The Synthesis and Oxidation of Mixed Cobalt(III) Complexes with Dimethyldithiocarbamato and Diamine Ligands, and the Crystal Structure of $(+)^{CD}_{500}$-Dimethyldithiocarbamato-bis(ethylenediamine)cobalt(III) Bis[μ-(*R*,*R*)-tartrato]diantimonate(III) Pentahydrate

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Dithiocarbamato complexes, $[Co(dtc)_{3-n}(diamine)_n]^{n+}$ (n=1 and 2 and dtc=dimethyldithiocarbamate) were newly prepared and characterized by means of their absorption, CD, and MCD spectra. $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot5H_2O$ crystallized in the monoclinic space group of $P2_1$ with a=14.630(3), b=9.300(1), c=12.023(5) Å, β=110.78(3)°, V=1529.4(8) Å^3, and Z=2. The refinement of 3346 reflections (Mo $K\alpha$ radiation) led to R=0.073. The dtc complex had a Δ configuration. The Co–N bond trans to the dtc sulfur atom was longer by 0.026 Å than the cis one. A novel oxidation derivative, $[Co\{(dimethylamino)thioxomethanesulfinato\text{-}O,S\}(en)_2]^{2+}$, was prepared and characterized by means of its XPS spectrum.

A large number of dithiocarbamato-metal complexes have been synthesized.[1] Several reports have been published on the crystal structures of dithiocarbamato cobalt(III) complexes: e.g., $[Co(S_2CNH_2)_3]$,[2] $[Co\{S_2CN(CH_3)_2\}_3]$,[3] and $[Co(S_2CN(C_2H_5)_2)_3]$.[4] No mixed chromophore systems of the $[Co(S)_2(N)_4]$ and $[Co(S)_4(N)_2]$ types have, however, been reported. The mixed chromophores are interesting in terms of their spectrochemistry because of the large difference in the ligand field strengths between dtc-sulfur and amine-nitrogen donors. Furthermore, sulfur donor groups with various chemical environments (thiolato, thioether, sulfenato, sulfinato, sulfito, thiosulfato, etc.) induce in cobalt(III) complexes the trans influence (structural trans effect) ranging in magnitude from 0.00 to 0.089 Å;[5] in contrast, however, no such trans influence of dithiocarbamato has yet been determined because the appropriate mixed complexes have not been synthesized.

This paper deals with the synthesis of a series of mixed cobalt(III) complexes with dimethyldithiocarbamate and diamine as the remaining ligands: $[Co(dtc)_{3-n}(diamine)_n]^{n+}$ (n=0, 1, and 2). The complexes were characterized by their electronic absorption, circular dichroism (CD), and magnetic circular dichroism (MCD) spectra. The X-ray crystal structure of $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot5H_2O$ was determined. The H_2O_2 oxidation of dithiocarbamato complexes was also attempted.

The following abbreviations of the ligands are used in this paper: Hdtc=dimethyldithiocarbamic acid $(CH_3)_2NCS_2H$; Hdtsi=(dimethylamino)thioxomethanesulfinic acid $(CH_3)_2NC(S)SO_2H$; Hmtz=2-mercapto-2-thiazoline $\overline{S\text{-}CH_2\text{-}CH_2N{=}C}\text{-}SH$; en=ethylenediamine $NH_2CH_2CH_2NH_2$; *R*-pn=(*R*)-propylenediamine $NH_2CH_2CH(CH_3)NH_2$.

Experimental

Preparation and Optical Resolution. (1) $[Co(dtc)(en)_2](ClO_4)_2$: To a solution of $Co(ClO_4)_2$ (0.018 mol) in 100 cm^3 of water we added a solution of ethylenediamine (2.2 g, 0.036 mol) in 100 cm^3 of methanol. To the mixture we then immediately added a solution of bis(dimethylthiocarbamyl) disulfide (2.2 g, 0.009 mol) in 200 cm^3 of ethanol, and the subsequent mixture was stirred at ca. 70 °C for 1 h. The resulting reddish purple precipitate was filtered off and washed with ethanol and diethyl ether. The precipitate was recrystallized by dissolving it in hot water (ca. 70 °C), filtering, and cooling to ca. 5 °C. The yield was 7.6 g (85%). Found: C, 16.75; H, 4.43; N, 13.81%. Calcd for $[Co(dtc)(en)_2](ClO_4)_2$=$C_7H_{22}N_5O_8S_2Cl_2Co$: C, 16.87; H, 4.45; N, 14.06%.

For optical resolution, to a solution of $[Co(dtc)(en)_2](ClO_4)_2$ (3.0 g, 0.006 mol) in 50 cm^3 of hot water we added a solution of $K_2[Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot3H_2O$ (1.9 g, 0.003 mol) in 50 cm^3 of hot water. After a few minutes, the red-plate diastereomer $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot5H_2O$ began to deposit; it was filtered off. The filtrate was cooled to induce the crystallization of $(-)^{CD}_{500}$-$[Co(dtc)(en)_2](ClO_4)_2$. The crystals were collected and recrystallized from hot water. Found for the less-soluble diastereomer: C, 19.64; H, 3.83; N, 7.58%. Calcd for $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot5H_2O$=$C_{15}H_{36}N_5O_{17}S_2CoSb_2$: C, 19.64; H, 3.92; N, 7.57%. Found for the $(-)^{CD}_{500}$-complex: C, 16.97; H, 4.48; N, 14.01%. Calcd for $(-)^{CD}_{500}$-$[Co(dtc)(en)_2](ClO_4)_2$=$C_7H_{22}N_5O_8Cl_2S_2Co$: C, 16.87; H, 4.45; N, 14.06%. An adequate amount of anion-exchange resin (QAE-Sephadex A-25, chloride form) was added to a suspension of the less-soluble diastereomer, $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot5H_2O$, in water, leading to a reddish brown supernatant. After the removal of the resin, sodium perchlorate was added to the filtrate; the crystals of $(+)^{CD}_{500}$-$[Co(dtc)(en)_2](ClO_4)_2$ were then deposited. Found: C, 16.80; H, 4.42; N, 13.98%. Calcd for $(+)^{CD}_{500}$-$[Co(dtc)(en)_2](ClO_4)_2$=$C_7H_{22}N_5O_8S_2Cl_2Co$: C, 16.87; H, 4.45; N, 14.06%.

(2) $[Co(dtc)_2(en)]ClO_4$: This green complex was obtained as a by-product (5%) from the mother liquor in the above preparation. The complex was also prepared in a

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high yield by the following method. Bis(dimethylthiocarbamyl) disulfide (4.3 g, 0.0183 mol) was stirred into a solution of $\mathrm{Co(ClO_4)_2}$ (0.036 mol) in 100 $\mathrm{cm^3}$ of ethanol. To the mixture we then added a mixed solution of sodium dimethyldithiocarbamate dihydrate (6.4 g, 0.036 mol) and ethylenediamine (2.2 g, 0.036 mol) in 50 $\mathrm{cm^3}$ of water. After a few minutes, the green precipitate began to deposit. The mixture was then stirred at ca. 70 °C for 1 h. The resulting green precipitate was filtered and washed with water (100 $\mathrm{cm^3}$), ethanol (20 $\mathrm{cm^3}$), chloroform (100 $\mathrm{cm^3}$ each, three times), and then ether (100 $\mathrm{cm^3}$). The water washings contained the complex $\mathrm{[Co(dtc)(en)_2](ClO_4)_2}$, and the chloroform ones, $\mathrm{[Co(dtc)_3]}$. The green precipitate was recrystallized by dissolving it in hot water–ethanol (2:1) and by then cooling it below 10 °C. The columnar green crystals were collected. The yield was 12 g (73%). Found: C, 20.80; H, 4.41; N, 12.17%. Calcd for $\mathrm{[Co(dtc)_2(en)]ClO_4{=}C_8H_{20}N_4O_4S_4ClCo}$: C, 20.94; H,4.39; N, 12.21%.

