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Characterization of *trans*(*O*)-*N*,*N'*-Ethylenebis(*S*-methyl-L-cysteinato)cobalt(III) Perchlorate and the Absolute Configuration of the Complex Determined by X-Ray Analysis

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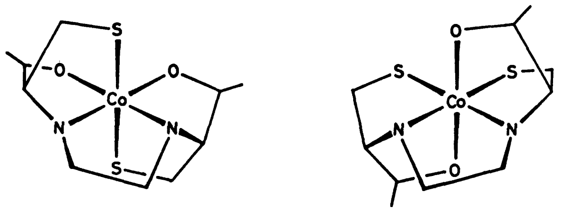
A cobalt(III) complex with the sexidentate ligand, *N*,*N'*-ethylenebis(*S*-methyl-L-cysteine), was newly synthesized and chromatographically isolated. Of two possible geometrical isomers, trans(O) and trans(N), one isomer was formed selectively. The dark-red crystals are orthorhombic, space group $P2_12_12_1$, $a=9.055(2)$, $b=22.123(7)$, $c=17.111(4)$ Å, and $Z=8$. The structure was solved by the direct method and refined to $R=0.066$ for 2380 nonzero reflections. The complex is trans(O) isomer and the crystal consists of two kinds of complex cations with respect to the absolute configurations of the coordinated asymmetric sulfur atom. One takes an *S*(S),*S*(S) configuration and the other an *R*(S),*S*(S) one. The changes in configuration between the asymmetric sulfur atoms in the crystal and those in aqueous solution are discussed on the basis of NMR (^{13}C and ^{1}H) spectral studies.

Cobalt(III) complexes with sulfur-containing amino carboxylates have been extensively investigated during the past several years.[1–12] However, the properties of the thioether type sulfur atom which takes *R* or *S* configuration by coordination have been little known yet. Recently, Jackson and Sargeson suggested that a sulfur inversion in the *S*-bonded thioether–cobalt(III) complexes occurs in aqueous solution.[5] The sexidentate ligand in this work, *N*,*N'*-ethylenebis(*S*-methyl-L-cysteine), has two chiral centers, *R*(C) and *R*(C).[13] As seen in Fig. 1, the possible geometrical isomers for the [Co(*R*,*R*-ebsmc)]$^+$ complex are limited to two, *trans*(*O*)-*R*(N),*R*(N) and *trans*(*S*)-*S*(N),*S*(N), where the abbreviation, *R*,*R*-ebsmc, is used for the present sexidentate ligand. For each of the two isomers, three other isomers, *S*(S),*S*(S), *R*(S),*S*(S), and *R*(S),*R*(S), due to the asymmetric sulfur atoms of the coordinated *R*,*R*-ebsmc are possible.



trans(S) trans(O)

Fig. 1. Two geometrical isomers of [Co(*R*,*R*-ebsmc)]$^+$.

In the present study, the *R*,*R*-H$_2$ebsmc ligand has been prepared from *S*-methyl-L-cysteine and 1,2-dibromoethane. The [Co(*R*,*R*-ebsmc)]$^+$ complex has been prepared and it has been chromatographically confirmed that only one geometrical isomer is formed. The crystal structure and absolute configuration of the isomer are established by X-ray diffraction studies. The chiral behavior of the sulfur atoms in solution is discussed on the basis of the ^{1}H and ^{13}C NMR spectra of the isomer, by comparison with the asymmetric sulfur atoms in the crystal. A preliminary report has been presented.[14]

Experimental

Preparation of R,R-*H$_2$ebsmc.* The *R*,*R*-H$_2$ebsmc ligand was prepared by a procedure modified from that used in the preparation of ethylenediaminedisuccinic acid.[15] *S*-Methyl-L-cysteine (16.9 g) was dissolved in 30 cm^3 of an aqueous solution containing sodium hydroxide (5.0 g). The solution was poured into a 100 cm^3 round bottom flask fitted with a condenser, and refluxed. To the solution were slowly added 1,2-dibromoethane (11.8 g) and sodium carbonate (6.6 g) over a period of 30 min. The mixture was continuously stirred under reflux for 3 h. The resulting reddish-brown mixture was cooled to room temperature and filtered to remove insoluble materials. When the pH of the filtrate was adjusted to 6 with concentrated hydrochloric acid, white crystals appeared (5.2 g). The crude product obtained was washed well with 80 cm^3 of warm water (*ca.* 60 °C). The product was recrystallized from a dilute aqueous solution of sodium hydroxide by adding concentrated hydrochloric acid. The crystals were collected, washed with water and then with acetone, and dried in a vacuum desiccator over $CaCl_2$. Yield 4.5 g. Found: C, 40.39; H, 6.67; N, 9.36; S, 21.41%. Calcd for $C_{10}H_{20}N_2O_4S_2$: C, 40.52; H, 6.80; N, 9.45; S, 21.63%.

