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Preparation and Characterization of Cobalt(III) Complexes with L-Cysteinate and *S*-Methyl-L-Cysteinate. Crystal Structure of (L-Cysteinato)(diethylenetriamine)cobalt(III) Perchlorate

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Of three possible isomers for the (L-cysteinato)(diethylenetriamine)cobalt(III) complex, $[Co(L\text{-}cys)(dien)]^+$, two isomers are selectively prepared. Of the two isomers, the crystal structure of the dominantly formed isomer has been determined by the X-ray diffraction method. The greenish brown needle crystal was orthorhombic, space group $P2_12_12_1$, $a=16.589(4)$, $b=20.510(9)$, $c=12.479(4)$ Å, and $Z=4$. The structure has been refined to $R=0.068$ on 5913 observed reflections. There are three crystallographically independent complex cations in an asymmetric unit. All the complex cations have trans(N_iS) configuration and the L-cysteinate coordinates facially to the cobalt atoms as terdentate-*N,O,S* ligand. The isomers of the (*S*-methyl-L-cysteinato)(diethylenetriamine)cobalt(III) complex were derived from $[Co(L\text{-}cys)(dien)]^+$ by the reaction with dimethyl sulfate. The electronic absorption, CD, and ^1H and ^{13}C NMR spectral behaviors for these complexes are discussed in relation to their geometrical configurations.

Cobalt(III) complexes with the thiolato or thioether type terdentate-*N,O,S* ligand such as *S*-methyl-L-cysteinate (L-smc), L-penicillaminate (L-pen), and *S*-methyl-L-penicillaminate (L-smp) have been investigated for the stereochemical and spectrochemical interests.[1–10] However, L-cysteinate (L-cys) usually coordinates to cobalt(III) as a bidentate-*N,S* ligand[11–16] or tends to form the stable *S*-bridged complexes.[17] So we attempted to prepare the (diethylenetriamine)cobalt(III) complex with L-cysteinate functioning as a terdentate-*N,O,S*, $[Co(L\text{-}cys)(dien)]^+$, and the result is able to compare with the stereochemistry of the corresponding L-penicillaminato complex.[5,7]

In the present paper, the (diethylenetriamine)cobalt(III) complex with L-cysteinate, which could not be prepared by a procedure similar to that used for $[Co(L\text{-}pen)(dien)]^+$,[5,7] was successfully obtained for the first time. Two isomers were selectively formed and the crystal structure of the dominantly formed isomer, $[Co(L\text{-}cys)(dien)]_3(ClO_4)_3\cdot 0.82H_2O$, was determined by X-ray diffraction method. The *S*-methyl-L-cysteinato complex, $[Co(L\text{-}smc)(dien)]^{2+}$, was prepared by the reaction of $[Co(L\text{-}cys)(dien)]^+$ with dimethyl sulfate. The absorption, CD, and ^1H and ^{13}C NMR spectra, and the stereochemical properties of $[Co(L\text{-}cys \text{ or } L\text{-}smc)(dien)]^{+ \text{ or } 2+}$ are discussed in comparison with those of the corresponding $[Co(L\text{-}pen \text{ or } L\text{-}smp)(dien)]^{+ \text{ or } 2+}$ complexes.[5,7]

Experimental

1) Preparation of Complexes. **a) $[Co(L\text{-}cys)(dien)]ClO_4$.** To a deoxygenated solution containing 4.8 g of $CoCl_2\cdot 6H_2O$ in 25 cm³ of water were successively added with stirring a deoxygenated solution containing 2.1 g of diethylenetriamine in 25 cm³ of water and 2.4 g of L-cystine powder. The mixture was continuously stirred under nitrogen atmosphere at room temperature for 1 h. The greenish brown solution was filtered and the filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 5 cm×45 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.15 mol dm^{-3} aqueous solution of $NaClO_4$. Only a greenish brown band (E-1) was eluted and the eluate was immediately concentrated to a small volume with a rotary evaporator below 25 °C. To the solution was added a small amount of ethanol and then the solution was kept in a refrigerator overnight. A small amount of crystals (A-1) appeared and was collected by filtration. The filtrate was concentrated and kept in a refrigerator again. The greenish brown crystals (A-2) which appeared were collected by filtration. When the A-1 isomer was recrystallized from as little water as possible by adding ethanol, the crystals contained a mixture of the A-1 and A-2 isomers as evidenced from the ^1H and ^{13}C NMR spectral measurements. This suggests that the A-1 isomer isomerized to the A-2 one. The A-2 isomer was obtained as pure crystals, collected by filtration, washed with ethanol, and dried in a desiccator. A piece of the crystals of the A-2 isomer was used for the X-ray crystal analysis. The A-1 and A-2 isomers could not be separated using a column chromatographic method because these isomers, especially A-1 isomer, were unstable in the column. Yield for A-2: 39%. Found for A-2: C, 21.94; H, 4.84; N, 14.61%. Calcd for $[Co(L\text{-}cys)(dien)]ClO_4\cdot 0.27H_2O = C_7H_{18}N_4O_6ClSCo\cdot 0.27H_2O$: C, 21.81; H, 4.85; N, 14.53%.