(3) $(+)^{\mathrm{CD}}_{580}$- and $(-)^{\mathrm{CD}}_{580}$-$\mathrm{[Co(dtc)_2(}\mathbf{\mathit{R}}\mathrm{\text{-}pn)]ClO_4}$: The $\mathrm{[Co(dtc)_2(}R\mathrm{\text{-}pn)]ClO_4}$ complexes were prepared by the same procedure as that used for $\mathrm{[Co(dtc)_2(en)]ClO_4}$, except for the use of R-pn instead of en. The yield was 11 g (85%). The green crystals of $\mathrm{[Co(dtc)_2(}R\mathrm{\text{-}pn)]ClO_4}$ were dissolved in a small amount of dimethyl sulfoxide (DMSO), adsorbed on a column of cation-exchange resin (SP-Sephadex C-25, $\mathrm{Na^+}$ form), and eluted with a 0.5 M NaCl aqueous solution (1 M=1 mol $\mathrm{dm^{-3}}$). The two green bands were eluted separately. The earlier eluate showed a negative CD at 17000 $\mathrm{cm^{-1}}$ and the latter one, a positive CD at 17000 $\mathrm{cm^{-1}}$. Each perchlorate salt was obtained by adding a saturated aqueous solution of $\mathrm{NaClO_4}$ to each eluate. Found for the $(-)^{\mathrm{CD}}_{580}$-complex: C, 22.76; H, 4.70; N, 11.86%. Calcd for $(-)^{\mathrm{CD}}_{580}$-$\mathrm{[Co(dtc)_2(}R\mathrm{\text{-}pn)]ClO_4{=}C_9H_{22}N_4O_4S_4ClCo}$: C, 22.86; H, 4.69; N, 11.85%. Found for the $(+)^{\mathrm{CD}}_{580}$-complex: C, 21.49; H, 4.86; N, 10.96%. Calcd for $(+)^{\mathrm{CD}}_{580}$-$\mathrm{[Co(dtc)_2(}R\mathrm{\text{-}pn)]ClO_4\cdot 1.5H_2O{=}C_9H_{25}N_4O_{5.5}S_4ClCo}$: C, 21.62; H, 5.04; N, 11.20%.

(4) $\mathrm{[Co(dtc)_3]}$: This complex was obtained according to the method in the literature.[3] Found: C, 25.75; H, 4.37; N, 9.84%. Calcd for $\mathrm{[Co(dtc)_3]{=}C_9H_{18}N_3S_6Co}$: C, 25.77; H, 4.32; N, 10.02%.

(5) $(-)^{\mathrm{CD}}_{490}$-$\mathrm{[Co(dtsi)(en)_2](ClO_4)_2}$: A mixed solution of 30% aqueous $\mathrm{H_2O_2}$ (10 g) and 60% aqueous $\mathrm{HClO_4}$ (10 g) was stirred into a solution of $(-)^{\mathrm{CD}}_{500}$-$\mathrm{[Co(dtc)(en)_2](ClO_4)_2}$ (5 g) in 50 $\mathrm{cm^3}$ of DMSO below 5 °C to give an orange-red solution instantly. To the resulting solution we immediately added a mixture of diethyl ether (700 $\mathrm{cm^3}$) and ethanol (300 $\mathrm{cm^3}$). Orange-red crystals separated out on the inside of a beaker within a few minutes and were filtered off. The yield was ca. 1 g. Found: C, 16.19; H, 4.20; N, 13.18%. Calcd for $(-)^{\mathrm{CD}}_{490}$-$\mathrm{[Co(dtsi)(en)_2](ClO_4)_2{=}C_7H_{22}N_5O_{10}S_2Cl_2Co}$: C, 15.86; H, 4.18; N, 13.20%. The compound was stable in the solid state on exposure to light, but was unstable in an aqueous or DMSO solution, even in the dark, probably because of the solvolysis.

(6) $\mathrm{[Co(mtz)(en)_2](ClO_4)_2}$: To a solution of $\mathrm{CoCl_2\cdot 6H_2O}$ (4.8 g, 0.020 mol) in 40 $\mathrm{cm^3}$ of ethanol–water (2:1) we added a solution of ethylenediamine (3.0 g, 0.050v mol) in 100 $\mathrm{cm^3}$ of ethanol. To the mixture we then added a solution of 2-mercapto-2-thiazoline (2.4 g, 0.020 mol)[6] in 200 $\mathrm{cm^3}$ of ethanol, after which the air oxidation was continued for 1 h. The resulting brown-purple precipitate was recrystallized by dissolving it in hot water, adding $\mathrm{NaClO_4}$ (10 g), and cooling the mixture to ca. 5 °C. The yield was 2.5 g (25%). Found: C, 17.05; H, 4.11; N, 13.92%. Calcd for $\mathrm{[Co(mtz)(en)_2](ClO_4)_2{=}C_7H_{20}N_5O_8S_2Cl_2Co}$: C, 16.94; H, 4.06; N, 14.11%.

For optical resolution, to a solution of $\mathrm{[Co(mtz)(en)_2](ClO_4)_2}$ (0.5 g, 0.001 mol) in 20 $\mathrm{cm^3}$ of hot water we added a solution of $\mathrm{K_2[Sb_2(}R,R\mathrm{\text{-}C_4H_2O_6)_2]\cdot 3H_2O}$ (0.3 g, 0.0005 mol) in 30 $\mathrm{cm^3}$ of hot water. After a few minutes, purple thin plate crystals $(+)^{\mathrm{CD}}_{506}$-$\mathrm{[Co(mtz)(en)_2][Sb_2(}R,R\mathrm{\text{-}C_4H_2O_6)_2]\cdot 5H_2O}$ began to deposit; they were filtered off. To the filtrate we added $\mathrm{NaClO_4}$ (10 g), and then the crystals of $(-)^{\mathrm{CD}}_{506}$-$\mathrm{[Co(mtz)(en)_2](ClO_4)_2}$ deposited were collected and recrystallized from hot water. Found for the less-soluble diastereomer: C, 19.42; H, 3.94; N, 7.46%. Calcd for $(+)^{\mathrm{CD}}_{506}$-$\mathrm{[Co(mtz)(en)_2][Sb_2(}R,R\mathrm{\text{-}C_4H_2O_6)_2]\cdot 5H_2O{=}C_{15}H_{38}N_5O_{17}S_2Cl_2CoSb_2}$: C, 19.43; H, 4.13; N, 7.55%. Found for $(-)^{\mathrm{CD}}_{506}$-complex: C, 16.87; H, 4.07; N, 13.73%. Calcd for $(-)^{\mathrm{CD}}_{506}$-$\mathrm{[Co(mtz)(en)_2](ClO_4)_2{=}C_7H_{20}N_5O_8S_2Cl_2Co}$: C, 16.94; H, 4.06; N, 14.11%.

Spectroscopic Determination. The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter, and the MCD spectra on the same instrument in a 1.5 T magnetic field. The absorption, CD, and MCD measurements were made in aqueous, DMSO, and/or $\mathrm{CHCl_3}$ solution at room temperature. The XPS measurements were carried out on a Shimadzu HIPS 70 apparatus. The binding energies relative to the Fermi level were determined by referring to the values of the Na-2s (64.0 eV) and S-$2\mathrm{p}_{3/2}$ (169.5 eV) of $\mathrm{Na_2SO_4}$, mixed with an appropriate amount of each sample.