Preparation of trans(O)-*[Co(*R,R-*ebsmc)]ClO$_4$.* To a suspension of *R*,*R*-H$_2$ebsmc (0.7 g) in 50 cm^3 of hot water (70 °C) were added $CoCl_2\cdot 6H_2O$ (0.55 g) and lead dioxide (1.5 g). The mixture was stirred at about 70 °C for 20 min, whereupon the solution became orange-red. The reaction mixture was cooled to room temperature and filtered to remove the excess of lead dioxide. The orange-red filtrate was poured onto an ion-exchange column (5 × 15 cm) containing SP-Sephadex C-25 resin (Na$^+$ form). After sweeping the column with water, the adsorbed band was eluted with 0.2 mol dm^{-3} aqueous solution of $NaClO_4$. Only one orange-red band was eluted and fractionated. It was found, from the absorption and CD spectra of the fractionated eluates, that the eluate contained only *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$. The eluate was concentrated to 20 cm^3 using a rotary evaporator below 30 °C, and then kept in a refrigerator. The dark-red crystals obtained were collected, washed with ethanol and then with ether, and dried in air. Yield 0.06 g. Found: C, 26.49; H, 4.18; N, 6.27%. Calcd for $CoC_{10}H_{18}N_2O_8S_2Cl$: C, 26.53; H, 4.01; N, 6.19%.

The halide (Cl$^-$, Br$^-$, or I$^-$) salt of this complex cation was also obtained by the elution with an aqueous solution of NaCl,

NH_4Br, or NaI instead of that of $NaClO_4$.

Measurements. The electronic absorption spectrum was recorded with a JASCO UVIDEC-1 spectrophotometer,and the CD spectrum with a JASCO J-20 spectropolarimeter. All measurements were carried out in aqueous solution at room temperature.

The ^1H and ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. For ^1H NMR spectrum, sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference. The ^{13}C chemical shifts were measured relative to external benzene and converted into the chemical shifts from TMS using the relation $\delta_{TMS}=\delta_{benzene}-128.50$ ppm.

The symmetry and approximate cell dimensions of the crystal were determined from Weisenberg and precession photographs. The more accurate cell dimensions were obtained by a least-squares analysis of 2θ measured on a Philips PW 1100 automated four circle diffractometer. The crystal data are summarized in Table 1.

TABLE 1. CRYSTAL DATA

Molecular formula	$CoC_{10}H_{18}N_2O_8S_2Cl$
Molecular weight	452.77
Space group	$P2_12_12_1$
Cell constants	$a=9.055(2)$ Å
	$b=22.123(7)$ Å
	$c=17.111(4)$ Å
Density obsd	1.77 g/cm^3
calcd	1.76 g/cm^3
	(for $Z=8$)

A crystal with dimensions of 0.4 mm × 0.2 mm × 0.1 mm was used for data collection. Intensity data were collected on the Philips PW 1100 automated four circle diffractometer with Mo $K\alpha$ radiation monochromatized by graphite. The ω-2θ scan technique was employed and reflections for $2\theta<70°$ were recorded. A total of 2380 independent non-zero reflections were used for the structure determination. The intensities were corrected for the Lorentz and polarization factors, but no absorption correction was applied.

Structure Determination

The structure was solved by the use of MULTAN.[16] Four sets of phases were calculated using the 180 $|E|$'s greater than 1.58. The set of phases with the highest confined figures of merit was used to calculate an E map which yielded the positions of the cobalt, sulfur, oxygen, nitrogen, and chlorine atoms. Fourier and difference-Fourier maps based on these atoms revealed the rest of the structure. The structure was refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters (program ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy was used). The final R value $(\sum||F_o|-|F_c||/\sum|F_o|)$ was 0.066 for all the non-hydrogen atoms. The atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[17] The calculations were carried out on an ACOS 800II computer at The University of Tsukuba. The final atomic parameters and their standard deviations are given in Table 2. A list of the anisotropic thermal parameters and a table of the observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8215).