b) $[Co(L\text{-}smc)(dien)](ClO_4)_2$. **Method 1.** To a solution containing 0.3 g of the A-2 isomer, $[Co(L\text{-}cys)(dien)]ClO_4\cdot 0.27H_2O$, in 12 cm³ of water was added 6 cm³ of dimethyl sulfate. When the mixture was allowed to stand in a refrigerator overnight, it was separated into two layers. The upper red layer was taken out and poured onto a column of QAE-Sephadex A-25 (ClO_4^- form, 2.5 cm×20 cm) in order to obtain the perchlorate salt. The eluate was concentrated to a small volume with a rotary evaporator and to this was added a small amount of ethanol. After the solution was kept in a refrigerator overnight, the needle crystals which appeared were collected by filtration, washed with ethanol, and dried in a desiccator. Found: C, 19.38; H, 4.26; N, 11.32%. Calcd for $[\mathrm{Co(L\text{-}smc)(dien)}](\mathrm{ClO_4})_2 = \mathrm{C_8H_{21}N_4O_{10}Cl_2SCo}$: C, 19.40; H, 4.27; N, 11.32%.

Method 2. The eluate containing $[\mathrm{Co(L\text{-}cys)(dien)}]^+$ (E-1) eluted from the SP-Sephadex column in 1a) was methylated by a similar procedure to that used in Method 1. The upper red layer was poured onto a column of Dowex 50W-X8 (200—400 mesh, $\mathrm{Na^+}$ form, 4.5 cm×40 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.5 mol $\mathrm{dm^{-3}}$ aqueous solution of NaCl. Two red bands, B-1 and B-2, were eluted in this order. The eluate B-2 showed the identical absorption and CD spectra with the isomer obtained in Method 1. The formation ratio of the isomers, B-1 and B-2, was about 1 : 3. Then the eluate B-1 was concentrated to a small volume with a rotary evaporator below 25 °C and the deposited NaCl was filtered off. The filtrate was passed through a column of Sephadex G-10 (3 cm×53 cm) in order to eliminate NaCl. The eluate was concentrated to a small volume and poured onto a column of QAE-Sephadex A-25 ($\mathrm{ClO_4^-}$ form, 2.5 cm×20 cm). The eluate converted to the perchlorate salt was concentrated to a small volume and to this was added a small amount of ethanol. The solution was kept in a refrigerator for several days. The crystals which appeared were collected by filtration, washed with ethanol, and dried in a desiccator. Found for B-1: C, 19.10; H, 4.43; N, 11.13%. Calcd for $[\mathrm{Co(L\text{-}smc)(dien)}](\mathrm{ClO_4})_2 \cdot 0.5\mathrm{H_2O}$: C, 19.06; H, 4.40; N, 11.11%.

2) **General Data.** The electronic absorption spectra were recorded on JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers and the CD spectra on a JASCO J-20 spectropolarimeter. All measurements were carried out in aqueous solution at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 or -FX-90Q NMR spectrometer at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference. The X-ray analysis calculations were carried out on a FACOM M-382 computer at the University of Tsukuba.

3) **X-Ray Data Collection.** Unit cell parameters and intensity data for the single crystal (A-2) (ca. 0.18×0.20×0.80 mm^3) were measured on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo Kα radiation. The unit cell parameters were determined by a least-squares refinement based on 25 reflections.