X-Ray Analysis. The X-ray analysis of $(+)^{\mathrm{CD}}_{500}$-$\mathrm{[Co(dtc)(en)_2][Sb_2(}R,R\mathrm{\text{-}C_4H_2O_6)_2]\cdot 5H_2O}$ was also performed. Crystal Data: monoclinic, $P2_1$, a=14.630(3) Å, b=9.300(1) Å, c=12.023(5) Å, β=110.78(3)°, V=1529.4(8) Å^3, Z=2, D_{calcd}=2.01, D_{obsd}=2.00 g $\mathrm{cm^{-3}}$. An orange-red crystal, of appropriate dimensions (0.375×0.250×0.075 mm), was used for X-ray work. The diffraction intensities were measured using a Rigaku four-circle diffractometer, with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Their intensities decreased progressively with the length of X-ray exposure. Furthermore, the linear absorption coefficient is $\mu(\mathrm{Mo}\ K\alpha)$=25.08 $\mathrm{cm^{-1}}$. Therefore the damage[7] and absorption[8] corrections were applied. Out of a total of 3654 reflections ($5°<2\theta<55°$), 3346 corresponded to those with $I>3\sigma(I)$. The atomic scattering factors of the neutral atoms were taken from Ref. 9 for all the atoms, both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all nonhydrogen atoms.

All the computations were performed on an ACOS-S700 apparatus at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The computer programs used were ABSC,[8] MFPA,[10] HBLS V and RHO,[11] DAPH,[12] and ORTEP.[13] The structure was solved by the usual heavy-atom method: conventional Patterson, Fourier, and least-squares refinement techniques. The absolute configurations of the asymmetric carbon atoms of bis[μ-(R,R)-tartrato(4−)]diantimonate(III) ion were fitted to those reported previously.[14] Therefore, the absolute configuration of the cobalt(III) complex, $(+)^{\mathrm{CD}}_{500}$-$\mathrm{[Co(dtc)(en)_2]^{2+}}$, was determined definitely. All nonhydrogen atoms except one water oxygen atom, which could not be found by the last

Table 1. Fractional Atomic Positional and Isotropic Thermal Parameters for Non-Hydrogen Atoms[a)]

Atom	x	y	z	B[b)]
				Å^2
Co	0.29075(9)	0.33340(16)	0.05600(10)	1.70(3)
S(1)	0.2834(2)	0.5189(3)	−0.0704(2)	2.03(6)
S(2)	0.1389(1)	0.3151(3)	−0.0795(2)	2.43(6)
N(1)	0.2490(6)	0.4633(12)	0.1554(6)	2.6(2)
N(2)	0.2717(7)	0.1756(12)	0.1562(7)	2.8(3)
N(3)	0.4294(6)	0.3584(10)	0.1573(7)	2.6(2)
N(4)	0.3418(6)	0.1966(9)	−0.0327(6)	1.9(2)
C″	0.1643(7)	0.4643(11)	−0.1450(9)	2.1(2)
N″	0.1028(6)	0.5306(12)	−0.2363(7)	2.7(2)
C(Me1)	0.0017(8)	0.4699(21)	−0.2923(11)	4.3(4)
C(Me2)	0.1269(9)	0.6564(17)	−0.2903(15)	5.2(5)
C(11)	0.2440(9)	0.3873(17)	0.2625(8)	3.6(4)
C(12)	0.2063(9)	0.2354(18)	0.2171(12)	4.1(4)
C(21)	0.4908(8)	0.3079(15)	0.0874(9)	2.9(3)
C(22)	0.4450(7)	0.1682(13)	0.0280(9)	2.3(3)
Sb(1)	0.64581(5)	0.94213(9)	0.33258(5)	2.08(2)
Sb(2)	0.67639(5)	0.41774(9)	0.47306(6)	2.38(2)
O(11)	0.5218(5)	0.8399(9)	0.1997(5)	2.6(2)
O(12)	0.3963(6)	0.6965(12)	0.1779(7)	3.6(3)
O(13)	0.5883(5)	0.8392(9)	0.4349(5)	2.4(2)
O(14)	0.5600(5)	0.5226(9)	0.3690(6)	2.5(2)
O(15)	0.6355(5)	0.5406(10)	0.6031(6)	2.7(2)
O(16)	0.5185(6)	0.6796(13)	0.6205(7)	3.8(3)
C(31)	0.4698(7)	0.7646(12)	0.2418(9)	2.5(3)
C(32)	0.4995(7)	0.7616(13)	0.3782(8)	2.4(2)
C(33)	0.5079(7)	0.6067(12)	0.4219(9)	2.2(3)
C(34)	0.5559(8)	0.6124(14)	0.5603(8)	2.7(3)
O(21)	0.7056(5)	0.4048(10)	0.3107(6)	3.1(2)
O(22)	0.8057(6)	0.4938(10)	0.2230(7)	3.1(2)
O(23)	0.7754(5)	0.5689(9)	0.5003(5)	2.5(2)
O(24)	0.7137(5)	0.7739(9)	0.2940(6)	2.3(2)
O(25)	0.7801(5)	0.9388(10)	0.4811(6)	2.9(2)
O(26)	0.9274(6)	0.8379(12)	0.5482(7)	4.1(3)
C(41)	0.7740(7)	0.4886(12)	0.3063(9)	2.1(2)
C(42)	0.8186(7)	0.5874(12)	0.4137(8)	2.0(2)
C(43)	0.8100(7)	0.7445(13)	0.3699(8)	2.3(3)
C(44)	0.8433(7)	0.8437(13)	0.4755(10)	2.8(3)
O(W1)	0.2692(7)	0.8961(10)	0.0092(7)	3.7(3)
O(W2)	0.0921(10)	0.8512(23)	0.0477(16)	9.7(8)
O(W3)	0.0488(9)	0.5779(15)	0.0751(11)	5.8(4)
O(W4)	0.0089(7)	0.5542(17)	0.2802(10)	6.7(5)

a) The e.s.d. are shown in parentheses. The numberings are shown in Fig. 7. b) B is evaluated from the corresponding anisotropic thermal parameters according to Ref. 14. The isotropic thermal parameters are of the $\exp\{-B(\sin^2\theta/\lambda^2)\}$ form.

difference Fourier synthesis, were located and were assigned anisotropic parameters. The hydrogen atoms, except for those belonging to methyl-carbon atoms and water-oxygen atoms, were introduced into their geometrical positions,[15)] but were not refined. The refinement of R and R_2 converged to 0.073 and 0.082 respectively.[16)] The final positional parameters, the corresponding isotropic thermal parameters as calculated from the respective anisotropic parameters by Hamilton's method,[17)] and their estimated standard deviations for nonhydrogen atoms are given in Table 1. The calculated positional parameters of the hydrogen atoms, the anisotropic thermal parameters for all the nonhydrogen atoms, and the complete list of $|F_o|$ and $|F_c|$ values are deposited as Document No. 8847 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Description of the Structure of $(+)^{CD}_{500}$-[Co(dtc)(en)$_2$][Sb$_2$(*R*,*R*-C$_4$H$_2$O$_6$)$_2$]·5H$_2$O and the Trans Influence Induced by the dtc Ligand. Figure 1 shows the numbering of the diastereomeric salt. Tables 2 and 3 show the nonhydrogen atom bond distances and angles respectively. Table 4 lists several selected plane equations, sets of deviations of atoms from the plane, and the dihedral angles between the pair of planes.

