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Preparation and Some Properties of Cobalt(III) Complexes with 1-Thio-β-D-glucose (H_5tg). Crystal Structure of Δ_D-[Co(H_3tg-O,S)(en)$_2$]NO_3

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Cobalt(III) complexes with 1-thio-β-D-glucose (H_5tg), [Co(H_4tg-S)$_2${(en)$_2$ or (tren)}]$^+$ and [Co(H_3tg-O, S){(en)$_2$ or (tren)}]$^+$, were newly prepared; where en and tren denote ethylenediamine and tris(2-aminoethyl)-amine, respectively. The oxidation products of [Co(H_3tg-O,S){(en)$_2$ or (tren)}]$^+$ were prepared by the addition of H_2O_2. These complexes were separated into their isomers by column chromatography. The crystal structure of $(+)^{CD}_{230}$-[Co(H_3tg-O,S)(en)$_2$]$NO_3\cdot H_2O$ was determined by X-ray diffraction: This complex, chemical formula $CoC_{10}H_{16}O_8N_5S$, crystallizes in orthorhombic, space group $P2_12_12_1$, $a=14.328(1)$, $b=14.617(1)$, $c=8.605(1)$ Å, $V=1802.2(3)$ Å^3, $Z=4$, and $R=0.055$. The geometry around the cobalt atom is approximately octahedral, coordinated by one 1-thio-β-D-glucose and two en ligands. 1-Thio-β-D-glucose takes the cyclic chair form and coordinates to cobalt(III) ion through the close-neighboring sulfur and oxygen atoms. This $(+)^{CD}_{230}$ isomer takes the Δ configuration. The other complexes were characterized by their absorption, CD, ^{13}C NMR spectra. For all of the isomers, the Δ configuration will be more preferentially formed than the Λ one.

Sugars can form complexes with metal ions, but the metal complexes with sugars or their related compounds are still largely unexplored.[1,2] In order to investigate the stereochemical relationship between the hexose-type sugars and cobalt(III) ion, 1-thio-β-D-glucose (H_5tg) of the cyclic form, which is a derivative of β-D-glucose, is chosen as a model sugar. 1-Thio-β-D-glucose contains a thiolate-type sulfur atom, which has a strong affinity for the cobalt(III) ion.[3—14] Then, we expect that 1-thio-β-D-glucose will coordinate selectively to the cobalt(III) ion through the sulfur atom and/or its close-neighboring oxygen atom, that is, it will act as a monodentate-S or didentate-O,S. From the structural point of view, therefore, the tetraamine cobalt(III) complexes will be favorable, that is, the cobalt(III) complexes with tris(2-aminoethyl)amine (tren) has two coordination sites restricted in only the cis position. For the bis(ethylenediamine) (en$_2$) complexes, two isomers, *trans* and *cis*, are possible. Furthermore, it is of interest to investigate the reactivity of the coordinated sulfur atom of the ligand.[5—8] In this paper, we report on the synthesis, spectrochemical and stereochemical properties of the novel cobalt(III) complexes with 1-thio-β-D-glucose, [Co(H_4tg-S)$_2$(tren)]$^+$ and [Co(H_3tg-O,S)(tren)]$^+$, *trans*(*S*)- and *cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$, and [Co(H_3tg-O,S)(en)$_2$]$^+$, together with their oxidation products, [Co(H_3sig-O,S)(en)$_2$]$^+$ and [Co(H_3sig-O, S)(tren)]$^+$ (H_3sig^{2-}; 1-thio-β-D-glucose-S-oxide).

Experimental

Materials. 1-Thio-β-D-glucose sodium salt (NaH_4tg) was purchased from Sigma Chemical Co., Ltd. Other reagents were purchased from Wako Pure Chemical Ind. Co., Ltd., and Tokyo Chemical Ind. Co., Ltd. All chemicals were of reagent grade and used without further purification.

Preparation of Complexes. 1) [Co(H_4tg-S)$_2$(tren)]$^+$ (1). To a solution containing 0.30 g (0.9 mmol) of [$CoCl_2$(tren)]Cl[15] in 2.5 cm^3 of deaerated water was added a solution containing 0.40 g (1.8 mmol) of NaH_4tg in 1.75 cm^3 of deaerated water. The mixture was stirred at room temperature for 30 min in a stream of nitrogen, whereupon the color of the solution turned from violet to dark brown. To this mixture was added a solution containing 0.38 g (1.1 mmol) of $NaB(C_6H_5)_4$ in 5 cm^3 of water. This was kept in a refrigerator. The resulting greenish brown crystals ($\mathbf{1}\cdot B(C_6H_5)_4\cdot 2H_2O$) were collected by filtration, washed with a small amount of water, and then air-dried. Found: C, 52.85; H, 6.98; N, 5.84%. Calcd for [Co(H_4tg-S)$_2$(tren)] $B(C_6H_5)_4\cdot 2H_2O = C_{42}H_{64}N_4O_{10}S_2BCo\cdot 2H_2O$: C, 52.82; H, 7.19; N, 5.87%.

2) [Co(H_4tg-S)$_2$(en)$_2$]$^+$ (2). This complex was prepared by a procedure similar to that used for 1), using *trans*-[$CoCl_2$(en)$_2$]Cl[16] [1.14 g (4.0 mmol) in H_2O (10 cm^3)] and NaH_4tg [1.75 g (8.0 mmol) in H_2O (15 cm^3)]. The dark brown reaction solution was poured onto an SP-Sephadex C-25 column (Na$^+$ form, 4 cm×100 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} NaCl aqueous solution. Four bands: greenish brown, reddish brown (**2a**), dark brown (**2b**), and reddish purple, were eluted in this order. From the absorption and CD spectral measurements, it was found that the eluates **2a** and **2b** contained *trans*(*S*)- and *cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$, respectively. **2a** could not be isolated because of the isomerization to **2b**. The concentration of **2a** was evaluated by the plasma emission spectral analysis.