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

Atom	X	Y	Z	B_{eq}/Å^2 a)	Atom	X	Y	Z	B_{eq}/Å^2 a)
CoA	0.44060(8)	0.15381(5)	0.59189(9)	2.00	CoD	0.93161(7)	0.02003(5)	0.38664(9)	1.87
SA	0.5615(2)	0.1777(1)	0.6667(2)	2.74	SD	1.0550(2)	0.0170(1)	0.3073(2)	2.54
OA1	0.4764(4)	0.0652(3)	0.5746(5)	2.76	OD1	0.9465(4)	0.1107(3)	0.4150(5)	2.42
OA2	0.5909(4)	0.0165(3)	0.5239(6)	3.94	OD2	1.0383(4)	0.1766(3)	0.4887(5)	3.39
NA1	0.4940(5)	0.1661(4)	0.4527(6)	3.23	ND1	0.9905(5)	0.0101(3)	0.5221(6)	2.39
NA2	0.3968(5)	0.1331(4)	0.7325(6)	2.88	ND2	0.8765(4)	0.0417(4)	0.2526(7)	2.82
NA3	0.3308(5)	0.1305(4)	0.5349(7)	2.73	ND3	0.8238(5)	0.0219(4)	0.4561(6)	2.59
NA4	0.4012(5)	0.2435(4)	0.5957(7)	3.19	ND4	0.9148(4)	−0.0723(3)	0.3664(7)	2.71
CA1	0.5445(6)	0.0629(4)	0.5254(7)	2.66	CD1	1.0114(6)	0.1226(5)	0.4725(7)	2.70
CA2	0.5672(6)	0.1264(4)	0.4668(7)	2.77	CD2	1.0528(5)	0.0618(4)	0.5137(7)	2.54
CA3	0.6208(6)	0.1648(5)	0.5439(8)	3.26	CD3	1.1128(6)	0.0382(5)	0.4268(8)	2.79
CA4	0.3078(7)	0.1161(6)	0.7281(10)	4.48	CD4	0.7859(6)	0.0370(6)	0.2651(9)	3.71
CA5	0.2927(6)	0.0875(6)	0.6167(10)	4.14	CD5	0.7670(6)	0.0548(6)	0.3814(9)	3.94
CA6	0.2814(7)	0.1924(5)	0.5166(11)	4.85	CD6	0.8017(7)	−0.0453(5)	0.4871(9)	3.86
CA7	0.3381(8)	0.2486(6)	0.5130(12)	5.56	CD7	0.8327(6)	−0.0930(5)	0.4033(10)	4.04
CoB	0.02560(7)	0.18535(6)	0.07290(9)	1.97	ClE	0.6520(2)	0.2175(2)	0.2174(2)	4.35
SB	−0.1015(1)	0.1914(1)	0.1365(2)	2.92	ClF	0.3508(2)	0.0597(2)	0.2557(2)	4.12
OB1	0.0312(4)	0.2790(3)	0.0753(5)	2.80	ClG	0.3582(3)	0.3719(3)	0.2735(3)	7.84
OB2	−0.0384(5)	0.3643(3)	0.0188(6)	3.98	OE1	0.6785(8)	0.1973(6)	0.1198(11)	9.87b)
NB1	−0.0208(5)	0.2010(3)	−0.0691(6)	2.65	OE2	0.6504(8)	0.2880(7)	0.2051(11)	10.56b)
NB2	0.0666(4)	0.1786(4)	0.2189(5)	2.23	OE3	0.7040(6)	0.2011(5)	0.3043(8)	6.71b)
NB3	0.1420(5)	0.1799(4)	0.0283(6)	3.07	OE4	0.5727(7)	0.2021(6)	0.2326(9)	8.68b)
NB4	0.0254(5)	0.0910(3)	0.0540(7)	3.10	OF1	0.3180(7)	0.0580(6)	0.1536(9)	8.69b)
CB1	−0.0237(6)	0.3055(4)	0.0185(7)	2.64	OF2	0.3608(8)	0.1298(7)	0.2734(11)	10.44b)
CB2	−0.0748(6)	0.2585(4)	−0.0496(7)	2.90	OF3	0.4231(11)	0.0352(8)	0.2651(14)	14.23b)
CB3	−0.1447(6)	0.2356(5)	0.0215(8)	3.37	OF4	0.2982(7)	0.0379(6)	0.3386(9)	8.33b)
CB4	0.1547(7)	0.1710(5)	0.2204(8)	3.71	OG1	0.3627(6)	0.3967(5)	0.1690(7)	6.05b)
CB5	0.1896(6)	0.2032(5)	0.1205(9)	3.49	OG2	0.3040(9)	0.3986(7)	0.3445(11)	11.05b)
CB6	0.1630(6)	0.1111(5)	−0.0048(9)	3.88	OG3	0.3152(19)	0.3068(16)	0.2678(25)	28.58b)
CB7	0.0855(7)	0.0745(5)	−0.0326(9)	4.06	OG4	0.4330(10)	0.3547(7)	0.3131(12)	12.49b)
					OW	0.5934(15)	0.0120(12)	0.2227(18)	16.74b)

