January, 1986] *Bull. Chem. Soc. Jpn.*, *59*, *277—283 (1986)*

Green and Brown Isomers of the ((*S*)-1-Amino-2-propanethiolato-*N*,*S*)(1,4,7,10-tetraazacyclododecane)cobalt(III) Ion and Crystal Structure of the Green Isomer

Masaaki Kojima, Kyoko Nakabayashi, Shigeru Ohba,† Satoshi Okumoto,†
Yoshihiko Saito,† and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464
† Department of Chemistry, Faculty of Science and Technology, Keio University,
Hiyoshi 3, Kohoku-ku, Yokohama 223

(Received July 18, 1985)

The $[Co(S\text{-apS})(cyclen)]^{2+}$ (*S*-apS=(*S*)-1-amino-2-propanethiolate ion, cyclen=1,4,7,10-tetraazacyclododecane) complex was prepared and separated into two isomers (green and brown) by column chromatography. The crystal structure of the green isomer, $[Co(S\text{-apS})(cyclen)]ZnCl_4 \cdot H_2O$ was determined by X-ray analysis. Crystal data are as follows: monoclinic, space group $P2_1$, a=9.382(2), b=13.124(3), c=8.934(2) Å, β=91.08(3)°, and Z=2. The complex ion has a cis-octahedral geometry with the cyclen ligand coordinated in a folded, butterfly-like configuration and the bidentate *S*-apS ligand in a δ-gauche form. One of the two "planar" NH hydrogens of the macrocycle with respect to the *S*-apS ligand is directed opposite the *S*-apS chelate ring (exo), while the other "planar" and the remaining two "apical" NH hydrogens are directed to the *S*-apS ring (endo). The green isomer can be represented by *endo*(S,NH), where NH denotes the planar NH hydrogen cis to the sulfur atom. The other brown isomer was assigned as the *exo*(S,NH) configuration, where the S and NH_2 coordination sites of *S*-apS in the green isomer are interchanged with each other, remaining the configuration of the macrocycle unchanged. Reversible isomerization between the two isomers occurred in aqueous solution and the kinetics was studied at 25.4 °C in the pH range of 5.98—6.97. The isomerization obeyed a rate law of the form, $R=k[OH^-]\cdot[complex]$, and was suggested to take place with synchronous inversion at the two nitrogen atoms of the macrocycle. The relative abundance of the two isomers at equilibrium is 1.0, and the forward and reverse second-order rate constants at 25.4 °C are $6.5 \times 10^3\ mol^{-1}\ dm^3\ s^{-1}$.

In the course of circular dichroism (CD) studies of cobalt(III) complexes containing a chiral aminoalkanethio(or seleno)late-*N*,*S*(or *Se*) chelate ligand,[1] we have obtained two isomers (green and brown) of $[Co(S\text{-apS})(cyclen)]^{2+}$ (*S*-apS=(*S*)-1-amino-2-propanethiolate ion, cyclen=1,4,7,10-tetraazacyclododecane). To our knowledge, no isomers of metal-cyclen complex have been reported. The isomers are stable in acidic solution, but easily isomerize to each other in basic solution. This report is concerned with the structures, absorption and CD spectra, and isomerization reactions of these isomers.

Experimental

Preparation of $[Co(S\text{-apS})(cyclen)]ZnCl_4$ (brown isomer) and $[Co(S\text{-apS})(cyclen)]ZnCl_4 \cdot H_2O$ (green isomer). An aqueous solution ($10\ cm^3$) containing cyclen·$2H_2SO_4$[2] (0.737 g, 2.00 mmol) and NaOH (0.32 g, 8.00 mmol) was deoxygenated by bubbling nitrogen, and then added to a deoxygenated aqueous solution ($5\ cm^3$) of $CoCl_2 \cdot 6H_2O$ (0.397 g, 1.67 mmol) with stirring. To the resulting brownish orange solution was added a deoxygenated aqueous solution ($5\ cm^3$) containing (*S*,*S*)-$(NH_2CH_2CH(CH_3)S\text{-})_2 \cdot 2HCl$[3,4] (0.212 g, 0.835 mmol) and NaOH (0.067 g, 1.67 mmol). The mixture was stirred under an atmosphere of nitrogen for 4 d at 30 °C, and then filtered to remove a small amount of insoluble substance. The brown filtrate was diluted with water ($500\ cm^3$) and applied on a column (ϕ2.7 cm×30 cm) of Dowex 50 W×2 (200—400 mesh, H^+ form). By elution with $2\ mol\ dm^{-3}$ HCl, a green and a brown band developed in this order. The eluate containing the green band was collected and evaporated to a small volume under reduced pressure. To the concentrate was added $ZnCl_2$ (0.5 g) in $3\ mol\ dm^{-3}$ HCl ($1\ cm^3$) to precipitate dark brown tetrachlorozincate of the complex. The precipitate was collected by filtration and washed with acetone. Yield: 0.2 g. Found: C, 23.81; H, 5.61; N, 12.60%. Calcd for $C_{11}H_{30}N_5Cl_4CoOSZn$: C, 24.17; H, 5.53; N, 12.81%.