This dtc complex has the *Λ*-(*δ*,*δ*) configuration, judged from the asymmetric carbon atoms of the bis[*μ*-(*R*,*R*)-tartrato(4−)]diantimonate(III) ion.[14)] The [Sb$_2$(*R*,*R*-C$_4$H$_2$O$_6$)$_2$]$^{2-}$ anion has reasonable bond distances and angles as compared with the results of an other structure analysis,[14)] as is shown in Table 5. Table 6 shows the selected bond distances and angles of the present [Co(dtc)(en)$_2$]$^{2+}$ in comparison with those of [Co(dtc)$_3$].[4)] There are no large differences between the two complexes concerning the dtc ligand, the Co–S distances, and the bite angle, S–Co–S. The cobalt atom lies nearly on the plane of S_2CN (Table 4), but the S(1)–Co–S(2), S(1)–Co–N(2), and S(2)–Co–N(3) angles are 76.9, 169.9, and 172.4° respectively, accounting for the rather distorted octahedral structure shown in Table 2. More remarkable is the mean of the trans Co–N(2) and Co–N(3) distances, which is longer by 0.026 Å than the mean of cis Co–N(1) and Co–N(4). The magnitude of the trans influence induced by the dtc ligand is between those induced by the

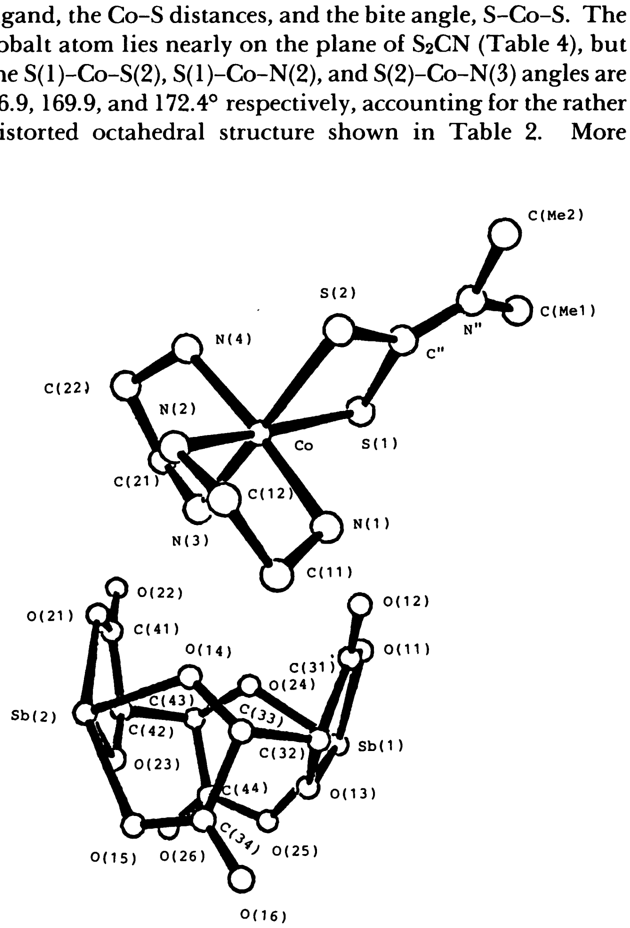


Fig. 1. A perspective view and numbering of $(+)^{CD}_{500}$-$[Co(dtc)(en)_2][Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot 5H_2O$ (50% probability thermal ellipsoids).

Table 2. Intramolecular Bond Distances (*l*/Å)

For the Co(III) complex:			
Co–S(1)	2.277(3)	Co–S(2)	2.249(3)
Co–N(1)	1.950(8)	Co–N(2)	1.990(9)
Co–N(3)	1.978(8)	Co–N(4)	1.966(8)
S(1)–C″	1.724(10)	S(2)–C″	1.694(10)
C″–N″	1.317(13)	N″–C(Mel)	1.495(15)
N″–C(Me2)	1.447(16)	N(1)–C(11)	1.473(16)
C(11)–C(12)	1.562(18)	C(12)–N(2)	1.509(15)
N(3)–C(21)	1.532(14)	C(21)–C(22)	1.510(16)
C(22)–N(4)	1.459(13)		
For bis[μ-(*R*,*R*)-tartrato(4−)]diantimonate(III):			
Sb(1)–O(11)	2.167(6)	Sb(1)–O(13)	1.966(6)
Sb(1)–O(24)	1.987(7)	Sb(1)–O(25)	2.131(7)
Sb(2)–O(14)	1.968(7)	Sb(2)–O(15)	2.180(7)
Sb(2)–O(21)	2.142(8)	Sb(2)–O(23)	1.961(7)
O(11)–C(31)	1.260(12)	O(12)–C(31)	1.227(13)
O(13)–C(32)	1.423(12)	O(14)–C(33)	1.399(12)
O(15)–C(34)	1.280(12)	O(16)–C(34)	1.219(13)
C(31)–C(32)	1.555(14)	C(32)–C(33)	1.512(14)
C(33)–C(34)	1.575(14)	O(21)–C(41)	1.296(13)
O(22)–C(41)	1.242(13)	O(23)–C(42)	1.406(12)
O(24)–C(43)	1.409(12)	O(25)–C(44)	1.302(13)
O(26)–C(44)	1.239(14)	C(41)–C(42)	1.526(14)
C(42)–C(43)	1.550(14)	C(43)–C(44)	1.494(15)

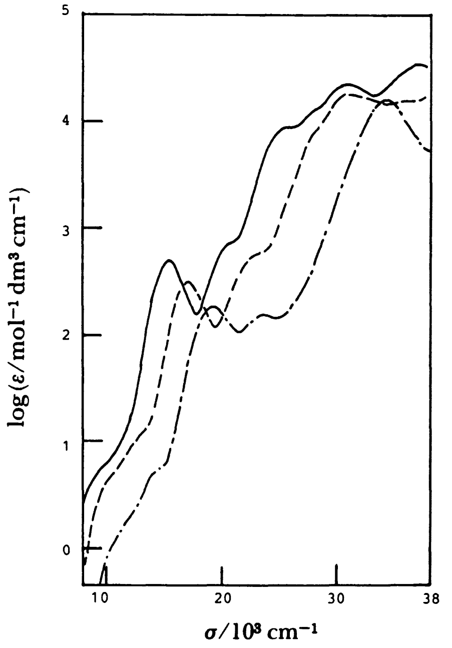


Fig. 2. Absorption spectra of $[Co(dtc)_{3-n}(en)_n](ClO_4)_n$ in DMSO solution: $n=0$ (——), $n=1$ (---), and $n=2$ (-·-).

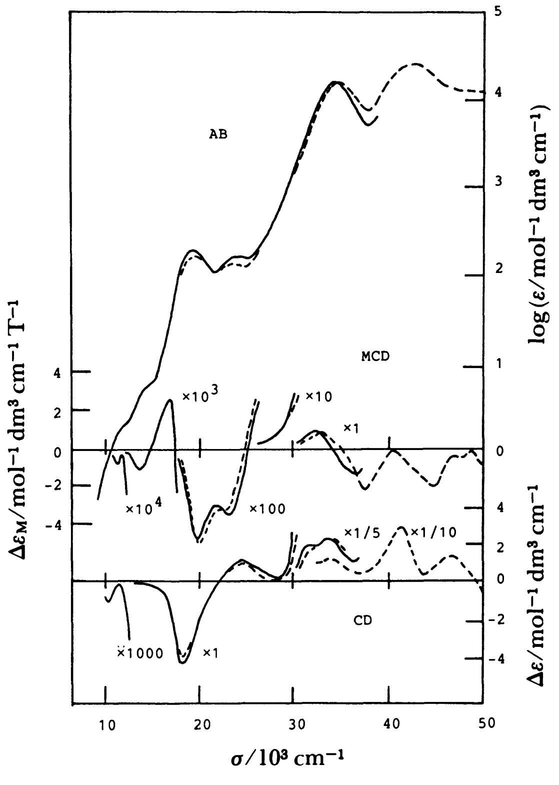


Fig. 3. Absorption, MCD, and CD spectra of $[Co(dtc)(en)_2](ClO_4)_2$ in DMSO (——) and H_2O (---) solution. For CD, $(-)^{CD}_{500}$-isomer (Δ-isomer) was used.