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

Systematic absences led to the space group $P2_12_12_1$. Crystal Data: $C_{21}H_{55.64}N_{12}O_{18.82}Cl_3S_3Co_3$, $M.W.$=1156.84, orthorhombic, space group $P2_12_12_1$, a=16.589(4), b=20.510(9), c=12.479(4) Å, V=4246(3) Å^3, D_x=1.810 g cm^{-3}, D_m=1.79 g cm^{-3} (by the flotation), Z=12, and μ(Mo Kα)=1.623 mm^{-1}.

The intensity data were collected by the ω-2θ scan technique up to 2θ=60° with scan rate of 3° min^{-1}. The intensity data were converted to the F_o data in the usual manner. Absorption corrections were not applied. A total of 5913 independent reflections with $|F_o|>3\sigma(|F_o|)$ of the measured 6881 reflections were considered as 'observed' and used for the structure analysis.

4) **Determination of the Crystal Structure.** The positions of three cobalt atoms and the coordinated sulfur, oxygen, and nitrogen atoms were determined by the direct method (program MULTAN[18]) was used). The difference-Fourier maps based on these atomic positions revealed the other nonhydrogen atoms. The structure was refined by a full-matrix least-squares refinement using the positional parameters, the anisotropic thermal parameters of the nonhydrogen atoms of the complex ions, and the isotropic thermal parameters of the oxygen atoms in the perchlorate ions and the water molecule (program RFINE[19]) was used). The occupancy for the oxygen atom of the water molecule was also refined and converged to 0.82(3), since the analytical result of the water molecule indicates the small value. The neutral atomic scattering factors for all the nonhydrogen atoms were taken from the literatures.[20,21]) The final residual values were R=0.068 and R_w=0.076, respectively. The configuration was determined on the basis of the known configuration of L-cysteinate.[22]) The final positional parameters are listed in Table 1. A list of structure factors (Table A) and anisotropic thermal parameters (Table B) are kept at the Chemical Society of Japan as Document No. 8738.

Results and Discussion

Description of the Structure. A perspective drawing of the typical complex cation (CoA species) is shown in Fig. 1, together with the numbering scheme. The packing mode is illustrated in Fig. 2. There are three crystallographically independent complex cations in an asymmetric unit, though their shapes and sizes remarkably resemble one another. The cobalt atom was octahedrally surrounded by the oxygen, sulfur, and four nitrogen atoms. The L-cysteinate and diethylenetriamine coordinate facially to the cobalt atom as terdentate ligands. The sulfur atom of the L-cys occupies the trans position to the imino nitrogen atom of the dien. Accordingly, all of these complex cations are determined to take a trans(N$_i$S) configuration (Figs. 1 and 2).[23])

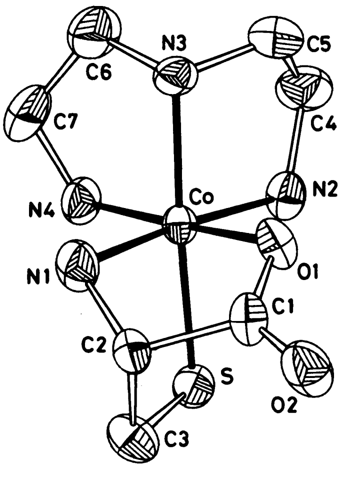

Fig. 1. A. perspective drawing of *trans*(N$_i$S)-[Co(L-cys)(dien)]$^+$ (CoA species) with the numbering scheme of atoms.

The bond lengths and angles in the three crystallographically independent complex cations are similar to those for the cobalt(III) complexes with diethylenetriamine and/or sulfur-containing amino carboxylates (Table 2).[1-3,5]) The average Co–N3 distance bonded trans to the sulfur atom is 2.005(8) Å and the average cis Co–N distance is 1.952(8) Å. A difference between the trans and cis Co–N distances, 0.053 Å, indicates the trans effect due to the coordinated sulfur atom, as in the case of the cobalt(III) complexes with the thiolato ligands such as L-penicillaminate[5]) and 2-aminoethanethiolate.[24]) Especially, the CoA and CoB complex cations exhibit the large trans effect, 2.013 Å.