The eluate containing the brown band was treated by the same method to yield brown plates. Yield: 0.15 g. Found: C, 24.82; H, 5.28; N, 13.19%. Calcd for $C_{11}H_{28}N_5Cl_4CoSZn$: C, 25.00; H, 5.34; N, 13.25%.

When the reaction product was chromatographed with a column of SP-Sephadex C-25 and an eluent $0.1\ mol\ dm^{-3}$ Na_2SO_4—$0.01\ mol\ dm^{-3}$ HCl, the order of elution was reversed; the brown isomer being eluted faster than the green one.

Spectral Measurements. Absorption spectra were recorded on a Hitachi 323 or a JASCO 610B spectrophotometer, and circular dichroism (CD) spectra on a JASCO J-40CS spectropolarimeter.

Kinetic Measurements. The rate of the change in absorption spectrum was measured for a phthalate buffer solution (pH range: 5.98—6.97) of each isomer (ca. $3 \times 10^{-3}\ mol\ dm^{-3}$) at 25.4 °C. The change in absorption spectrum was recorded in the region of 800—400 nm. The reaction was followed at least three half-lives.

Crystal Structure Determination. A dark brown crystal was ground into approximate sphere 0.45 mm in diameter and mounted on an automated Rigaku four-circle diffractometer AFC-5. The cell dimensions were refined based on 20 2θ values ($20 < 2\theta < 28°$) with λ(Mo $K\alpha$)=0.71073 Å. The crystal data are: $[Co(C_3H_8NS)(C_8H_{20}N_4)]^{2+}[ZnCl_4]^{2-} \cdot H_2O$, F.W.=546.5, monoclinic, space group $P2_1$, a=9.382(2), b=13.124(3), c=8.934(2) Å and β=91.08(3)°, V=1099.9(4) $Å^3$, Z=2, D_m(ether/bromoform)=1.65, D_x=1.65 Mg m^{-3}, μ=2.46 mm^{-1}. Intensity measurement was performed to 2θ=55° by θ—2θ scan technique with scan speed 6° min^{-1} (θ). The ratio of structure factors of five standard reflections, $|F_o|/|F_o|_{\text{initial}}$, was from 0.98 to 1.06. 2814 reflections were measured and 2573 reflections with $|F_o|>3\sigma(|F_o|)$ were regarded as observed, of which 2423 reflections were unique. Lorentz-polarization and absorption corrections were applied ($0.447\leqq$transmission factor$\leqq 0.457$). The structure was solved by Patterson-Fourier method. The atomic parameters were refined by block-diagonal least squares. The function minimized was $\sum w||F_o|-|F_c||^2$, $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$. After the introduction of anisotropic thermal parameters (R=0.050), 9 among 28 hydrogen atoms were found from the difference synthesis and others were calculated (R=0.039). The difference synthesis at this stage of the refinement showed a peak of 1.7 eÅ^{-3} with three satellite peaks of 0.7—1.0 eÅ^{-3}, suggesting positional disorder of the water of crystallization. D_m indicated one water molecule for each asymmetric unit. O(W)1 atom was included in the calculation with 0.25 occupancy factor tentatively (R=0.034). Anisotropic thermal parameter of the O(W)1 atom became non-positive definite. Thus, O(W)2, O(W)3, and O(W)4 atomic positions which separate from the most populated O(W)1 position with distances from 0.88(5) to 1.14(3) Å were added. The population parameters of four O(W) atoms were estimated by the trial and error method in such a way that each isotropic thermal parameter took nearly equal value. The R value reduced to 0.028, wR=0.035 and S=1.6.[5] All the shifts in the final cycle of the refinement were less than 0.6σ for non-hydrogen atoms except O(W). Maximum and minimum height in the final difference synthesis was 0.5 and −0.4 eÅ^{-3}. The calculations were carried out on a FACOM M-380R computer at Keio University with UNICS III program system.[6]