Table 3. Intramolecular Bond Angles (ϕ/°)

	For the Co(III) complex:		
Metal coordination angles			
S(1)-Co-S(2)	76.90(9)	S(1)-Co-N(1)	89.5(3)
S(1)-Co-N(2)	169.9(3)	S(1)-Co-N(3)	96.7(3)
S(1)-Co-N(4)	93.6(2)	S(2)-Co-N(1)	92.7(3)
S(2)-Co-N(2)	94.0(3)	S(2)-Co-N(3)	172.4(3)
S(2)-Co-N(4)	91.2(2)	N(1)-Co-N(2)	86.5(3)
N(1)-Co-N(3)	91.3(3)	N(1)-Co-N(4)	175.5(3)
N(2)-Co-N(3)	92.7(4)	N(2)-Co-N(4)	90.9(3)
N(3)-Co-N(4)	85.1(3)		
Intraligand angles			
Co-S(1)-C″	85.3(3)	Co-S(2)-C″	86.9(4)
Co-N(1)-C(11)	111.7(7)	Co-N(2)-C(12)	105.8(7)
Co-N(3)-C(21)	106.8(6)	Co-N(4)-C(22)	111.8(6)
S(1)-C″-S(2)	110.8(6)	S(1)-C″-N″	124.4(8)
S(2)-C″-N″	124.8(8)	C″-N″-C(Me1)	119.0(9)
C″-N″-C(Me2)	123.4(9)	C(Me1)-N″-C(Me2)	117.5(9)
N(1)-C(11)-C(12)	104.9(9)	C(11)-C(12)-N(2)	107.1(9)
N(3)-C(21)-C(22)	106.2(9)	C(21)-C(22)-N(4)	106.6(8)
	For bis[μ-(*R*,*R*)-tartrato(4−)]diantimonate(III):		
O(11)-Sb(1)-O(13)	79.2(3)	O(11)-Sb(1)-O(24)	80.7(3)
O(11)-Sb(1)-O(25)	153.1(3)	O(13)-Sb(1)-O(24)	97.9(3)
O(13)-Sb(1)-O(25)	86.7(3)	O(24)-Sb(1)-O(25)	78.5(3)
O(14)-Sb(2)-O(15)	78.8(3)	O(14)-Sb(2)-O(21)	81.4(3)
O(14)-Sb(2)-O(23)	100.1(3)	O(15)-Sb(2)-O(21)	150.9(3)
O(15)-Sb(2)-O(23)	82.8(3)	O(21)-Sb(2)-O(23)	79.9(3)
Sb(1)-O(11)-C(31)	115.1(6)	Sb(1)-O(13)-C(32)	118.1(6)
Sb(1)-O(24)-C(43)	117.8(6)	Sb(1)-O(25)-C(44)	114.8(7)
Sb(2)-O(14)-C(33)	118.8(6)	Sb(2)-O(15)-C(34)	115.4(6)
Sb(2)-O(21)-C(41)	114.2(6)	Sb(2)-O(23)-C(42)	117.1(5)
O(11)-C(31)-O(12)	123.9(10)	O(11)-C(31)-C(32)	116.2(9)
O(12)-C(31)-C(32)	119.9(9)	C(31)-C(32)-O(13)	111.4(8)
C(31)-C(32)-C(33)	110.0(8)	O(13)-C(32)-C(33)	112.0(8)
C(32)-C(33)-O(14)	111.8(8)	C(32)-C(33)-C(34)	106.6(8)
C(33)-C(34)-O(15)	114.2(8)	C(33)-C(34)-O(16)	120.7(9)
O(15)-C(34)-O(16)	125.1(9)	O(21)-C(41)-O(22)	124.9(9)
O(21)-C(41)-C(42)	115.3(9)	O(22)-C(41)-C(42)	119.8(9)
C(41)-C(42)-O(23)	113.2(8)	C(41)-C(42)-C(43)	108.8(8)
O(23)-C(42)-C(43)	111.2(8)	C(42)-C(43)-O(24)	110.3(8)
C(42)-C(43)-C(44)	109.2(8)	C(43)-C(44)-O(25)	116.4(9)
C(43)-C(44)-O(26)	120.9(10)	O(25)-C(44)-O(26)	122.6(10)
O(14)-C(33)-C(34)	112.5(8)	O(24)-C(43)-C(44)	112.2(8)

thiolato and thiosulfato ligands: SO_3^{2-}(0.089)>RSO^-(0.072)>RSO_2^-(0.049)>RS^-(0.040)>dtc^-(0.026)>$S_2O_3^{2-}$(0.019)>RSR′, RSSR′, or $RSNH_2$(0.000),[5] where the figures in parentheses indicate the difference (Å) between the trans Co-N distance and the average of the cis distances in the $[Co(S)(N)_5]$ type. The dtc sulfur donor atoms do not induce so large a trans influence, presumably because of the little overlapping between the σ(dtc) MO and metal dσ AO attributable to the 4-membered acute chelation.

Results and Discussion

Synthesis and Characterization of $[Co(dtc)_{3-n}(diamine)_n](ClO_4)_n$($n$=0, 1, and 2, and diamine means en or *R*-pn). The reduction of dialkyl disulfide by 2-equiv cobalt(II) ions with 10-equiv amines yields several $[Co(thiolato)(amine)_5]^{2+}$-type complexes.[18] In the present series, $[Co(dtc)_{3-n}(diamine)_n]^{n+}$ (n=0, 1, and 2, and diamine means en or *R*-pn), such a redox reaction between the disulfide and cobalt(II) ions produced the desired complexes in high yields, as has been described in the Experimental section.

The absorption spectra of three complexes $[Co(dtc)_{3-n}(en)_n](ClO_4)_n$($n$=0, 1, and 2) in a DMSO solution are shown in Fig. 2. The energies of both the spin-allowed first (15000—20000 cm^{-1}) and second (20000—25000 cm^{-1}) d-d bands decrease with the increase in the number of dtc ligands. Such shifts correspond the weaker ligand field of the dtc sulfur donor than that of the en nitrogen one. The observed increase in the band intensity can be accounted for through the partial release of the Laporte forbidden d-d transitions by the mixing between the dπ(Co) and n(dtc) or π(dtc) and by the distortion from the octahedral-site structure around the central cobalt(III)

Table 4. Displacements of Atoms from the Least-Squares Plane and the Dihedral Angles between Planes

For the Co(III) complex:

Plane 1. [Co, S(1), S(2), N(2), and N(3)]

$0.5239X-0.6451Y-0.5562Z+0.2536=0$

Co 0.0070, S(1) −0.0891, S(2) 0.1035, N(2) −0.0465, N(3) 0.0509, C″ −0.0426, N″ −0.1439, C(Me1) −0.0691, C(Me2) −0.2346

Plane 2. [Co, S(1), N(1), N(2), and N(4)]

$-0.7902X-0.1947Y-0.5812Z+4.1017=0$

Co −0.0409, S(1) 0.1075, N(1) −0.1064, N(2) 0.1466, N(4) −0.0948

Plane 3. [Co, S(2), N(1), N(3), and N(4)]

$-0.3522X-0.7682Y+0.5346Z+3.4924=0$

Co 0.0321, S(2) −0.0724, N(1) 0.0710, N(3) −0.1009, N(4) 0.0773

Plane 4. [S(1), S(2), C″, and N″]

$-0.5517X+0.5697Y+0.6091Z+0.1889=0$

S(1) 0.0022, S(2) 0.0047, C″ −0.0101, N″ 0.0039, Co 0.1234, C(Me1) −0.0283, C(Me2) −0.0423

Dihedral angles ($\phi/°$)

Between Planes 1 and 2	88.0
Between Planes 1 and 3	89.2
Between Planes 1 and 4	174.5
Between Planes 2 and 3	83.3

The X, Y, and Z coordinates in Å refer to the crystallographic axes.