The conformations of the L-cys in the three complex

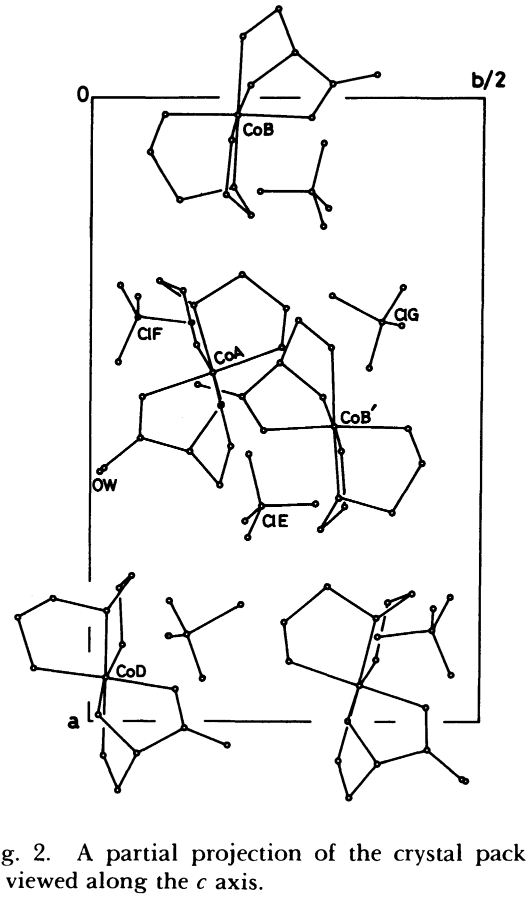

Fig. 2. A partial projection of the crystal packing viewed along the c axis.

Table 2. Interatomic Distances and Bond Angles (with e.s.d.'s) for *trans*(N_iS)-[Co(L-cys)(dien)]$ClO_4 \cdot 0.27H_2O$

(a) Bond distances (l/Å)

	A	B	D		A	B	D
Co-S	2.266(3)	2.256(3)	2.274(3)	N1-C2	1.472(12)	1.501(12)	1.485(11)
Co-O1	1.925(6)	1.922(6)	1.910(6)	N2-C4	1.517(14)	1.470(13)	1.515(12)
Co-N1	1.966(8)	1.959(7)	1.963(8)	N3-C5	1.489(14)	1.475(13)	1.487(13)
Co-N2	1.946(8)	1.950(7)	1.957(8)	N3-C6	1.527(14)	1.511(14)	1.477(13)
Co-N3	2.013(8)	2.013(8)	1.988(8)	N4-C7	1.474(16)	1.508(14)	1.499(12)
Co-N4	1.952(8)	1.949(7)	1.930(7)	C1-C2	1.542(13)	1.540(13)	1.513(13)
S-C3	1.841(10)	1.843(10)	1.825(10)	C2-C3	1.527(14)	1.534(14)	1.550(13)
O1-C1	1.287(11)	1.275(11)	1.318(11)	C4-C5	1.530(18)	1.525(15)	1.529(16)
O2-C1	1.224(12)	1.230(11)	1.209(12)	C6-C7	1.489(17)	1.529(15)	1.522(16)

(b) Bond angles (ϕ/°)

	A	B	D		A	B	D
S-Co-O1	88.7(2)	89.1(2)	89.5(2)	Co-N1-C2	101.3(6)	102.5(5)	102.2(5)
S-Co-N1	86.4(2)	86.7(2)	85.7(2)	Co-N2-C4	112.4(6)	111.5(6)	111.2(6)
S-Co-N2	90.4(3)	90.0(2)	93.1(2)	Co-N3-C5	106.4(6)	106.2(6)	107.8(6)
S-Co-N3	176.2(2)	175.5(2)	179.5(2)	Co-N3-C6	109.9(6)	110.4(6)	108.7(6)
S-Co-N4	94.7(2)	95.5(3)	92.7(2)	C5-N3-C6	111.6(8)	113.1(8)	115.5(8)
O1-Co-N1	83.3(3)	82.5(3)	83.0(3)	Co-N4-C7	106.7(7)	108.0(6)	111.7(6)
O1-Co-N2	90.6(3)	92.3(3)	89.9(3)	O1-C1-O2	126.0(8)	124.0(8)	124.1(9)
O1-Co-N3	90.9(3)	90.8(3)	91.0(3)	O1-C1-C2	114.2(8)	115.6(7)	113.7(8)
O1-Co-N4	174.7(3)	173.4(3)	176.8(3)	O2-C1-C2	119.8(9)	120.4(8)	122.1(9)
N1-Co-N2	173.1(3)	173.9(3)	172.7(3)	N1-C2-C1	108.8(8)	104.6(7)	107.3(7)
N1-Co-N3	97.2(3)	97.8(3)	94.3(3)	N1-C2-C3	105.7(7)	107.7(7)	105.8(7)
N1-Co-N4	93.0(3)	93.0(3)	94.8(3)	C1-C2-C3	106.3(7)	106.8(7)	108.1(7)
N2-Co-N3	85.9(3)	85.4(3)	87.0(3)	S1-C3-C2	106.7(7)	107.9(6)	108.0(6)
N2-Co-N4	93.4(3)	92.5(3)	92.4(3)	N2-C4-C5	106.2(9)	108.7(8)	106.6(8)
N3-Co-N4	85.9(3)	85.0(4)	86.9(3)	N3-C5-C4	109.0(9)	107.1(8)	110.9(8)
Co-S-C3	95.7(3)	96.7(3)	96.3(3)	N3-C6-C7	108.0(9)	109.1(8)	109.6(9)
Co-O1-C1	111.0(5)	112.6(5)	112.8(5)	N4-C7-C6	111.8(11)	106.5(8)	109.6(8)