The eluate **2b** was changed on the top of another SP-Sephadex C-25 column (Na$^+$ form, 4 cm×70 cm). When the adsorbed band was eluted with a 0.02 mol dm^{-3} $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ aqueous solution, it was separated into two brown bands, **2bI** and **2bII**, in this order. After this column was swept with water, each band was eluted with a 0.05 mol dm^{-3} NaCl aqueous solution. From the absorption and CD spectral measurements, it was found that the eluates **2bI** and **2bII** contained Δ_{DD}-$(+)^{CD}_{230}$-*cis*(*S*)- and Λ_{DD}-$(-)^{CD}_{230}$-*cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$, respectively. **2bII** could not be isolated as a crystal because of the isomerization to **2bI**, and the concentration of **2bII** was also evaluated by the plasma emission spectral analysis.

The eluate **2bI** was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. The filtrate was passed through a Sephadex G-10 column (2.5 cm×100 cm) by eluting with water. The chloride form was converted into the nitrate one by use of a QAE-Sephadex A-25 column (NO_3^- form, 2.5 cm×30 cm). The eluate was concentrated to a small volume and to this was added a solution containing ca. 0.5 g of $NaB(C_6H_5)_4$ in a small amount of water. After the resulting precipitate had been filtered off, the filtrate was concentrated to a small volume with a rotary evaporator and kept in a refrigerator overnight. The brown crystals (**2bI**$\cdot B(C_6H_5)_4\cdot H_2O\cdot 2/3NaNO_3$) which appeared were collected by filtration, and then dried in a vacuum desiccator. Found: C, 49.86; H, 6.74; N, 7.55%. Calcd for $[Co(H_4tg\text{-}S)_2(en)_2]B(C_6H_5)_4\cdot H_2O\cdot 2/3NaNO_3 = C_{10}H_{62}N_4O_5SBCo\cdot H_2O\cdot 2/3NaNO_3$: C, 49.65; H, 6.68; N, 7.24%.

The complexes were also prepared using *cis*-$[CoCl_2(en)_2]$-$Cl^{16)}$ instead of *trans*-$[CoCl_2(en)_2]Cl$ as a starting complex.

3) $[Co(H_3tg\text{-}O,S)(tren)]^+$ (3). To a solution containing 0.50 g (1.5 mmol) of $[CoCl_2(tren)]Cl\cdot H_2O^{15)}$ in 10 cm^3 of deaerated water was added a solution containing 0.40 g (1.8 mmol) of NaH_4tg in 2 cm^3 of deaeraed water and 1.8 cm^3 of a 1 $mol\,dm^{-3}$ NaOH aqueous solution. The mixture was stirred at 50 °C for 30 min in a stream of nitrogen, whereupon the color of the solution turned from violet to dark purple. The reaction solution was poured onto an SP-Sephadex C-25 column (Na^+ form, 4.5 cm×50 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.05 $mol\,dm^{-3}$ NaCl aqueous solution. Two bands, greenish brown and reddish purple (**3**), were eluted in this order. The absorption spectral measurements showed that the earlier eluate contained $[Co(H_4tg\text{-}S)_2(tren)]^+$ (**1**) as described in 1), and eluate **3** contained $[Co(H_3tg\text{-}O,S)(tren)]^+$ which consists of only one species. Then, eluate **3** was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. The filtrate was passed through a QAE-Sephadex A-25 column (ClO_4^- form, 2.5 cm×35 cm) by eluting with water. The eluate was concentrated to a small volume again and kept in a refrigerator overnight. The resulting reddish purple crystals (**3**$\cdot ClO_4\cdot H_2O$) were collected by filtration. Found: C, 27.74; H, 5.94; N, 10.75%. Calcd for $[Co(H_3tg\text{-}O,S)(tren)]ClO_4\cdot H_2O = C_{12}H_{28}N_4O_9SClCo\cdot H_2O$: C, 27.88; H, 5.86; N, 10.84%.

4) $[Co(H_3tg\text{-}O,S)(en)_2]^+$ (4). This complex was prepared by a procedure similar to that used for 3), using *cis*-$[CoCl_2(en)_2]Cl^{16)}$ [0.65 g (2.3 mmol) in H_2O (5 cm^3)], NaH_4tg [0.50 g (2.3 mmol) in H_2O (2.5 cm^3)] and a 1 $mol\,dm^{-3}$ NaOH aqueous solution (2.3 cm^3). The dark purple reaction solution was chromatographed by a procedure similar to that used in 3). Three bands: dark brown, reddish purple (**4**), and red, were eluted in this order. The absorption and CD spectral measurements showed that the earlier dark brown eluate contained *cis*(*S*)-$[Co(H_4tg\text{-}S)_2(en)_2]^+$ (**2b**) as described in 2) and the eluate **4** contained only $(+)^{CD}_{230}$-$[Co(H_3tg\text{-}O,S)(en)_2]^+$. The eluate **4** was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. The filtrate was passed through a Sephadex G-10 column (2.5 cm×100 cm) by eluting with water. The eluate was concentrated to a small volume and kept in a refrigerator overnight. The reddish purple crystals (**4**$\cdot Cl\cdot 2H_2O$) which appeared were collected by filtration and dried in a vacuum desiccator. Found: C, 27.23; H, 6.92; N, 12.59%. Calcd for $[Co(H_3tg\text{-}O,S)(en)_2]$-$Cl\cdot 2H_2O = C_{10}H_{26}O_5N_4SClCo\cdot 2H_2O$: C, 27.00; H, 6.81; N, 12.62%.

The complex was also prepared by using *trans*-$[CoCl_2(en)_2]Cl$ instead of *cis*-$[CoCl_2(en)_2]Cl$ as a starting complex. The nitrate and perchlorate salts of **4** were obtained by converting the corresponding chloride salt using a QAE-Sephadex A-25 column (NO_3^- or ClO_4^- form, 2.5 cm×30 cm). The crystals suitable for X-ray analysis were obtained as the nitrate salt. Nitrate salt: Found: C, 26.74; H, 6.43; N, 15.67%. Calcd for $C_{10}H_{26}O_8N_5SCo\cdot H_2O$: C, 26.49; H, 6.24; N, 15.45%. Perchlorate salt: Found: C, 25.25; H, 5.62; N, 11.87%. Calcd for $C_{10}H_{26}O_9N_4SClCo$: C, 25.25; H, 5.52; N, 11.78%.

