steric regulation between the chiral sulfur donor atoms in the complexes. The CD contribution due to the chiral sulfur donor atoms in *trans*(O)-[Co(D-smp)$_2$]$^+$ is probably canceled, because the D-smp complex is a mixture of three isomers (*R*(S),*R*(S), *R*(S),*S*(S), and *S*(S),*S*(S)).[4] While, the *S,S*-bridged five-membered ring of *trans*(O)-[Co(*S,S*-ebp)]$^+$ takes a gauche form with the λ conformation, and accordingly, the two sulfur donor atoms are regulated to the *S*(S),*S*(S) configuration. In contrast with the *S,S*-ebp complex, *trans*(O)-[Co(*N,N*-ebsmp)]$^+$ shows a similar CD spectral pattern to *trans*(O)-[Co(D-smp)$_2$]$^+$ over the whole region (Fig. 4 and Table 3).[4] This similarity suggests that the *N,N*-ebsmp complex consists of two isomers, *R*(S),*R*(S) and *R*(S),*S*(S), in solution as mentioned above. Here, it takes notice that the *N,N*-bridged five-membered ring of the *N,N*-ebsmp complex takes a gauche form with the δ conformation, that is, *S*(N),*S*(N) with regard to the bridged nitrogen donor atoms. However, the contribution to the CD spectral pattern will be minor in this case, because the chiral sulfur donor atoms contribute to the CD spectral pattern much larger than the chiral nitrogen atoms do.[16,17] The similar consideration is applicable to the similarity in CD spectral behavior between [Co(*cyc*-etmbp)]$^+$ and *trans*(O)-[Co(*S,S*-tmbp)]$^+$ over the whole region (Fig. 5 and Table 3). Namely, each of the chiral sulfur donor atoms of both complexes are fixed to the *R*(S) configuration because of the twist chair form with the λ conformation of the *S,S*-bridged seven-membered ring.

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3) Abbreviation used in this paper: D- or L-pen=D- or L-penicillaminate, D-smp=*S*-methyl-D-penicillaminate, L-smc=*S*-methyl-L-cysteinate, *N,N*-ebsmp=*N,N'*-ethylenebis(*S*-methyl-D-penicillaminate), *N,N*-ebsmc=*N,N'*-ethylenebis(*S*-methyl-L-cysteinate), *N,N*-ebp=*N,N'*-ethylenebis(D-penicillaminate), *S,S*-ebp=*S,S'*-ethylenebis(D-penicillaminate), *S,S*-ebc=*S,S'*-ethylenebis(L-cysteinate), *S,S*-tmbp=*S,S'*-tetramethylenebis(*S*-methyl-D-penicillaminate), *cyc*-etmbp=*N,N'*-ethylene-*S,S'*-tetramethylenebis(*S*-methyl-D-penicillaminate) or (3*S*,8*S*)-2,2,9,9-tetramethyl-1,10-dithia-4,7-diazacyclotetradecane-3,8-dicarboxylate.

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