cations resemble one another and the average displacements of the relevant atoms from the Co–O1–N1 or Co–S–N1 plane are somewhat different from those of *trans*(N_iN)-[Co(L-pen)(dien)]$^+$ (C1 and C2 for the L-cys (L-pen) complex, 0.599(0.371) and 0.942(0.838) Å, λ form; C2 and C3, 1.101(1.154) and 0.590(0.780) Å, δ form).[5] The conformation of the dien in the CoD complex cation are quite similar to those in *trans*(N_iN)-[Co(L-pen)(dien)]$^+$ (the displacement of the CoD–ND2–ND3 or CoD–ND3–ND4 plane: CD4 and CD5 for the L-cys (L-pen) complex, −0.237(−0.239) and 0.366(0.362) Å, δ form; CD6 and CD7, 0.437(0.431) and −0.093(−0.097) Å, λ form). On the contrary, the conformations of the dien in the CoA and CoB complex cations are significantly different from those of the CoD and L-pen ones; namely, both of the diamine chelate rings in the former take an asymmetric skew with λ form (the average displacement of the Co–N2–N3 or Co–N3–N4 plane: C4 and C5, −0.070 and 0.568 Å; C6 and C7, 0.130 and 0.681 Å).

Preparation and Characterization. Three geometrical isomers, trans(N_iN), trans(N_iS), and trans(N_iO),[23] are possible for [Co(L-cys)(dien)]$^+$, as in the case of [Co(L-pen)(dien)]$^+$.[5,7] The L-cys complex was prepared for the first time by the reaction of cobalt(II) chloride with L-cystine under a nitrogen atmosphere. In this preparative reaction, two isomers, A-1 and A-2 (trans(N_iS) based on the X-ray crystal structure analysis) were selectively formed. The absorption and CD spectra of the A-1 isomer, which were shown by the arbitrary scale in Fig. 3, exhibit quite similar spectral patterns to those of *trans*(N_iN)-[Co(L-pen)(dien)]$^+$ whose structure was determined by the X-ray crystal structure analysis.[7] Therefore, the A-1 isomer can be assigned to the trans(N_iN) configuration.

The absorption, CD, and ^1H and ^{13}C NMR spectra of *trans*(N_iN)-[Co(L-cys)(dien)]$^+$ (A-1) changes with time and these spectral behaviors suggest that the trans(N_iN) isomer isomerizes to the trans(N_iS) one, though *trans*(N_iN)-[Co(L-pen)(dien)]$^+$ did not isomerize in an aqueous solution.[5,7] *trans*(N_iS)-[Co(L-cys)(dien)]$^+$ (A-2) did not isomerize in an aqueous solution and gave only one isomer of [Co(L-smc)(dien)]$^{2+}$ by the reaction with dimethyl sulfate. This fact suggests that the methylation for the A-2 isomer proceeded with retention of the trans(N_iS)