5) $[Co(H_3sig\text{-}O,S)(tren)]^+$ (5). To the dark purple reaction solution prepared as in 3) was added an excess amount of 8 cm^3 of 5% H_2O_2 solution, followed by the addition of 0.75 cm^3 of a 30% $HClO_4$ solution. The mixture was stirred for 1 h in an ice bath, whereupon the color of the solution turned from dark purple to reddish orange. After being kept in a refrigerator overnight, the solution was concentrated to a small volume with a rotary evaporator. This was chromatographed by a procedure similar to that used in 3). One main band (**5**) tinged with reddish orange was eluted. Eluate **5** was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. The filtrate was passed through a Sephadex G-10 column (2.5 cm×100 cm) by eluting with water. The eluate was concentrated to a small volume again and to this was added a small amount of the saturated $NaB(C_6H_5)_4$ aqueous solution. After the resulting precipitate had been filtered off, the filtrate was concentrated to a small volume and then kept in a refrigerator overnight. The reddish orange crystals (**5**$\cdot B(C_6H_5)_4\cdot 3H_2O$) which appeared were collected by filtration and dried in a vacuum desiccator. Found: C, 53.73; H, 6.78; N, 6.96%. Calcd for $[Co(H_3sig\text{-}O,S)(tren)]B(C_6H_5)_4\cdot 3H_2O = C_{36}H_{48}O_7N_4SBCo\cdot 3H_2O$: C, 53.11; H, 6.72; N, 6.88%.

This complex was also prepared by the oxidation reaction of $[Co(H_3tg\text{-}O,S)(tren)]ClO_4\cdot H_2O$ (**3**) with H_2O_2.

6) $[Co(H_3sig\text{-}O,S)(en)_2]^+$ (6). This complex was prepared and chromatographed by a procedure similar to that used in 5), using *cis*-$[CoCl_2(en)_2]Cl^{16)}$ instead of $[CoCl_2(tren)]Cl$. Two reddish-orange bands, which partially overlapped each other, were fractionated with a fraction collector. From the absorption and CD spectral measurements for each fraction, the earlier and slower moving eluates **6a** and **6b** contained Δ_D-$(+)^{CD}_{230}$- and Λ_D-$(-)^{CD}_{230}$-$[Co(H_3sig\text{-}O,S)(en)_2]^+$, respectively. These isomers could not be isolated because of their high hygroscopicity. The concentrations of the complex cations were evaluated by the plasma emission spectral analysis.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-505 or JASCO UVIDEC-610C spectrophotometer. The CD spectra were recorded with a JASCO J-600 spectropolarimeter. All measurements were carried out in aqueous solution at room temperature. The ^{13}C NMR spectra were recorded with Bruker-AM-500 NMR spectrometer at a probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. Plasma emission spectral analysis was recorded with a Jarrell-Ash, Model 975, emission spectrophotometer.

Crystallography. X-Ray Data Collection. A single crystal (ca. 0.23×0.23×0.40 mm^3) of **4** ($(+)^{CD}_{230}$ isomer) was used for data collection on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo $K\alpha$ (0.70926 Å) radiation at 40 kV and 150 mA. Unit cell parameters were determined by least-squares refinement based on 25 reflections with $20° < 2\theta < 25°$.

Crystal data: $CoC_{10}H_{16}O_8N_5S$, $M_r=453.42$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a=14.328(1)$, $b=14.617(1)$, $c=8.605(1)$ Å, $V=1802.2(3)$ Å^3, $Z=4$, $D_x=1.67$ g cm^{-3}, $F(000)=872$, $\mu(\text{Mo } K\alpha)=10.5$ cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan technique up to $2\theta=60°$ ($0 \leqq h \leqq 20$, $0 \leqq k \leqq 20$, $0 \leqq l \leqq 12$) with scan rate 3° min^{-1} and scan width $(1.0+0.4 \tan\theta)°$. The three intensity and orientation standards were monitored after every 50th scan, and the intensities have remained constant within experimental error throughout data collection. The intensity data were converted to the F_o data in the usual manner. Absorption corrections were not applied. A total of 2578 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 3015 reflections were considered as 'observed' and used for structure determination.

Determination of Crystal Structure. The position of cobalt atom was determined by the heavy atom method. The successive difference Fourier maps based on the Co atom position revealed the other non-hydrogen atom positions. The hydrogen atoms on the C–H unit, except for the O–H and N–H units, were fixed by geometrical and thermal constrains (C–H=0.95 Å and $U=0.05$ Å^2). The structure was refined by a full-matrix least-squares treatment on F using the anisotropic thermal parameters for non-hydrogen atoms on FACOM M1800/20 computer, in which the program SHELX76[17] was used. Scattering factors were taken from International Tables for X-Ray Crystallography.[18] When the refinements were carried out by use of a set of the atomic parameters containing the Δ configuration of the complex cation, the residual values converged to $R=0.055$, $R_w=0.055$ and $w=1.0000/\{\sigma^2(F_o)+0.004114(F_o)^2\}$; $S=1.00$, respectively. On the contrary, the refinement in the enantiometric atomic parameters (the Λ configuration) results in the residual values of $R=0.064$, $R_w=0.068$, $w=1.5174/\{\sigma^2(F_o)+0.002789(F_o)^2\}$; $S=1.77$, respectively. These fact indicated that the former is probably the correct choice, namely, the $(+)^{CD}_{230}$ complex cation has the Δ_D configuration. This absolute configuration is supported from the result that the asymmetric carbon atom of the $(H_3tg\text{-}O,S)^{2-}$ in the Δ configuration is in line with the known D configuration. The final atomic coordinates for non-hydrogen atoms are given in Table 1.[19]