TABLE 2. THE ATOMIC POSITIONAL PARAMETERS, WITH THEIR e.s.d.'s IN PARENTHESES ($\times 10^4$)

Atom	x	y	z	B_{eq}/Å^2 [a]	Atom	x	y	z	B_{eq}/Å^2 [a]
Co(1)	7181(2)	884(1)	1761(1)	2.59	N(1)	3991(12)	5469(4)	2462(6)	3.06
Co(2)	7416(2)	3542(1)	3207(1)	2.56	N(2)	4589(10)	5917(5)	3872(5)	3.04
Cl(1)	2347(5)	98(2)	4128(2)	4.51	N(3)	6133(10)	2962(4)	2702(6)	2.88
Cl(2)	2826(5)	2279(2)	983(3)	5.61	N(4)	8589(9)	3553(4)	2244(5)	2.60
S(1)	9188(4)	718(2)	2513(2)	3.97	C(1)	−68(17)	6435(6)	2235(8)	4.74
S(2)	8262(4)	1451(2)	820(2)	3.67	C(2)	1863(17)	5573(6)	1585(8)	4.46
S(3)	5968(4)	3494(2)	4277(2)	4.03	C(3)	3505(16)	5757(5)	1722(7)	4.00
S(4)	1080(4)	9289(2)	1352(2)	3.73	C(4)	3590(15)	6424(6)	1915(7)	3.65
O(1)	3308(9)	6577(3)	2618(4)	3.21	C(5)	105(16)	6057(7)	4528(10)	5.30
O(2)	3874(13)	6793(4)	1390(5)	5.18	C(6)	3052(17)	6249(6)	4956(7)	4.93
O(3)	7561(10)	172(3)	1180(4)	3.30	C(7)	4051(15)	5732(6)	4656(7)	3.75
O(4)	2913(13)	4762(5)	4958(6)	6.79	C(8)	3055(17)	5165(7)	4485(8)	4.95
O(5)	4021(8)	9113(4)	2158(4)	3.13	C(9)	4375(17)	555(6)	2353(8)	4.76
O(6)	3638(8)	4183(4)	2454(5)	3.82	C(10)	4266(14)	505(6)	1449(7)	3.37
O(7)	1201(9)	7958(3)	1470(4)	2.96	C(11)	3364(17)	7900(7)	61(8)	4.89
O(8)	1197(9)	2729(4)	3347(5)	4.20	C(12)	4395(15)	3125(6)	3787(8)	4.24
O(9)	1295(16)	9649(8)	3708(11)	15.38	C(13)	4597(13)	3217(6)	2866(8)	3.56
O(10)	3801(13)	9757(7)	3919(6)	8.60	C(14)	4736(15)	3886(6)	2685(8)	3.33
O(11)	2105(14)	9929(7)	4922(6)	10.10	C(15)	273(17)	9039(7)	411(8)	5.52
O(12)	2251(18)	554(6)	3903(8)	11.19	C(16)	417(14)	4137(6)	2940(8)	3.68
O(13)	3242(35)	2062(8)	342(9)	24.04	C(17)	−108(13)	8538(6)	2443(7)	2.98
O(14)	1343(15)	2310(7)	1012(15)	17.84	C(18)	105(13)	3027(5)	3180(7)	3.14
O(15)	3241(19)	1927(6)	1598(9)	12.89	C(19)	3530(13)	7961(6)	3144(8)	3.29
O(16)	3289(17)	2871(6)	1130(8)	10.86	C(20)	1836(13)	8008(6)	3237(7)	3.33

a) $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$ where U_1, U_2, and U_3 are the principal components of the U matrix.

Results and Discussion

Description of the Structure. Perspective drawings of the complex cations obtained are given in Fig. 2 and their packing mode is illustrated in Fig. 3. The bond lengths and angles with their estimated standard deviations in the complex ions are given in Tables 3 and 4, respectively. There are two crystallographically independent complex cations in an asymmetric unit. In both complex cations, the *R*,*R*-ebsmc ligand is sexidentate and the coordination around cobalt atoms is approximately octahedral. The cobalt atoms are surrounded by two *cis* sulfur, two *cis* nitrogen, and two trans oxygen atoms. Both cations can be designated as trans(O) configuration. The preferred *cis* configiration of the two coordinated sulfur atoms was also recognized in the case of the cobalt(III) complexes with the sulfur-containing amino carboxylates.[10,11] The absolute configuration of the complex cations in the crystal can be confirmed on the basis of the asymmetric carbon atoms, *R*(C),*R*(C), in the coordinated sexidentate ligand. As a result, the absolute configurations of the two nitrogen atoms in each of the two complex cations are determined to be *R*(N),*R*(N), as expected. Each of the two sulfur atoms in these cations becomes chiral by coordination. This means, as seen in Fig. 2, that the two sulfur atoms take the *S*(S),*S*(S) configuration in complex (a), whereas the sulfur atoms are in the *R*(S),*S*(S) one in complex (b). The *S*(S),*S*(S) complex has a pseudo-twofold axis through the Co(1) which bisects the S(1)–S(2) edge of the octahedron, whereas the *R*(S),*S*(S) complex takes a C_1 symmetry (Fig. 2).