Table 5. Selected Bond Distances (l/Å) and Angles ($\phi/°$) for the $[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]^{2-}$ Ion

	This work	$K_2[Sb_2(R,R\text{-}C_4H_2O_6)_2]\cdot 3H_2O$[11]
Bond	Average l/Å	Average l/Å
Sb-O[a]	2.155	2.16
Sb-O[b]	1.971	1.99
O[a]-C	1.285	1.27
O[b]-C′	1.409	1.40
Angle	Average $\phi/°$	Average $\phi/°$
O[a]-Sb-O[b]	79.1	78.3
Sb-O[a]-C	114.9	115.2
Sb-O[b]-C′	118.0	117.5

a) and b) oxygen atoms indicate the carboxyl and hydroxyl oxygen atoms of a tartrato(4−) anion.

Table 6. Selected Bond Distances (l/Å) and Angles ($\phi/°$) for the Cobalt(III) Complexes Containing the dtc Ligand

	This work	$[Co(dtc)_3]$[19]
Bond	Average l/Å	Average l/Å
Co-S	2.263	2.264
S-C″	1.709	1.705
C″-N″	1.317	1.320
N″-C(Me)	1.460	1.450
Angle	Average $\phi/°$	Average $\phi/°$
S-Co-S	76.9	76.4
Co-S-C″	86.1	86.6
S-C″-S	110.8	110.4
S-C″-N″	124.6	124.9
C″-N″-C(Me)	121.2	121.4
C(Me)-N″-C(Me)	117.5	117.2

ion because of the 4-membered chelation of the dtc ligand. In the higher energy region (25000—35000 cm^{-1}), the energy of ligand-to-metal charge-transfer (LMCT) band, $d\sigma^*(Co)\leftarrow\sigma(dtc)$, decreases and the band is split and widened with the increase of the number of the dtc ligands. These features may result from the increase in the sets of combination of the σ MOs of the dtc ligands.

The absorption, MCD, and CD spectra of the complex compound $(-)^{CD}_{500}$-$[Co(dtc)(en)_2](ClO_4)_2$, which has a *cis*-$[Co(S)_2(N)_4]$ chromophore, are shown in Fig. 3, while the numerical data are listed in Tables 7, 8, and 9. The weak shoulders in the absorption spectrum at ca. 12000 cm^{-1} and ca. 15000 cm^{-1} can be assigned to the spin-forbidden d-d transitions, $^3T_1$ and $^3T_2\leftarrow{}^1A_1$ (O_h) respectively. In the MCD spectra, the negative peak at 11360 cm^{-1} and the pair of the negative peak at 13700 cm^{-1} and the positive one at 17000 cm^{-1} correspond to the transitions of $^3T_1$ (the first peak) and $^3T_2$ (the latter two peaks)$\leftarrow{}^1A_1(O_h)$. The absorption band at 19400 cm^{-1}, the negative CD peak at 18300 cm^{-1}, and the negative MCD at 19900 cm^{-1} are assigned to the spin-allowed first d-d transition of $^1T_1\leftarrow{}^1A_1$ (O_h), and the absorption band at 23700 cm^{-1} the negative MCD peak at 23200 cm^{-1}, and the positive CD one at 24500 cm^{-1}, to the second d-d transition of $^1T_2\leftarrow{}^1A_1$. The intense absorption bands at 34300 cm^{-1} and at 41000 cm^{-1} can be assigned to the LMCT band $\sigma^*(Co)\leftarrow\sigma$(dtc or sulfur) and the intra-

Table 7. Absorption Spectral Data

Complex/Solvent	$\sigma_{\max}(\log \varepsilon)^{a)}$
$[Co(dtc)(en)_2](ClO_4)_2$	
DMSO	12.05(0.27)^{sh}, 14.93(0.76)^{sh}, 19.40(2.25), 23.71(2.18), 34.30(4.24)
H_2O	14.94(0.80)^{sh}, 19.60(2.21), 23.29(2.11), 34.75(4.21), 41.10(4.35)^{sh}, 42.90(4.43)
$[Co(dtc)_2(en)]ClO_4$	
DMSO	10.00(0.56)^{sh}, 12.99(1.06)^{sh}, 17.24(2.51), 23.00(2.76)^{sh}, 27.47(3.79)^{sh}, 31.25(4.27)
H_2O	17.39(2.49), 23.00(2.70)^{sh}, 28.17(3.78)^{sh}, 31.75(4.22), 35.71(4.11)^{sh}, 40.00(4.34)^{sh}, 41.90(4.45)
$[Co(dtc)_3]$	
DMSO	10.00(0.78)^{sh}, 15.38(2.70), 21.05(2.88)^{sh}, 25.74(3.95)^{sh}, 25.74(3.95)^{sh}, 27.89(4.08)^{sh}, 30.91(4.35), 35.90(4.49)^{sh}
H_2O	10.00(0.74)^{sh}, 15.60(2.66), 21.05(2.85)^{sh}, 25.53(3.98)^{sh}, 25.53(3.98)^{sh}, 28.03(4.13)^{sh}, 31.08(4.34), 36.14(4.53)^{sh}, 37.40(4.55), 41.00(4.52)
Δ-$[Co(dtc)_2\{(R)\text{-pn}\}]ClO_4$	
DMSO	10.00(0.56)^{sh}, 12.99(1.03)^{sh}, 17.24(2.53), 23.00(2.77)^{sh}, 27.78(3.87)^{sh}, 31.25(4.29)
H_2O	17.39(2.52), 23.00(2.73)^{sh}, 28.17(3.84)^{sh}, 31.75(4.28), 35.71(4.17)^{sh}, 40.00(4.41)^{sh}, 41.67(4.52)
Λ-$[Co(dtc)_2\{(R)\text{-pn}\}]ClO_4$	
DMSO	10.00(0.57)^{sh}, 12.99(1.01)^{sh}, 17.24(2.54), 23.00(2.77)^{sh}, 27.78(3.89)^{sh}, 31.25(4.29)
H_2O	17.39(2.52), 23.00(2.75)^{sh}, 28.17(3.88)^{sh}, 31.25(4.29), 35.71(4.18)^{sh}, 40.00(4.42)^{sh}, 41.67(4.53)
Δ-$[Co(dtsi)(en)_2](ClO_4)_2$	
DMSO	20.94(2.49), 29.00(3.40)^{sh}, 37.74(4.40)
$[Co(mtz)(en)_2](ClO_4)_2$	
DMSO	11.95(0.43), 16.00(1.47)^{sh}, 19.20(2.18), 23.30(2.11), 33.33(3.66)^{sh}
H_2O	19.50(2.10), 23.20(2.05), 33.33(3.68)^{sh}, 38.20(4.21), 44.00(4.25)^{sh}, 48.00(4.33)

a) Wavenumbers are given in $10^3\,cm^{-1}$ units, the $\log(\varepsilon/mol^{-1}\,dm^3\,cm^{-1})$ values are in parentheses, and sh indicates a shoulder.