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2)[a] for Non-H Atoms of Δ_D-[$Co(H_3tg\text{-}O,S)(en)_2$]$NO_3 \cdot H_2O$

Atom	x	y	z	B_{eq}
Co	0.09637(3)	0.02167(4)	0.23315(6)	1.32(2)
S	0.25198(6)	0.03576(7)	0.2627(1)	1.63(3)
O(1)	0.0800(2)	0.1465(2)	0.2917(4)	1.55(10)
O(2)	0.0754(2)	0.3275(2)	0.4348(4)	1.82(11)
O(3)	0.2393(2)	0.4287(2)	0.3510(6)	2.72(15)
O(4)	0.4141(2)	0.3205(3)	0.5767(4)	2.34(13)
O(5)	0.3271(2)	0.1935(2)	0.3555(4)	1.73(11)
N(1)	0.0779(3)	−0.0202(3)	0.4491(5)	2.14(14)
N(2)	0.1115(3)	−0.1095(3)	0.1808(5)	2.02(13)
N(3)	0.1090(2)	0.0609(3)	0.0191(5)	1.85(13)
N(4)	−0.0405(2)	0.0215(3)	0.1893(5)	2.03(13)
C(1)	0.2474(3)	0.1592(3)	0.2760(5)	1.50(13)
C(2)	0.1591(3)	0.1871(3)	0.3607(5)	1.44(13)
C(3)	0.1528(3)	0.2906(3)	0.3505(5)	1.52(14)
C(4)	0.2432(3)	0.3364(3)	0.4025(5)	1.58(14)
C(5)	0.3308(3)	0.2906(3)	0.3378(5)	1.64(14)
C(6)	0.4183(3)	0.3270(3)	0.4129(6)	2.09(16)
C(7)	0.0692(4)	−0.1211(4)	0.4528(7)	2.97(21)
C(8)	0.1331(4)	−0.1588(4)	0.3293(8)	3.00(22)
C(9)	0.0202(4)	0.0444(4)	−0.0663(6)	2.86(20)
C(10)	−0.0561(4)	0.0699(4)	0.0425(7)	2.96(21)
N(N)	0.6368(4)	0.2238(4)	0.1825(7)	3.54(22)
O1(N)	0.6380(5)	0.2938(4)	0.2563(7)	5.24(26)
O2(N)	0.6120(5)	0.1511(5)	0.2444(7)	5.97(30)
O3(N)	0.6576(5)	0.2238(5)	0.0422(7)	5.83(30)
O(W)	0.8278(4)	0.9618(3)	0.4503(6)	3.78(19)

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

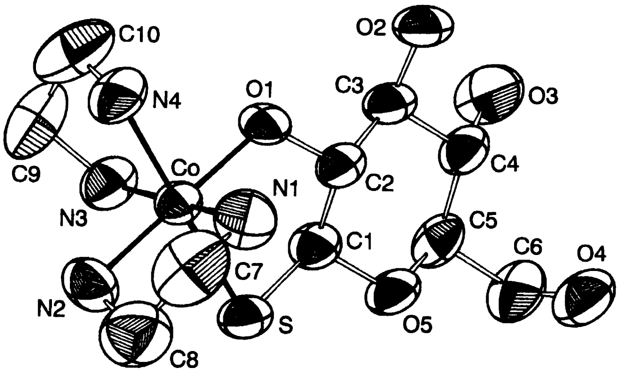

Fig. 1. Perspective view of $(+)^{CD}_{230}$-[$Co(H_3tg\text{-}O,S)(en)_2$]$NO_3 \cdot H_2O$ with the atomic labeling scheme.

Results and Discussion

Crystal Structure of Δ_D-$(+)^{CD}_{230}$-[$Co(H_3tg\text{-}O,S)(en)_2$]$^+$. A perspective drawing of the complex cation **4** ($(+)^{CD}_{230}$ isomer) is given in Fig. 1, together with a numbering scheme. The selected bond distances and angles in the complex cation are summarized in Table 2. The coordination geometry around the cobalt atom is approximately octahedral. Two coordination sites are occupied by a didentate H_3tg^{2-} ligand and the remaining four coordination sites are occupied by two en ligands. The H_3tg^{2-} ligand coordinates to the cobalt atom through a sulfur atom on the C(1) atom and a oxygen atom on the C(2) atom to form the five-membered chelate ring. In this complex, [$Co(H_3tg\text{-}O,S)(en)_2$]$^+$, the Co–N(4) distance (1.997(3) Å) being the

Table 2. Selected Bond Distances and Angles for Δ_{D}-$[\mathrm{Co(H_3tg\text{-}O,S)(en)_2}]^+$

(a) Distance (Å)			
Co–S	2.254(1)	Co–O(1)	1.907(3)
Co–N(1)	1.974(4)	Co–N(2)	1.982(4)
Co–N(3)	1.938(4)	Co–N(4)	1.997(3)
S–C(1)	1.809(4)	O(5)–C	av 1.425(5)
O–C (tg)[a)]	av 1.421(5)	O(4)–C(6)	1.413(6)
N–C (en)	av 1.484(7)	C–C (tg)[a)]	av 1.522(6)
C(5)–C(6)	1.507(6)	C–C (en)	av 1.497(9)
(b) Bond angles (°)			
S–Co–O(1)	90.24(8)	N(1)–Co–N(2)	85.9(2)
S–Co–N(4)	173.2(1)	N(3)–Co–N(4)	85.0(2)
O(1)–S–N(2)	177.7(2)	N(1)–Co–N(3)	177.5(2)
Co–S–C(1)	93.6(1)	Co–O(1)–C(2)	114.5(2)
Co–N–C (en)	av 108.8(4)	S–C(1)–O(5)	110.7(3)
S–C(1)–C(2)	109.2(3)	O–C–C (tg)[a)]	av 110.1(4)
N–C–C (en)	av 107.2(4)	C(1)–O(5)–C(5)	109.3(3)
O(5)–C(5)–C	av 110.5(4)	O(4)–C(6)–C(5)	111.6(4)
C–C–C (tg)[a)]	av 110.7(3)	C(4)–C(5)–C(6)	111.9(4)

a) Pyranose ring.