The cobalt-ligand bond lengths are all similar to those for the cobalt(III) complexes with the sulfur-containing amino carboxylates.[7–12] The bond angles at the cobalt atoms of both complex cations are slightly distorted from their idealized values, that is, *cis* angles are in the range of 82.6—98.5° and *trans* angles 171.8—177.4° (Table 4). The interatomic distances and bond angles in the two crystallographically independent complex cations corre-

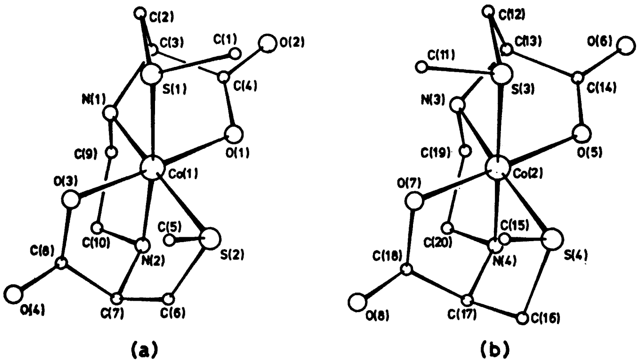


Fig. 2. Structure of *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ ion; (a) *S*(S),*S*(S) and (b) *R*(S),*S*(S) isomers.

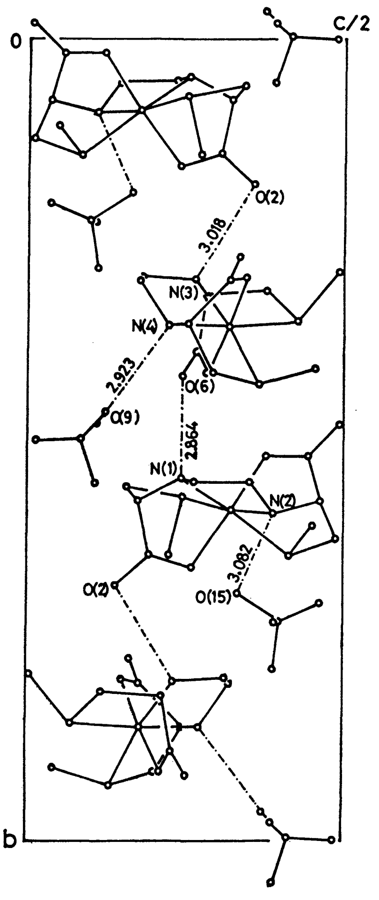


Fig. 3. A projection of the crystal packing viewed along a axis.

Table 3. Intramolecular distances (with e.s.d.'s) for *trans*(*O*)-[Co(*R*,*R*-ebsmc)]ClO_4