The absolute structure was determined by the anomalous-scattering technique. The enantiomeric structure gave R=0.032, wR=0.040 and could be rejected at the 0.005 significance level by the Hamilton test.[7] The absolute configuration of optically active apS in the present complex cation, which was obtained from $(+)_{589}$-apS·HCl,[1] was determined to be S in agreement with the assignment based on the isomer distribution and CD spectra of [Co(apS){(*R*,*R*)-1,2-cyclohexanediamine}$_2$]$^{2+}$ and related complexes.[1]

Results and Discussion

Preparation and Characterization of the Complexes. The [Co(*S*-apS)(cyclen)]$^{2+}$ complex was prepared by oxidizing Co$^{\text{II}}$–cyclen species with the disulfide according to the method for analogous aminoalkanethiolate-*N,S* complexes of cobalt(III).[8,9] The complex was separated into two isomers (green and brown) by column chromatography on Dowex 50W×2 (eluent: 2 mol dm^{-3} HCl) or on SP-Sephadex C-25 (eluent: 0.1 mol dm^{-3} Na_2SO_4—0.01 mol dm^{-3} HCl). The isomers are stable in acidic water and show no measurable change in absorption and CD spectra, but isomerize in neutral or alkaline solution to give an equilibrium mixture of the two isomers (vide infra).

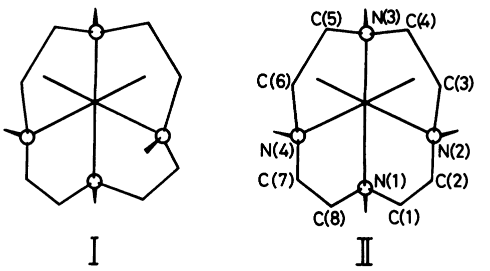
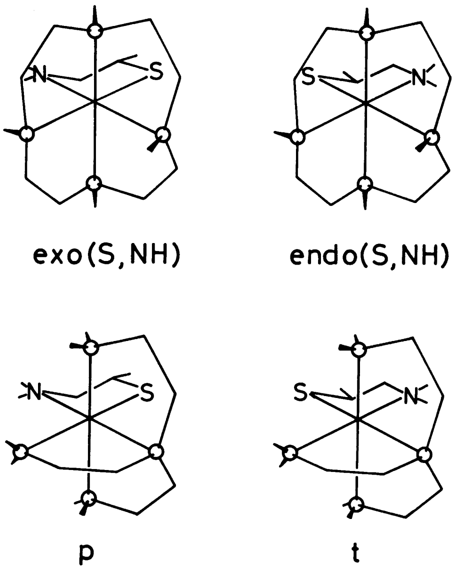


Fig. 1. Two possible configurations for cis-octahedral complexes of cyclen.



exo(S,NH) endo(S,NH)

p t

Fig. 2. Structures of *exo*(S, NH)- and *endo*(S, NH)-[Co(*S*-apS)(cyclen)]$^{2+}$, and *p*- and *t*-[Co(*S*-apS)(tren)]$^{2+}$.