trans position to the sulfur atom is a little longer than the Co–N distances (1.938(4)—1.982(4) Å) being the cis position (Table 2). This indicates that the thiolato sulfur atom of $(\mathrm{H_3tg\text{-}O,S})^{2-}$ causes slight structural trans influence, in analogy with the sulfur atom of other thiolate type ligands coordinated to the cobalt(III) ion.[9—12)] The C–C distances (av 1.522(6) Å) for the pyranose ring are quite similar to the corresponding distances in β-D-glucose (av 1.521(4) Å) (Table 2).[20)] The C–O distances (av 1.421(5) Å) are also in good agreement with the corresponding distances in β-D-glucose (av 1.427(4) Å).[20)] The C–C–C (av 111.0°) and O–C–C (av 110.3°) angles are close to a normal tetrahedral angle. In the pyranose ring of **4** there will thus be no significant strain upon coordination.

Of the two diastereomers, Δ_{D} and Λ_{D}, possible for $[\mathrm{Co(H_3tg\text{-}O,S)(en)_2}]^+$, it turns out that the $(+)^{\mathrm{CD}}_{230}$ isomer takes the Δ_{D} configuration (Fig. 1). Each of the $(\mathrm{H_3tg\text{-}O,S})^{2-}$ and two en ligands takes the gauche form with the λ conformation, that is, they take the *lel* (parallel) conformation against a C_3 axis. The pyranose ring of $(\mathrm{H_3tg\text{-}O,S})^{2-}$ takes the β chair conformation, which is also adopted in the free 1-thio-β-D-glucose ligand.[21)] The same conformation was observed for $[\mathrm{Ni(D\text{-}}N\mathrm{\text{-}gl\text{-}en)_2}]^{2+}$ (D-*N*-gl-en=1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-glucose).[2)] Therefore, the gauche conformation of the chelate ring for $(\mathrm{H_3tg\text{-}O,S})^{2-}$ coordinated to the cobalt(III) ion is regulated by the absolute configuration D around the anomeric the C(1) atom, having the usual β chair conformation of the pyranose ring (Fig. 1).

Characterization. The ^{13}C NMR spectra of the isolated complexes with 1-thio-β-D-glucose are summarized in Table 3. **1** and **2bI** exhibit two sets of six resonance lines due to six carbon atoms of 1-thio-β-D-glucose, while **3** and Δ_{D}-$[\mathrm{Co(H_3tg\text{-}O,S)(en)_2}]^+$ (**4**) show only one set of six resonance lines. Further, **1** and **3** show six resonance lines due to the tren ligand and **2bI** and **4** show four resonance lines due to two en ligands. Judging from such NMR spectral behavior and the elemental analytical results, we conclude that **1** and **2bI** are $[\mathrm{Co(H_4tg)_2(tren)}]^+$ and $[\mathrm{Co(H_4tg)_2(en)_2}]^+$, respectively, in which $\mathrm{H_4tg^-}$ acts as the monodentate, while **3** is $[\mathrm{Co(H_3tg)(tren)}]^+$ in which $\mathrm{H_3tg^{2-}}$ acts as the didentate.

In the complexes with two monodentate ligands, only a cis isomer is possible for $[\mathrm{Co(H_4tg)_2(tren)}]^+$ (**1**) and two geometrical isomers, trans and cis, are possible for $[\mathrm{Co(H_4tg)_2(en)_2}]^+$ (**2**), and the $\mathrm{H_4tg^-}$ ligands will coordinate to cobalt(III) ion through the sulfur and/or oxygen atoms. In **1** and **2bI**, the ^{13}C NMR chemical shifts for the two monodentate $\mathrm{H_4tg^-}$ ligands appear at similar positions (Table 3), suggesting the similarity of each coordination geometry around the ligands. Further, the absorption spectra of **1** and **2b** are quite similar to each other over the whole region, and especially exhibit the broad intense absorption bands in the region of 30—36×10^3 cm^{-1}, which are assigned to the sulfur-to-metal charge transfer (SMCT) transition (Fig. 2 and Table 4). Similar absorption spectral behavior was also observed for the *cis*(*S*)-$[\mathrm{Co(S)_2(N)_4}]$-type isomers containing two thiolato donor atoms.[4)] Accordingly, these indicate that both of the monodentate $\mathrm{H_4tg^-}$ ligands in **1** and **2b** bind to the cobalt(III) ion through the sulfur atom, that is, the structures of **1** and **2b** are $[\mathrm{Co(H_4tg\text{-}S)_2(tren)}]^+$ and *cis*(*S*)-$[\mathrm{Co(H_4tg\text{-}S)_2(en)_2}]^+$, respectively. Furthermore, **2a** shows a sharp SMCT band

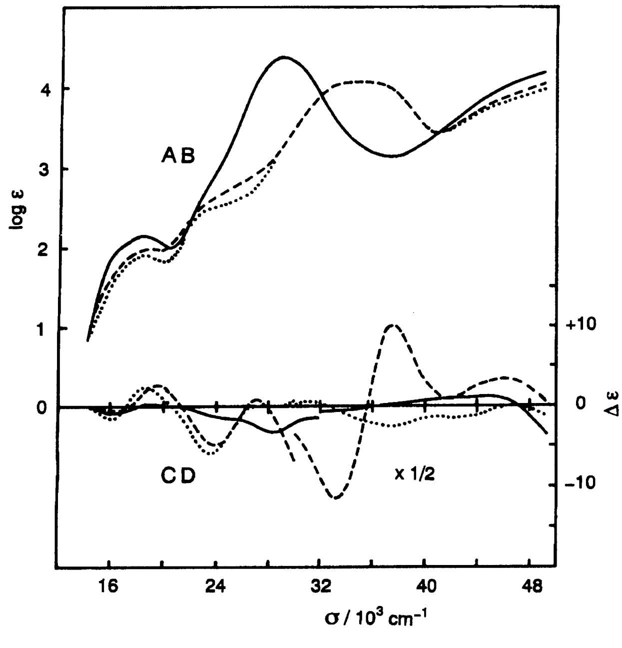

Fig. 2. Absorption and CD spectra of $[\mathrm{Co(H_4tg\text{-}S)_2(en)_2}]^+$: *trans*(*S*) (—), Δ_{DD}-*cis*(*S*) (---), and Λ_{DD}-*cis*(*S*) (····).