	l/Å		l/Å
Complex (a)		Complex (b)	
Co(1)–S(1)	2.257(4)	Co(2)–S(3)	2.253(4)
Co(1)–S(2)	2.264(4)	Co(2)–S(4)	2.270(4)
Co(1)–O(1)	1.916(8)	Co(2)–O(5)	1.918(8)
Co(1)–O(3)	1.895(7)	Co(2)–O(7)	1.883(8)
Co(1)–N(1)	1.933(10)	Co(2)–N(3)	1.935(10)
Co(1)–N(2)	1.936(10)	Co(2)–N(4)	1.962(9)
S(1)–C(1)	1.828(13)	S(3)–C(11)	1.838(13)
S(1)–C(2)	1.842(14)	S(3)–C(12)	1.843(14)
S(2)–C(5)	1.816(15)	S(4)–C(15)	1.851(14)
S(2)–C(6)	1.838(14)	S(4)–C(16)	1.849(12)
O(1)–C(4)	1.276(13)	O(5)–C(14)	1.262(14)
O(2)–C(4)	1.240(13)	O(6)–C(14)	1.256(14)
O(3)–C(8)	1.267(14)	O(7)–C(18)	1.334(14)
O(4)–C(8)	1.212(15)	O(8)–C(18)	1.222(13)
N(1)–C(3)	1.483(16)	N(3)–C(13)	1.527(15)
N(1)–C(9)	1.525(17)	N(3)–C(19)	1.479(16)
N(2)–C(7)	1.486(15)	N(4)–C(17)	1.477(14)
N(2)–C(10)	1.486(15)	N(4)–C(20)	1.510(14)
C(2)–C(3)	1.559(20)	C(12)–C(13)	1.600(18)
C(3)–C(4)	1.515(16)	C(13)–C(14)	1.516(17)
C(6)–C(7)	1.547(18)	C(16)–C(17)	1.505(17)
C(7)–C(8)	1.573(18)	C(17)–C(18)	1.554(16)
C(9)–C(10)	1.554(18)	C(19)–C(20)	1.546(16)
ClO_4^- Ion		ClO_4^- Ion	
Cl(1)–O(9)	1.317(12)	Cl(2)–O(13)	1.256(14)
Cl(1)–O(10)	1.401(11)	Cl(2)–O(14)	1.345(14)
Cl(1)–O(11)	1.377(10)	Cl(2)–O(15)	1.361(13)
Cl(1)–O(12)	1.497(13)	Cl(2)–O(16)	1.396(12)