The structure of the green isomer was determined by the X-ray method to be *endo*(S,NH) isomer of configuration I (vide infra, Figs. 1 and 2). We could not obtain good crystals of the brown isomer suitable for X-ray analysis. However, this isomer can be assigned to the other isomer of configuration I, *exo*(S,NH) from comparisons of the behavior in column chromatography, and the absorption and CD spectra with those of two isomers of [Co(*S*-apS)(tren)]$^{2+}$[1] (tren=tris(2-aminoethyl)amine). The steric relations of the sulfur and amine hydrogen atoms of the p- and t-isomers of [Co(*S*-apS)(tren)]$^{2+}$ can be compared to those of the *exo*(S,NH) and *endo*(S,NH) isomers of [Co(*S*-apS)(cyclen)]$^{2+}$, respectively (Fig. 2). The *exo*(S,NH) isomer of the cyclen complex and the p-isomer of the tren complex have two sets of three N–H bonds capable of forming hydrogen bonds with a sulfate ion. Thus, the isomers will be eluted faster in column chromatography than the other isomers (*endo*(S,NH) and t-isomers), since the former isomers will form a stronger ion pair with a sulfate ion than the latter ones which have no such a set of three N–H bonds.[10] The brown isomer of the cyclen complex and p-isomer of the tren complex[1)] are eluted faster than the other respective isomers. Thus the brown isomer can be assigned to the *exo*(S,NH) isomer. Similarity of the absorption and CD spectra between the *exo*(S,NH) and p-isomers, and between the *endo*(S,NH) and t-isomers support the assignment. The relative intensities of the two absorption components in the first absorption band region are considerably different between the two pairs of the complexes; the brown and p-isomers exhibit only a weak shoulder around 17000 cm^{-1}, while the green (*endo*(S,NH)) and t-isomers show a rather strong, distinct band in this region (Fig. 3 and Table 1). The CD spectral pattern of the green isomer resembles that of the t-isomer in the d-d absorption band region. On the other hand, the brown isomer shows a CD spectrum rather different from that of *p*-[Co(*S*-apS)(tren)]$^{2+}$. However, there is something in common between them; the spectra are weak in magnitude and complicated in pattern, and seem to consist of several components with opposite signs. Thus, all these results support the assignment of the brown isomer to *exo*(S,NH).

Figure 1 shows the two possible configurations (I and II) for cis-octahedral complexes of cyclen. Several Co^{III}–cyclen complexes have been prepared, and all of the cobalt(III) complexes whose structures have been determined by X-ray crystallography have configuration I.[2,11,12)] Configuration II was found only in [NiBr(H$_2$O)(Me$_2$cyclen)]Br (Me$_2$cyclen=1,7-dimethyl-1,4,7,10-tetraazacyclododecane), where the two methyl groups are attached to the two "apical" nitrogen atoms (N(1) and N(3) in Fig. 1).[13)] On the other hand, the Me$_2$cyclen ligand takes configuration I in [Co(CO$_3$)(Me$_2$cyclen)]ClO$_4$.[14)] ^{13}C NMR spectroscopy suggests that Co^{III}–cyclen and Co^{III}–Me$_2$cyclen complexes in solution also assume configuration I.[2,14)] Examination of molecular models indicates that when a complex with cyclen (or Me$_2$cyclen) has configuration II, steric interactions occur between the methylene groups of the macrocycle (C(3)···C(6) and C(2)···C(7) in Fig. 1). The interactions will increase as the M–N bond distances decrease. On the other hand, configuration I does not have such interactions between the methylene groups. Thus, the shorter bond distance of Co–N than Ni–N will be responsible for the preference of configuration I over II in Co^{III}–cyclen (or Co^{III}–Me$_2$cyclen) complexes. If the brown isomer were configuration II, the strain energy would be large and the relative abundance of the isomer at equilibrium would become small. The fact that the ratio of the brown to green isomer is 1.0 also supports the assignment for the brown isomer. A similar isomerism to the *exo*(S,NH) and *endo*(S,NH)

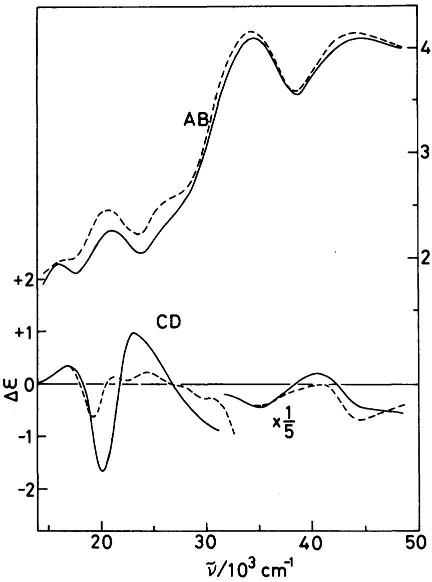


Fig. 3. Absorption (AB) and CD spectra of the green (——) and the brown (----) isomers of [Co(*S*-apS)-(cyclen)]$^{2+}$ in 0.01 mol dm^{-3} HClO$_4$.