Table 3. ^{13}C NMR Chemical Shift Data of the Complexes[a)]

Complex ion		tren or en					
[Co(H$_4$tg-S)$_2$(tren)]$^+$	**1**	47.47	48.39	49.48	62.33	63.20	63.88
Δ_{DD}-*cis*(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$	**2bI**	45.41	45.96	47.56	47.84		
t-[Co(H$_3$tg-O,S)(tren)]$^+$	**3**	47.50	49.18		61.00	62.37	62.85
Δ_{D}-[Co(H$_3$tg-O,S)(en)$_2$]$^+$	**4**	45.72	46.35	47.60	48.09		
t-[Co(H$_3$sig-O,S)(tren)]$^+$	**5**	47.73	48.43	49.08	60.95	62.46	63.38
p-[Co(aet)(tren)]$^{2+}$ [b)]		46.70	47.67	47.84	64.20	66.96	
p-[Co(aesi)(tren)]$^{2+}$ [b)]		46.48	48.11		64.96	65.61	
		β-D-Glucose moiety					
[Co(H$_4$tg-S)$_2$(tren)]$^+$	**1**	64.07	72.82	76.93	79.69	82.17	87.23
		64.40	73.06	77.84	79.81	82.23	88.31
Δ_{DD}-*cis*(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$	**2bI**	63.90	72.85	77.13	79.61	81.94	87.84
		63.94	72.88	77.14	79.68	81.98	88.11
t-[Co(H$_3$tg-O,S)(tren)]$^+$	**3**	63.79	72.37	80.73	83.67	88.12	88.53
Δ_{D}-[Co(H$_3$tg-O,S)(en)$_2$]$^+$	**4**	63.81	72.30	81.18	83.72	88.87	89.09
t-[Co(H$_3$sgi-O,S)(tren)]$^+$	**5**	63.60	72.00	77.58	80.23	83.86	101.79
[Co(H$_3$sgi-O,S)(trien)]$^+$ [c)]		63.26	71.88	76.75	80.18	83.72	100.10

a) δ/ppm from DSS. b) Ref. 13. c) Ref. 24.

Table 4. Absorption and CD Spectral Data of the Complexes

	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})
[CoH$_4$tg-S)$_2$(tren)]$^+$ (**1**)	18.69 (2.23)	15.67 (−0.62)
	24.10 (2.81 sh)	17.61 (+0.99)
	32.68 (4.18 sh)	23.15 (−3.69)
	34.97 (4.27)	26.32 (+1.68)
		32.68 (−10.4)
		36.50 (+11.1)
		45.46 (+11.1)
trans(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$ (**2a**)	16.81 (2.00)	16.39 (−1.03)
	18.69 (2.15)	19.05 (+0.41)
	23.92 (2.95 sh)	28.41 (−3.13)
	29.07 (4.38)	45.05 (+2.58)
Δ_{DD}-*cis*(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$ (**2bI**)	17.09 (1.84 sh)	16.26 (−0.57)
	19.05 (1.99)	19.42 (+2.77)
	25.32 (2.77 sh)	23.81 (−4.97)
	34.25 (4.06)	27.03 (+0.85)
	36.23 (4.05 sh)	33.11 (−22.6)
		37.59 (+20.1)
		45.87 (+6.97)
Λ_{DD}-*cis*(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$ (**2bII**)	17.09 (1.78 sh)	16.13 (−1.57)
	18.52 (1.93)	18.52 (+2.55)
	23.81 (2.52)	23.53 (−5.80)
	34.01 (4.06)	27.78 (+0.19)
	36.23 (4.04 sh)	30.86 (+1.31)
		37.59 (−5.10)
t-[Co(H$_3$tg-O,S)(tren)]$^+$ (**3**)	17.39 (2.01 sh)	16.50 (−1.61)
	19.05 (2.20)	19.23 (+4.72)
	26.67 (2.53)	23.37 (−2.31)
	35.71 (4.15)	28.90 (+3.66)
	38.76 (4.12 sh)	33.56 (−7.93)
		40.00 (+8.65)
		48.08 (+1.30)
Δ_{D}-[Co(H$_3$tg-O,S)(en)$_2$]$^+$ (**4**)	17.24 (1.92 sh)	17.09 (−4.83)
	18.87 (2.13)	19.42 (+7.00)
	27.40 (2.50 sh)	25.00 (−1.45)
	37.04 (4.11)	28.17 (+2.75)
	39.37 (4.09)	32.90 (−6.97)
		40.32 (+23.1)
t-[Co(H$_3$sig-O,S)(tren)]$^+$ (**5**)	19.23 (2.05 sh)	18.87 (+1.39)
	22.22 (2.71)	21.98 (−3.21)
	34.25 (4.14)	27.47 (+2.69)
	38.46 (3.96)	32.05 (−5.72)
	45.87 (4.01)	36.23 (+7.97)
		44.64 (+2.13)
		49.02 (−2.74)
Δ_{D}-[Co(H$_3$sig-O,S)(en)$_2$]$^+$ (**6a**)	18.69 (1.82 sh)	17.54 (−0.09)
	21.98 (2.42)	22.47 (+1.18)
	34.48 (3.98)	25.64 (−1.52)
	39.06 (3.48 sh)	28.57 (+0.15)
		32.05 (−3.90)
		36.77 (+7.65)
		45.87 (+2.55)
Λ_{D}-[Co(H$_3$sig-O,S)(en)$_2$]$^+$ (**6b**)	18.69 (1.84 sh)	20.83 (+1.26)
	21.98 (2.40)	25.32 (−1.33)
	34.25 (3.97)	28.57 (+0.27)
	39.06 (3.85 sh)	32.05 (−3.97)
		35.97 (+4.88)
		42.37 (−1.61)
		48.54 (−5.85)

sh denote a shoulder.