Table 4. Bond angles(with e.s.d.'s) for *trans*(*O*)-[Co(*R*,*R*-ebsmc)]ClO_4

	ϕ/°		ϕ/°
Complex (a)		S(4)–Co(2)–N(4)	86.88(29)
S(1)–Co(1)–S(2)	98.47(15)	O(5)–Co(2)–N(3)	83.33(36)
S(1)–Co(1)–O(1)	90.05(27)	O(5)–Co(2)–N(4)	94.86(35)
S(1)–Co(1)–O(3)	90.99(27)	O(7)–Co(2)–N(3)	94.29(38)
S(2)–Co(1)–O(1)	92.94(25)	O(7)–Co(2)–N(4)	83.98(35)
S(2)–Co(1)–O(3)	90.48(26)	N(3)–Co(2)–N(4)	87.56(40)
S(1)–Co(1)–N(1)	88.44(32)	O(5)–Co(2)–O(7)	177.40(34)
S(2)–Co(1)–N(2)	86.50(29)	S(3)–Co(2)–N(4)	176.51(29)
O(1)–Co(1)–N(1)	82.60(37)	S(4)–Co(2)–N(3)	172.46(31)
O(1)–Co(1)–N(2)	95.05(39)	Co(2)–S(3)–C(11)	110.08(48)
O(3)–Co(1)–N(1)	93.82(38)	Co(2)–S(3)–C(12)	95.84(42)
O(3)–Co(1)–N(2)	83.60(41)	C(11)–S(3)–C(12)	102.66(66)
N(1)–Co(1)–N(2)	87.05(42)	Co(2)–S(4)–C(15)	107.96(55)
O(1)–Co(1)–O(3)	176.25(36)	Co(2)–S(4)–C(16)	95.14(42)
S(1)–Co(1)–N(2)	172.70(34)	C(15)–S(4)–C(16)	103.12(63)
S(2)–Co(1)–N(1)	171.81(33)	Co(2)–O(5)–C(14)	114.32(83)
Co(1)–S(1)–C(1)	110.12(49)	Co(2)–O(7)–C(18)	112.30(72)
Co(1)–S(1)–(C2)	95.13(48)	Co(2)–N(3)–C(13)	102.71(71)
C(1)–S(1)–C(2)	100.27(68)	Co(2)–N(3)–C(19)	108.35(72)
Co(1)–S(2)–C(5)	108.64(54)	C(13)–N(3)–C(19)	111.60(100)
Co(1)–S(2)–C(6)	95.72(41)	Co(2)–N(4)–C(17)	101.44(67)
C(5)–S(2)–C(6)	100.00(70)	Co(2)–N(4)–C(20)	108.07(69)
Co(1)–O(1)–C(4)	110.96(75)	C(17)–N(4)–C(20)	114.60(89)
Co(1)–O(3)–C(8)	113.70(94)	S(3)–C(12)–C(13)	107.65(83)
Co(1)–N(1)–C(3)	102.76(74)	N(3)–C(13)–C(12)	103.78(106)
Co(1)–N(1)–C(9)	109.33(76)	N(3)–C(13)–C(14)	104.34(101)
C(3)–N(1)–C(9)	114.33(103)	C(12)–C(13)–C(14)	109.50(110)
Co(1)–N(2)–C(7)	102.90(72)	O(5)–C(14)–O(6)	124.37(121)
Co(1)–N(2)–C(10)	110.33(72)	O(5)–C(14)–C(13)	114.81(122)
C(7)–N(2)–C(10)	113.17(101)	O(6)–C(14)–C(13)	120.61(123)
S(1)–C(2)–C(3)	107.70(90)	S(4)–C(16)–C(17)	108.00(85)
N(1)–C(3)–C(2)	107.42(110)	N(4)–C(17)–C(16)	108.08(100)
N(1)–C(3)–C(4)	102.53(97)	N(4)–C(17)–C(18)	105.34(91)
C(2)–C(3)–C(4)	109.61(110)	C(16)–C(17)–C(18)	110.06(100)
O(1)–C(4)–O(2)	123.43(119)	O(7)–C(18)–O(8)	123.44(121)
O(1)–C(4)–C(3)	116.92(108)	O(7)–C(18)–C(17)	113.13(99)
O(2)–C(4)–C(3)	119.60(113)	O(8)–C(18)–C(17)	123.41(120)
S(2)–C(6)–C(7)	108.56(79)	N(3)–C(19)–C(20)	107.83(108)
N(2)–C(7)–C(6)	106.71(106)	N(4)–C(20)–C(19)	104.47(99)
N(2)–C(7)–C(8)	103.88(97)	ClO_4^- Ion	
C(6)–C(7)–C(8)	108.45(111)	O(9)–Cl(1)–O(10)	116.32(84)
O(3)–C(8)–O(4)	124.25(157)	O(9)–Cl(1)–O(11)	116.23(106)
O(3)–C(8)–C(7)	114.19(120)	O(9)–Cl(1)–O(12)	103.12(113)
O(4)–C(8)–C(7)	121.56(125)	O(10)–Cl(1)–O(11)	114.24(80)
N(1)–C(9)–C(10)	105.04(113)	O(10)–Cl(1)–O(12)	102.09(85)
N(2)–C(10)–C(9)	106.28(108)	O(11)–Cl(1)–O(12)	101.63(88)
Complex (b)		O(13)–Cl(2)–O(14)	110.53(180)
S(3)–Co(2)–S(4)	96.55(14)	O(13)–Cl(2)–O(15)	111.94(126)
S(3)–Co(2)–O(5)	84.34(25)	O(13)–Cl(2)–O(16)	115.13(120)
S(3)–Co(2)–O(7)	96.68(26)	O(14)–Cl(2)–O(15)	106.04(131)
S(4)–Co(2)–O(5)	92.07(26)	O(14)–Cl(2)–O(16)	104.23(102)
S(4)–Co(2)–O(7)	90.18(26)	O(15)–Cl(2)–O(16)	108.32(96)
S(3)–Co(2)–N(3)	88.96(31)		

spond well with each other. Only the S–Co–S angles are significantly different. The angles S(1)–Co(1)–S(2) and S(3)–Co(2)–S(4) are 98.5° and 96.6°, respectively. The values are significantly larger than the normal ones; these deviations may be attributed to the repulsion between methyl groups on the sulfur atoms.

Several hydrogen bonds are recognized between the two complex ions, and between the complex ions and the perchlorates: *e.g.*, N(1)–O(6), N(3)–O(2), N(2)–O(15), and N(4)–O(9) (Fig. 3). The bond lengths of the Co(1)–O(1) and Co(2)–O(5) are apparently longer than those of the Co(1)–O(3) and Co(2)–O(7), respec-