Table 8. MCD Spectral Data

Complex/Solvent	$\sigma_{ext}(\Delta\varepsilon_M)^{a)}$
$[Co(dtc)(en)_2](ClO_4)_2$	
DMSO	11.36(−0.00008), 13.70(−0.0011), 16.95(+0.0026), 19.92(−0.048), 23.15(−0.035), 32.47(+0.983), 37.76(−1.37)
H_2O	20.00(−0.050), 22.73(−0.032), 33.11(0.898), 37.40(−2.10), 44.44(−2.04)
$[Co(dtc)_2(en)]ClO_4$	
DMSO	12.11(−0.0018), 14.29(+0.0031), 17.54(−0.066), 21.98(−0.041), 29.41(+1.91), 31.65(−1.96)
H_2O	29.85(+1.57), 32.26(−1.51), 42.55(−2.16)
$[Co(dtc)_3]$	
DMSO	11.24(−0.0025), 12.66(+0.0036), 15.95(−0.120), 20.53(−0.075), 24.10(+0.279), 27.17(+3.12), 28.99(−1.63), 35.71(−0.80)
$CHCl_3$	10.99(−0.0025), 12.82(−0.0033), 16.05(−0.106), 20.62(−0.064), 24.10(+0.317), 27.03(+3.35), 28.65(−1.96), 30.77(−0.66)^{sh}

a) Wavenumbers are given in $10^3\,cm^{-1}$ units, the $\Delta\varepsilon_M$ (in parentheses) are given in $mol^{-1}\,dm^3\,cm^{-1}\,T^{-1}$ units, and sh indicates a shoulder.

ligand transition π^*(dtc or delocalized MO on S_2NC fragment)←n(dtc) respectively.

Figure 4 shows the absorption and MCD spectra of $[Co(dtc)_2(en)]ClO_4$, which has a *cis*-$[Co(S)_4(N)_2]$ chromophore. The first eluted $(-)^{CD}_{580}$-$[Co(dtc)_2(R\text{-pn})]ClO_4$, which shows a negative CD at 17000 cm^{-1}, is assigned to the Δ absolute configuration by analogy with the assignment for $[Co(dtc)(en)_2](ClO_4)_2$. The CD curve due to the configurational contribution was calculated from these CD spectra on the basis of the assumed additivity of the CD contributions. It is noteworthy that the CD intensities of the bis-

Table 9. CD Spectral Data

Complex/Solvent	$\sigma_{\text{ext}}(\Delta\varepsilon)$[a)]
Δ-[Co(dtc)(en)$_2$](ClO$_4$)$_2$	
DMSO	10.20(−0.0011), 18.25(−4.26), 24.51(+1.14), 31.45(+9.34), 33.56(+10.94)
H_2O	18.21(−3.87), 24.51(+0.99), 32.26(+9.24), 34.13(+11.13), 41.32(+28.47), 46.73(+12.87)
Δ-[Co(dtc)$_2${(R)-pn}]ClO$_4$	
DMSO	17.01(−9.79), 20.20(−1.04)$^{\text{sh}}$, 23.26(+3.98)$^{\text{sh}}$, 28.82(+57.16), 31.25(+41.25), 35.71(−44.71)$^{\text{sh}}$, 37.04(−64.73)
H_2O	17.24(−8.75), 20.41(−0.84)$^{\text{sh}}$, 23.26(+3.14)$^{\text{sh}}$, 29.07(+53.74), 31.75(+38.11), 37.59(−43.10), 40.49(+27.44), 43.29(+23.15), 46.51(−44.78)
Λ-[Co(dtc)$_2${(R)-pn}]ClO$_4$	
DMSO	16.86(+9.68), 20.41(+1.51)$^{\text{sh}}$, 22.99(−2.44)$^{\text{sh}}$, 28.49(−60.52), 31.25(−37.67), 36.90(+67.82)
H_2O	17.04(+9.11), 20.20(+1.36)$^{\text{sh}}$, 23.26(−2.21)$^{\text{sh}}$, 28.99(−58.97), 31.85(−37.51), 37.31(+49.28), 40.32(−30.16), 42.74(−16.15), 46.51(+53.27)
Δ-[Co(dtsi)(en)$_2$](ClO$_4$)$_2$	
DMSO	20.41(−0.443), 28.90(+0.645), 37.04(+3.827)
Δ-[C(mtz)(en)$_2$](ClO$_4$)$_2$	
DMSO	19.76(−2.26), 24.94(+1.02), 32.89(+5.17)

a) Wavenumbers are given in 10^{-1} cm^{-1} units, the $\Delta\varepsilon$ (in parentheses) are given in mol^{-1} dm^3 cm^{-1} units, and sh indicates a shoulder.

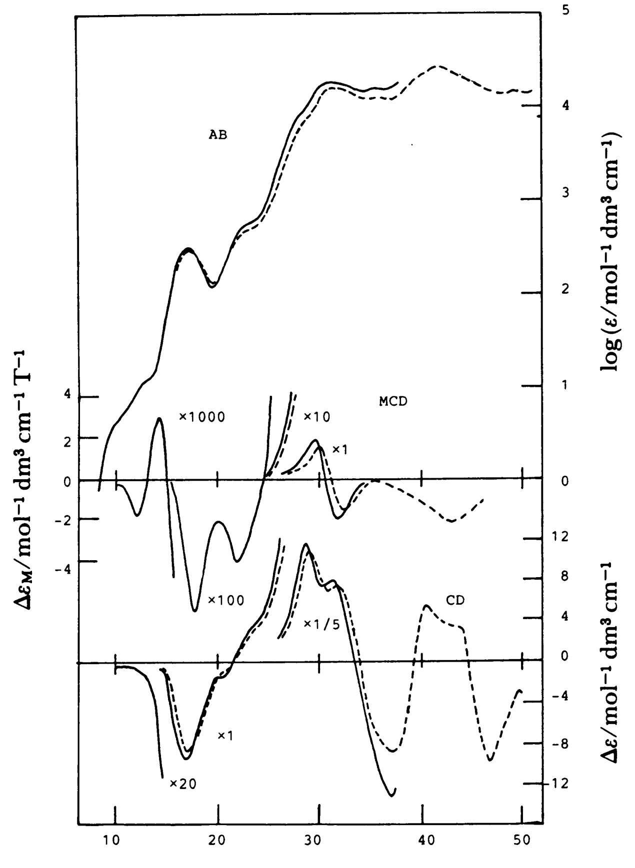


Fig. 4. Absorption and MCD spectra of [Co(dtc)$_2$(en)]ClO$_4$, and CD curve of [(Δ-[Co(dtc)$_2$(R-pn)]ClO$_4$)−(Λ-[Co(dtc)$_2$(R-pn)]ClO$_4$)]/2 in DMSO (——) and H_2O (---) solutions.