at ca. 29×10^3 cm^{-1} (Fig. 2), which appears at an energy side lower than those of **2b** and was also observed for *trans*(*S*)-[Co(S)$_2$(N)$_4$]-type isomers.[4)] These indicate, therefore, that **2a** is *trans*(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$.

cis(*S*)-[Co(H$_4$tg-S)$_2$(en)$_2$]$^+$ (**2b**) was isolated into two isomers, $(+)^{\mathrm{CD}}_{230}$ (**2bI**) and $(-)^{\mathrm{CD}}_{230}$ (**2bII**), by the column chromatographic method using $[Sb_2(d\text{-tart})_2]^{2-}$ as an eluent. **2bI** and **2bII** exhibit mutually quasi-enantiomeric CD spectral pattern in the SMCT band region, although **2bI** has a CD spectral pattern similar to that of **2bII** in the d–d transition band region (Fig. 2). This suggests that each of **2bI** and **2bII** is one of the two possible diastereomers, Δ_{DD} or Λ_{DD}. The CD spectral pattern of **2bI** resembles that of Δ_D-[Co(H_3tg-O,S)(en)$_2$]$^+$ over the whole region. Accordingly, these results suggest that **2bI** is the Δ_{DD} configuration of *cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$ and **2bII** is the Λ_{DD} one.

The absorption spectrum of **3** appears quite similar to that of **4** over the whole region (Fig. 3 and Table 4). This indicates that the didentate H_3tg^{2-} ligand in **3** coordinates to the cobalt(III) ion through the sulfur and oxygen atoms, [Co(H_3tg-O,S)(tren)]$^+$. Of two geometrical isomers, p and t,[22] possible for [Co(H_3tg-O,S)(tren)]$^+$, **3** formed only one geometrical isomer, as was confirmed by the column chromatography and NMR spectral behavior (Table 3). The oxidation reaction of **3** gave only **5**. It has been recognized that a similar oxidation reaction of the thiolato cobalt(III) complexes proceeds with retention of the geometrical configuration.[8,23] In fact, **5** exhibits six ^{13}C NMR resonance lines due to the H_3sig^{2-} ligand and six resonance lines due to the tren ligand (Table 3), indicating no mixture of the *p* and *t* isomers. The chemical shifts of the H_3sig^{2-} ligand in **5** correspond well to those of the didentate H_3sig-O,S in *cisβ*-[Co(H_3sig-O,S)(trien)]$^+$, whose structure is determined by the single crystal structure analysis.[24] Thus, it is assumed that **3** and **5** take the same configuration, *p* or *t*. Kojima et al.[25] pointed out that the spectral pattern of the *t*-isomer for [Co(SCHRCOO)(tren)]$^+$ (R=H, CH_3) exhibits a strong absorption shoulder on the lower energy side of the first absorption band. **3** exhibits a spectral pattern similar to *t*-[Co(SCHRCOO)(tren)]$^+$. It has been found, furthermore, that the resonance lines due to some carbon atoms of the tren ligand on *p*-[Co(aet)(tren)]$^{2+}$ (aet=2-aminoethanethiolate) shift toward the higher magnetic field by the conversion to *p*-[Co(aesi)(tren)]$^{2+}$ (aesi=2-aminoethanesulfinate).[13] However, such a tendency is not observed in the conversion of **3** to **5**. Accordingly, it is likely that **3** and **5** are *t*-[Co(H_3tg-O,S)(tren)]$^+$ and *t*-[Co(H_3sig-O,S)(tren)]$^+$, respectively.

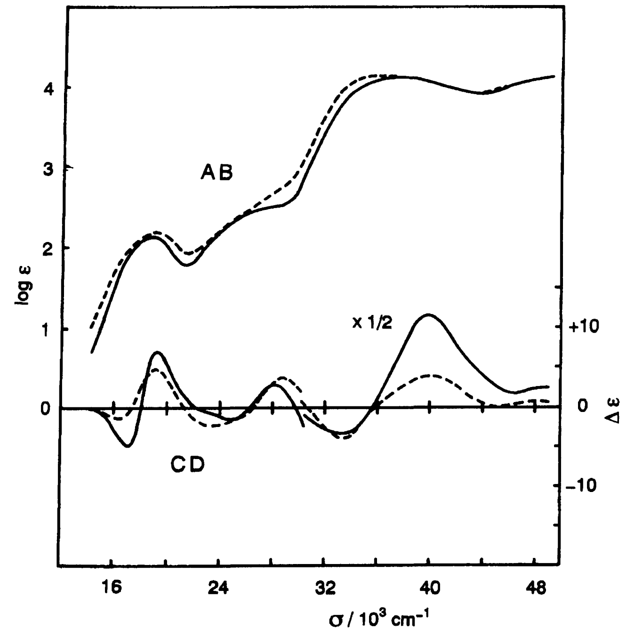

Fig. 3. Absorption and CD spectra of Δ_D-[Co(H_3tg-O,S)(en)$_2$]$^+$ (—) and *t*-[Co(H_3tg-O,S)(tren)]$^+$ (- - -).

The absorption spectral behavior of **6** is quite similar to that of *t*-[Co(H_3sig-O,S)(tren)]$^+$ (**5**) (Table 4), suggesting that **6a** and **6b** are the diastereomer of [Co(H_3sig-O,S)(en)$_2$]$^+$, Δ_D and Λ_D. **6a** exhibits a CD spectral behavior similar to that of Δ_{DD}-*cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$ in the region of 32—50×10^3 cm^{-1}, although the CD spectral patterns of **6a** and **6b** resemble each other in the d–d transition band region (Table 4). Taking account of this result and of the oxidation reaction proceeding with the retention of the configuration for **4**, we assigned **6a** to take the Δ_D configuration, and **6b** to take the Λ_D one.