Table 5. Displacements of atoms from the least-squares plane

Diamine chelate ring			
Plane 1(a);[c)] $0.2394X-0.8781Y-0.4144Z+1.4094=0$			
Co(1)*	0.0000	C(9)	−0.3905
N(1)*	0.0000	C(10)	0.3246
N(2)*	0.0000		
Plane 2(b);[c)] $0.5636X+0.7475Y+0.3516Z-16.5225=0$			
Co(2)*	0.0000	C(19)	−0.3344
N(3)*	0.0000	C(20)	0.3957
N(4)*	0.0000		
S-Methyl groups			
Plane 3(a); $0.2018X-0.8285Y-0.5224Z+1.8826=0$			
Co(1)*	0.0000	C(1)	−1.3804
S(1)*	0.0000	C(5)	1.3309
S(2)*	0.0000		
Plane 4(b); $0.6105X+0.6852Y+0.3973Z-15.5951=0$			
Co(2)*	0.0000	C(11)	1.7199
S(3)*	0.0000	C(15)	1.4636
S(4)*	0.0000		
S–N chelate ring			
Plane 5(a); $0.1581X-0.8674Y-0.4719Z+2.0899=0$			
Co(1)*	0.0000	C(2)	−0.6010
S(1)*	0.0000	C(3)	−1.0788
N(1)*	0.0000		
Plane 6(a); $0.2832X-0.8326Y-0.4761Z+1.2217=0$			
Co(1)*	0.0000	C(6)	0.6668
S(2)*	0.0000	C(7)	1.1189
N(2)*	0.0000		
Plane 7(b); $0.5598X+0.7477Y+0.3572Z-16.5354=0$			
Co(2)*	0.0000	C(12)	−0.4878
S(3)*	0.0000	C(13)	−1.1001
N(3)*	0.0000		
Plane 8(b); $0.6168X+0.6855Y+0.3868Z-15.5849=0$			
Co(2)*	0.0000	C(16)	0.5965
S(4)*	0.0000	C(17)	1.0801
N(4)*	0.0000		

The *X*, *Y*, and *Z* coordinates in Å are referred to the crystallographic axies. c): (a) and (b) denote the *S*(S),-*S*(S) and *R*(S),*S*(S) isomers, respectively.

tively (Table 3). These differences may be reflected by the stronger hydrogen bondings caused by the O(2) and O(6) atoms.

In order to examine the conformations of chelate rings, the displacements of relevant atoms from the chelate ring plane, which is defined by the central cobalt atom and the two coordinated atoms in the chelate ring, were calculated. The results are given in Table 5. The diamine chelate rings in both cations have asymmetric gauche form with λ conformation. This is in line with the case of diamines such as ethylenediamine and its derivatives.[18)]

Electronic Absorption and CD Spectra. The electronic absorption and CD spectra of the *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ are shown in Fig. 4 and their data are summarized in Table 6. The electronic absorption spectrum of the trans(O) complex shows an explicit shoulder on the lower energy side of the major peak in the first absorption band region. The splitting behavior is in line with the results from the semi-empirical calculation on the basis of the ligand field strength order N>S>O.[2,3,6)] The sulfur-to-metal charge transfer band of the complex is observed at 34010 cm^{-1}.

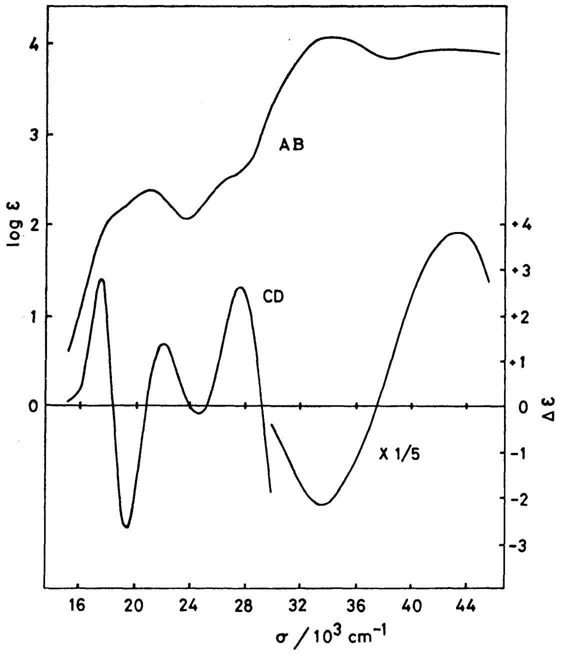


Fig. 4. Absorption and CD spectra of *trans*(*O*)-[Co-(*R*,*R*-ebsmc)]$^+$.

Table 6. Absorption and CD spectral data of *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ ion

Absorption maxima $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
18.35(2.1 sh[a)])	17.33(+2.82)
20.83(2.37)	19.27(−2.68)
	21.93(+1.38)
26.67(2.5 sh)	24.57(−0.17)
	27.47(+2.64)
34.01(4.07)	33.67(−10.8)
42.55(3.92)	43.48(+19.2)
48.78(3.85)	

a) sh: Shoulder.