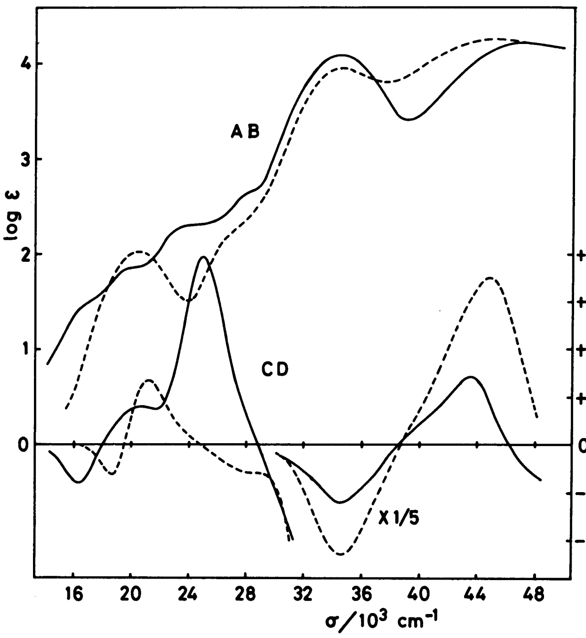

Fig. 3. Absorption and CD spectra of *trans*(N_iN)-[Co(L-cys or L-smc)(dien)]$^{+ \text{ or } 2+}$: L-cys (—) and L-smc (------).

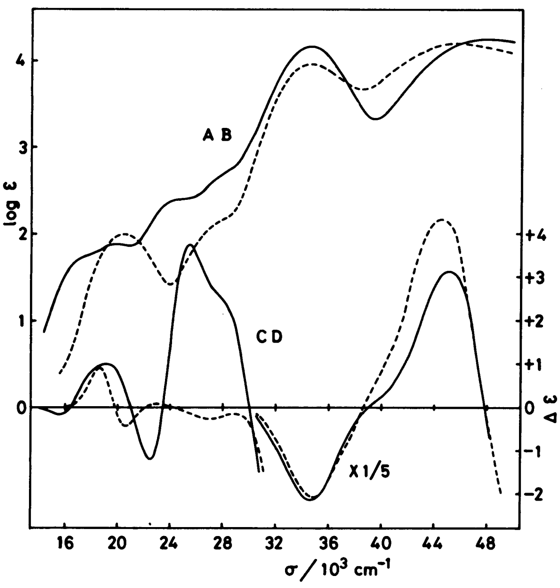

Fig. 4. Absorption and CD spectra of *trans*(N_iS)-[Co(L-cys or L-smc)(dien)]$^{+ \text{ or } 2+}$: L-cys (——) and L-smc (------).

Table 3. Absorption and CD Spectral Data of [Co(L-cys)(dien)]$^+$ and [Co(L-smc)(dien)]$^{2+}$

Complex	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)
trans(N_iN)-[Co(L-cys)-(dien)]$^+$	14.39 (——sh)	16.31 (−)
	20.00 (——sh)	20.64 (+)
	24.39 (——sh)	24.94 (+)
	28.09 (——sh)	34.48 (−)
	34.48 (——)	43.48 (+)
	47.17 (——)	
trans(N_iS)-[Co(L-cys)-(dien)]$^+$	17.51 (1.74 sh)	15.46 (−0.16)
	19.88 (1.88)	19.12 (+1.01)
	24.69 (2.40 sh)	22.42 (−1.19)
	28.09 (2.71 sh)	25.41 (+3.78)
	34.60 (4.16)	27.70 (+2.59 sh)
	48.08 (4.24)	34.48 (−10.76)
		45.05 (+15.68)
trans(N_iN)-[Co(L-smc)-(dien)]$^{2+}$	20.49 (2.02)	18.62 (−0.61)
	27.03 (2.21 sh)	21.19 (+1.35)
	34.58 (3.95)	28.74 (−0.58 sh)
	45.05 (4.26)	34.48 (−11.50)
		44.84 (+17.59)
trans(N_iS)-[Co(L-smc)-(dien)]$^{2+}$	20.41 (1.99)	18.62 (+0.91)
	27.47 (2.12 sh)	20.62 (−0.43)
	34.60 (3.97)	22.88 (+0.09)
	45.66 (4.21)	26.88 (−0.26)
		34.72 (−10.53)
		44.44 (+21.78)

sh denotes a shoulder.