Properties. The present cobalt(III) complexes of [Co(H_4tg-S)$_2$(N)$_4$]$^+$- and [Co(H_3tg-O,S)(N)$_4$]$^+$-type ((N)$_4$; tren and (en)$_2$) were prepared by the reaction of [$CoCl_2$(N)$_4$]$^+$ with NaH$_4$tg in water. When the reaction was conducted at room temperature, the [Co(H_4tg-S)$_2$(N)$_4$]$^+$-type complexes were dominantly formed. The [Co(H_3tg-O,S)(N)$_4$]$^+$-type complexes were dominantly formed by the reaction at a high temperature (ca. 50 °C). This suggests that NaH$_4$tg coordinates at first to the metal ion through the sulfur atom, and then rearrangement to the didentate (H_3tg-O,S)$^{2-}$ is accompanied by some crowdness around the metal ion and the chelate effect of the ligand.

For [Co(H_4tg-S)$_2$(en)$_2$]$^+$, both the *cis*(*S*) and the *trans*(*S*) isomers were formed. The sharp SMCT band at 29.07×10^3 cm^{-1}, which is characteristic for the *trans*(*S*) isomer, decreased with time, while the SMCT band in the region of 37—39×10^3 cm^{-1}, which is observed for [Co(H_3tg-O,S)(en)$_2$]$^+$ increased. This indicates that the *trans*(*S*) isomer tended to convert to [Co(H_3tg-O,S)(en)$_2$]$^+$. These are consistent with the fact that the cobalt(III) complexes containing two or three thiolato groups are unstable and tend to initiate a rearrangement, because of the structural trans influence due to the thiolato donor atoms.[9—12]

Of the two diastereomers, **2bII** of [Co(H_4tg-S)$_2$(en)$_2$]$^+$ is isomerized to **2bI**, and **2bII** could not be isolated as a crystal. The Λ_D isomer of [Co(H_3tg-O,S)(en)$_2$]$^+$ could not be isolated. These reaction processes seem to indicate that the Δ_{DD} and Δ_D isomers of these complexes are more stable than the Λ_{DD} and Λ_D ones, respectively. These facts and molecular model constructions suggest that the stability of Δ_D-[Co(H_3tg-

O,S)(en)$_2$]$^+$ will depend on the conformation, *lel* in Δ_D and *ob* (oblique) in Λ_D, for the (H_3tg-O,S)$^{2-}$ chelate rings, and that of *cis*(*S*)-[Co(H_4tg-S)$_2$(en)$_2$]$^+$ will exist with a little energy difference for the Δ_{DD} and Λ_{DD} isomers arising from the steric repulsion between the hydrogen atoms on the two (H_4tg-S)$^-$ ligands.

The [Co(H_3tg-O,S)(N)$_4$]$^+$-type complexes are fairly stable in an aqueous solution. When methanol or ethanol was added to an aqueous solution of these complexes, however, the color of the solution gradually changed from reddish purple to reddish orange. When the reddish orange solution was chromatographed on a cation exchange column (SP-Sephadex C-25, Na^+ form), the band which contained the sulfinato complex, [Co(H_3sig-O,S)(N)$_4$]$^+$, was eluted with a 0.05 mol dm^{-3} NaCl aqueous solution. This means that the coordinated thiolato atom in [Co(H_3tg-O,S)(N)$_4$]$^+$ is easily oxidized in alcohol.

The [Co(H_3tg-O, S)(N)$_4$]$^+$- and [Co(H_3sig-O, S)-(N)$_4$]$^+$-type complexes, which have only one sulfur donor atom, exhibit and intense absorption component at ca. 39×10^3 cm^{-1} besides the SMCT band at 35×10^3 cm^{-1} (Fig. 3 and Table 4), although the [Co(thiolato-S)(O)(N)$_4$]$^+$-type complexes with the aliphatic thiolate ligand exhibit the only sharp SMCT band in the corresponding region.[11] A similar intense band is observed in the absorption spectra of the alcoholato complexes such as [Co{$NH_2CH(CH_3)CH_2O$-N,O}(en)$_2$]$^{2+}$.[26] These indicate that the intense band at ca. 39×10^3 cm^{-1} depends on the coordinated oxygen atom of the (H_3tg-O,S)$^{2-}$ ligand; namely, this band will be assigned as arising from the oxygen-to-cobalt charge transfer transition. In fact, this band is not observed for [Co(H_4tg-S)$_2$(tren or (en)$_2$)]$^+$, indicating that the oxygen atoms do not coordinate to the cobalt(III) ion (Fig. 2).

t-[Co(H_3tg-O,S)(tren)]$^+$, [Co(H_4tg-S)$_2$(tren)]$^+$, and Δ_D-[Co(H_3tg-O,S)(en)$_2$]$^+$ show similar CD patterns and intensities to one another over the whole region (Table 4). The CD spectral behavior of the tren complexes will contribute to the chirality due to the asymmetric carbon atoms of the 1-thio-β-D-glucose ligands and/or due to the additional rigid chelate ring conformation of the didentate (H_3tg-O,S)$^{2-}$ ligand. In addition to that due to *t*-[Co(H_3tg-O,S)(tren)]$^+$, Δ_D-[Co-(H_3tg-O,S)(en)$_2$]$^+$ has the CD contribution from the configurational chirality due to the skew pair of chelate rings of two en ligands. Taking the similarity of the CD spectral behavior into consideration, these results suggest that the CD spectral behavior of the present complexes are mainly affected by the chirality due to the 1-thio-β-D-glucose ligand. A similar CD pattern is observed for [Co(β-CDX)(en)$_2$]$^+$ (β-CDX; β-cyclodextrin, which is a cyclic oligosaccharide consisting of six or more β-D-glucopyranose units).[27] Therefore, care must be taken in relating the CD spectra to the absolute configurations of the complexes with the 1-thio-β-D-glucose.

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