The CD spectrum shows (+), (−), and (+) bands, listing from the lower energy side in the first absorption band region. A similar splitting pattern was observed in those of the $(-)_{576}$-[Co(*S*,*S*-edds)]$^-$[15)] and $(-)_{589}$-[Co(*S*,*S*-ebm)]$^+$[1)] which have a similar framework to that of the present trans(O) complex, where *S*,*S*-edds and *S*,*S*-ebm denote the *S*,*S*-ethylenediaminedisuccinate and ethylenebis(*S*-methioninate), respectively.

NMR Spectra. The ^{13}C and ^{1}H NMR spectra of the *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ complex were measured in D$_2$O solution. The results are shown in Figs. 5 and 6. Taking the absolute configurations of the coordinated sulfur atoms into consideration, the ^{13}C NMR spectrum of the *S*(S),*S*(S) or *R*(S),*R*(S) isomer having a twofold axis is expected to show a single peak for each of the *S*-methyl, methylene, and methine

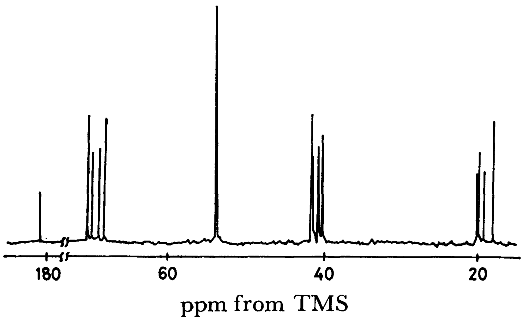


Fig. 5. ^{13}C NMR spectrum of *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ in D_2O.

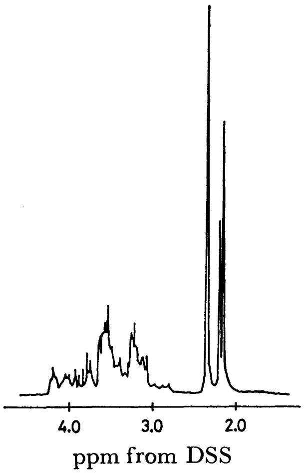


Fig. 6. ^{1}H NMR spectrum of *trans*(*O*)-[Co(*R*,*R*-ebsmc)]$^+$ in D_2O.

carbons. On the other hand, the *R*(S),*S*(S) isomer is expected to show two peaks for each of them because of a C_1 symmetry of the complex. If the configurations, *S*(S),*S*(S) and *R*(S),*S*(S), in crystal are retained in solution, the ^{13}C NMR spectrum will show the three peaks for each of the *S*-methyl, methylene, and methine carbons. As seen in Fig. 5, the spectrum exhibits the four peaks for each of the *S*-methyl (18.3—20.3 ppm from TMS), methylene (40.3—41.8 ppm), and methine (68.1—70.3 ppm) carbons, respectively. This fact suggests that the sulfur atoms of the *trans*(*O*)-*R*,*R*-ebsmc complex in solution take a different configuration from those in the crystal, that is, the present spectrum indicates a mixture of the *S*(S),*S*(S), *R*(S),*S*(S), and *R*(S),*R*(S) configurations. A similar trend was also observed for the ^{1}H NMR spectrum.

The ^{1}H NMR spectrum of *trans*(*O*)-*R*,*R*-ebsmc complex shows three peaks, at 2.19, 2.23, and 2.38 ppm (in the ratio 1.5 : 1.0 : 2.4) from DSS in the *S*-methyl proton region, soon after its dissolution (Fig. 6). It may be considered that the peak at 2.38 ppm is caused by partial overlap of the two peaks due to the two isomers. The peaks did not change significantly in the range from 5 °C to 60 °C. These facts are in agreement with the suggestion from the ^{13}C NMR study and suggest that the rate of the sulfur inversion in the present complex cations is slow on the NMR time scale. The complex chromatographed, however, gave only one adsorbed band and all of its fractionated eluates showed the same CD spectra. The attempt to precipitate fractionally as ClO_4^-, Cl^-, Br^-, and I^- salts from water yielded homogeneous crystals, which exhibited identical CD and NMR spectra. These results suggest that in aqueous solution a sulfur inversion similar to that for the *S*-bonded thioether-cobalt(III) complexes[5] occurs also in the present complex at room temperature, *i.e.*, *S*(S),*S*(S)$\rightleftarrows$*R*(S),*S*(S)$\rightleftarrows$*R*(S),*R*(S).

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