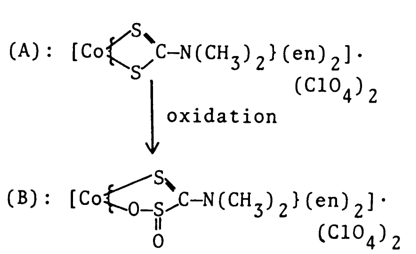
(dithiocarbamate) complexes are about twice larger than that of the monodithiocarbamate one. This means the larger distortion from the octahedral-site structure is due to the increase in the numbers of the 4-membered dtc ligand. The shoulders of the absorption spectra at 10000 cm^{-1} and 13000 cm^{-1} are assigned to the spin-forbidden d-d transitions. A negative CD peak at 16900 cm^{-1} and a negative MCD peak at 17500 cm^{-1} are assigned to the splitting components of the first d-d transition. The two LMCT absorption bands at 27500 and 31300 cm^{-1} correspond to the two peaks of MCD at 29400 and 31700 cm^{-1} or to the two peaks of CD at 28700 and 31300 cm^{-1}. The absorption bands at 40000 and 41900 cm^{-1} are assigned to the dtc intraligand $\pi^*\leftarrow n$ transitions. The vicinal contribution of asymmetric carbon or R-pn to the CD spectrum of [Co(dtc)$_2$(R-pn)]ClO$_4$ is shown in Table 9. It is interesting to note that the contribution depends significantly on the kind of solvent.

The absorption and MCD spectra of [Co(dtc)$_3$] with a [Co(S)$_6$] chromophore are shown in Tables 7 and 8. The absorption bands at 11200 and 12700 cm^{-1} are assigned to the spin-forbidden d-d transitions. The bands at 24100, 27200, and 29000 cm^{-1} are assigned to the LMCT transitions, and the band at 35900 cm^{-1}, to the dtc intraligand transitions. The positions of the absorption bands are the same as those of the MCD ones throughout the region observed.

The splitting components of the first d-d transition of the cis-S$_2$N$_4$- and cis-S$_4$N$_2$-type complexes were calculated semiempirically[21)] on the basis of the observed d-d transition energies of [Co(en)$_3$]$^{3+}$ and

$[Co(dtc)_3]$. The calculated values are fairly consistent with the observed splittings: the energetically lower component corresponds to the CD peak, and the higher one, to the MCD extreme, as is shown in Table 10.

Synthesis and Characterization of the Oxidation Product $[Co(dtsi)(en)_2](ClO_4)_2$. The orange-red oxidation complex was prepared via the H_2O_2 oxidation of $[Co(dtc)(en)_2](ClO_4)_2$. The H_2O_2 oxidation of the coordinated dtc ligand in neutral aqueous solution was ineffective, but it was effective in acid media.



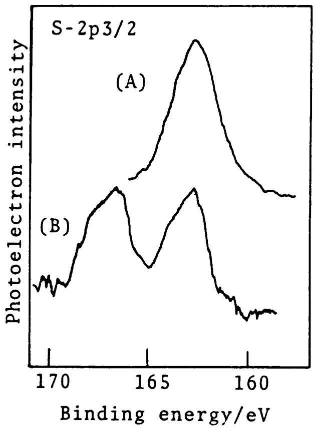


Fig. 5. XPS spectra of (A) $[Co(dtc)(en)_2](ClO_4)_2$ and (B) $[Co(dtsi)(en)_2](ClO_4)_2$ in the region of S-2p binding energy.

Elemental analysis indicates that the calculated formula weight of the resulting species is consistent with two additional oxygen atoms compared with the starting material. Since it is reasonable to consider that the oxidation takes place at the sulfur moieties of the dtc ligand, there are two possibilities, $(CH_3)_2NC(SO)SO^-$ or $(CH_3)_2NC(S)SO_2^-$, as the oxidized dtc ligand. The XPS spectra of the $[Co(dtc)(en)_2](ClO_4)_2$ and $[Co(dtsi)(en)_2](ClO_4)_2$ are given in Fig. 5: they indicate the presence of two kinds of sulfur in the latter complex. The lower S-2p$_{3/2}$ binding energy (162.7 eV) in the dtsi complex is the same as that in the dtc complex. The higher peak (166.6 eV) is due to the oxidized sulfur atom with two oxygen atoms, for the S-2p$_{3/2}$ binding energy increases with the increase in

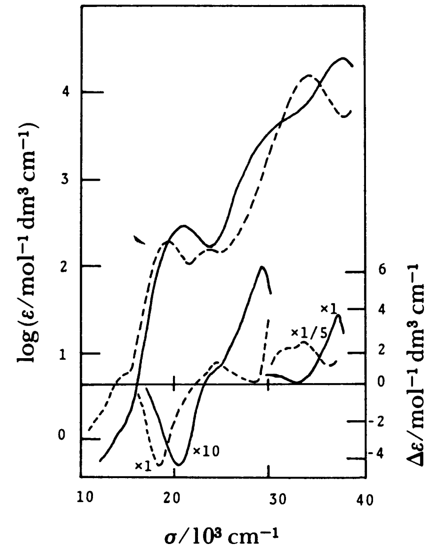


Fig. 6. Absorption and CD spectra of Δ-$[Co(dtsi)(en)_2](ClO_4)_2$ (——) and Δ-$[Co(dtc)(en)_2](ClO_4)_2$ (---) in DMSO solution.

Table 10. Splittings of the 1st Spin-Allowed d-d Transition.
(The wavenumber is given in $10^3\,cm^{-1}$ units)

Type/Complex	Method	Splittings of the 1st d-d band
N_6		
$[Co(en)_3]^{3+}$	AB	21.3 (Standard)
Δ-isomer	CD	20.5(−)
S_6		
$[Co(dtc)_3]$	AB	15.4 (Standard)
	MCD	16.0(−)
cis-S_2N_4	Calcd	18.3, 19.8
$[Co(dtc)(en)_2]^{2+}$	AB	19.4
Δ-isomer	CD	18.3(−)
	MCD	19.9(−)
cis-S_4N_2	Calcd	16.8, 18.3
$[Co(dtc)_2(en)]^+$	AB	17.2
$(\Delta\varepsilon_{\Delta\text{-}R}-\Delta\varepsilon_{\Lambda\text{-}R})/2$	CD	16.9(−)
	MCD	17.5(−)
Δ-$[Co(dtc)_3]$	CD	15.50(−0.14) from Ref. 2

the sulfur oxidation numbers.[22] Since the intensities of the lower and higher energy bands are approximately equal, the dtsi complex should have oxidized and nonoxidized sulfur atoms compared with those of the original dtc complex. Thus, the dtsi ligand is represented by this formula: $(CH_3)_2NC(S)SO_2^-$. The present dtsi complex exhibits a new absorption band at ca. 29000 cm^{-1} as a broad shoulder in addition to the $\sigma^*(Co) \leftarrow \sigma(S)$ LMCT band at 37000 cm^{-1}, as is shown in Fig. 6. The *O*-bonded sulfinato cobalt(III) complex, $[Co(NH_2CH_2CH_2SO_2\text{-}O,N)(en)_2]^{2+}$, shows a similar absorption band at 31000 cm^{-1} without the $\sigma^*(Co) \leftarrow \sigma(S)$ LMCT band.[5] This fact indicates that the dtsi ligand coordinates through the sulfinato oxygen and thiocarbonyl sulfur atoms. This indicates the occurrence of the chelate ring expansion from a four-membered ring to a five-membered one during the oxidation process. The optically active complex $(-)^{CD}_{490}\text{-}[Co(dtsi)(en)_2]^{2+}$ can be assigned to the Δ-configuration on the basis of the CD sign at 20400 cm^{-1} in the first d–d band region (Fig. 6). Therefore, the oxidation reaction proceeds with a retention of the initial configuration of Δ-$[Co(dtc)(en)_2]^{2+}$, whose configuration was determined by X-ray structure analysis as has been described in the preceding section.

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