configuration, as in the case of [Co(L-pen)(dien)]$^+$.7) When the reaction mixture containing [Co(L-cys)-(dien)]$^+$ reacted with dimethyl sulfate, two isomers, B-1 and B-2, of [Co(L-smc)(dien)]$^{2+}$ were obtained after the column chromatographic separation. The B-2 isomer showed the identical absorption and CD spectra with *trans*(N_iS)-[Co(L-smc)(dien)]$^{2+}$ (Fig. 4 and Table 3) and the B-1 isomer exhibits quite similar absorption and CD spectra to *trans*(N_iN)-[Co(L-smp)(dien)]$^{2+}$ (Fig. 3 and Table 3), in which the L-smp has a similar framework to the L-smc. This fact seems to indicate that the B-1 isomer has the trans(N_iN) configuration. The formation ratio of the trans(N_iN) and trans(N_iS) isomers was about 1:3 and the two isomers were stable in an aqueous solution. The trans(N_iO) isomer could not be detected. The difference in formation seems to depend on the nitrogen donor atoms, imino and terminal amino nitrogens, in the dien occupying the trans position of the sulfur one in the L-cys.

In the former paper,7) we assigned the trans(N_iS) and trans(N_iO) configurations for [Co(L-pen)(dien)]$^+$ and [Co(L-smp)(dien)]$^{2+}$ on the basis of the CD spectral patterns of the (diethylenetriamine)cobalt(III) complexes with iminodiacetate, *N*-(carboxylatomethyl)-L-alaninate, and D- or L-aspartate. However, the present assignment for *trans*(N_iS)-[Co(L-cys)(dien)]$^+$ based on the X-ray crystal analysis and the spectral behaviors of the isomers of the derivative, [Co(L-smc)(dien)]$^{2+}$ (Fig. 4), point out that the assignments in the former paper should be reversed.7)

The ^{1}H NMR spectrum of *trans*(N_iS)-[Co(L-smc)(dien)]$^{2+}$ exhibits two resonance lines at σ=2.18 and 2.35 (intensity ratio; 9.3:1) in the *S*-methyl protons

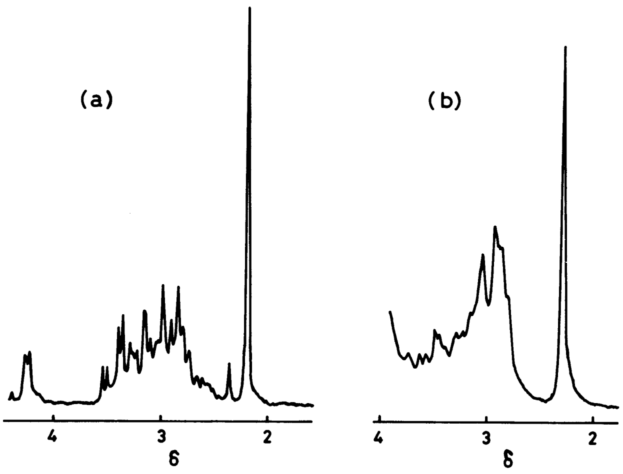

Fig. 5. ^{1}H NMR spectra of $[\mathrm{Co(L\text{-}smc)(dien)}]^{2+}$: (a) trans($N_iS$) and (b) trans($N_iN$).

region (Fig. 5). The corresponding resonance lines were also observed for the ^{13}C NMR spectrum at σ=19.8 and 21.8, respectively. For the asymmetric sulfur donor atom, R or S, in the trans(N_iS) isomer, the interligand interaction, which exists between an *S*-methyl group and the amino group of the dien, of the S configuration can be expected to be weaker than that of the R one. The *S*-methyl protons of the S configuration in the trans(N_iS) isomer lies above the carboxyl group, while there is no such steric relation for the *S*-methyl group of the R configuration. Taking account of the model inspections mentioned above and the up field shift due to the methyl group lying above the carboxyl group,[25,26] it is suggested that the major species (2.18 ppm) in the *trans*(N_iS)-$[\mathrm{Co(L\text{-}smc)(dien)}]^{2+}$ has the S configuration and the minor one (2.35 ppm) has the R configuration. On the other hand, *trans*(N_iN)-$[\mathrm{Co(L\text{-}smc)(dien)}]^{2+}$ exhibits only one resonance line at 2.29 ppm (for ^{1}H NMR) or at 20.69 ppm (for ^{13}C NMR) in the *S*-methyl region (Fig. 5). The model inspection concerning the interligand interaction between the *S*-methyl group and an ethylenediamine moiety in the dien also suggests that the coordinated sulfur atom has only S configuration. These results are in line with the fact that *trans*(N_iN)- and *trans*(N_iS)-$[\mathrm{Co(L\text{-}smp)(dien)}]^{2+}$, which exhibit only resonance line in the *S*-methyl protons region, take the S configuration.[7]

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