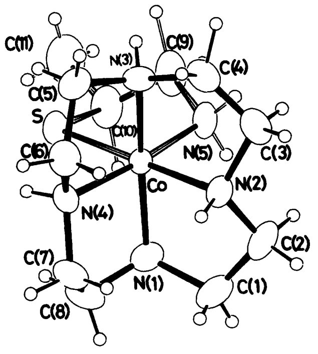


Fig. 4. An ORTEP drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level.[17)] Hydrogen atoms are represented by circles of radius 0.08 Å.

Table 1. Absorption (AB) and CD Spectral Data of the Isomers of [Co(*S*-apS)(cyclen)]$^{2+}$ in 0.01 mol dm^{-3} HClO$_4$

Isomer	AB: $\tilde{\nu}_{max}/10^3$ cm^{-1}(log(ε/mol^{-1} dm^3 cm^{-1})	CD: $\tilde{\nu}_{ext}/10^3$ cm^{-1}($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
exo(S,NH) (brown isomer)	16.7(sh, 1.99), 20.6(2.44), 26.7(sh, 2.56), 34.1(4.15), 44.2(4.15)	16.7(+0.36), 19.3(−0.63), 21.4(+0.15), 24.5(+0.22), 27.2(sh, −0.02), 29.5(sh, −0.28), 35.0(−2.16), 44.0(−3.40)
endo(S,NH) (green isomer)	16.0(1.95), 21.0(2.27), 26.3(sh, 2.33), 34.5(4.10), 44.5(4.10)	17.0(+0.34), 20.2(−1.68), 23.2(+1.00), 35.1(−2.18), 40.7(+1.14)

isomers of $[Co(S\text{-apS})(cyclen)]^{2+}$ was found in *trans*-(O,X)-$[CoX(\text{amino acidato})(dien)]^+$ ($X^-=CN^-$, NO_2^-, Cl^-; dien=diethylenetriamine).[15)]

Structure of $[Co(S\text{-apS})(cyclen)]ZnCl_4\cdot H_2O$ (green isomer). Final atomic coordinates and bond lengths and angles are listed in Tables 2 and 3. Figure 4 is a perspective drawing of the complex cation. This is the *endo*(S,NH) isomer (Fig. 2) in agreement with the prediction based on the order of elution in column chromatography and spectral data. Edge-on views of the five-membered chelate rings are shown in Fig. 5. The cyclen ligand has a pseudo-mirror symmetry through N(2)–Co–N(4) plane.

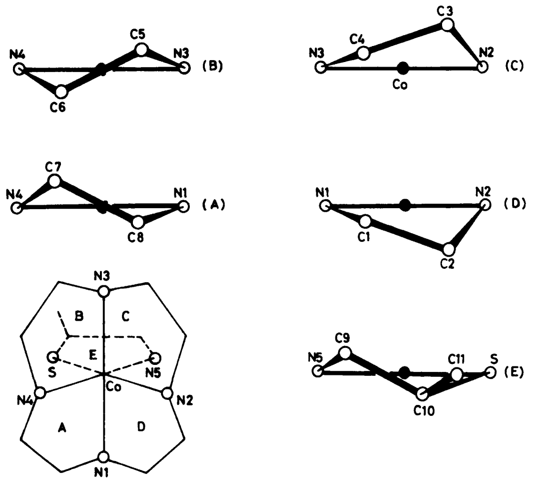


Fig. 5. Edge-on views of the five-membered chelate rings. The black circles stand for the Co atom.

Table 2. Positional Parameters ($\times 10^4$; for O(W) $\times 10^3$) and Equivalent Isotropic Temperature Factors

Atom	X	Y	Z	B_{eq}(Å^2)
Zn	17438(5)	0*	24307(5)	3.0
Co	46480(5)	57631(5)	25282(5)	1.9
Cl (1)	3491(1)	1222(1)	2434(1)	3.6
Cl (2)	1960(2)	−961(1)	325(2)	5.7
Cl (3)	−340(2)	762(2)	2550(2)	8.1
Cl (4)	2161(2)	−1064(1)	4387(2)	5.3
S	5675(1)	7300(1)	2536(1)	2.7
N (1)	4418(4)	5679(3)	338(4)	2.9
N (2)	3815(4)	4375(3)	2499(4)	2.7
N (3)	4389(3)	5660(3)	4713(4)	2.6
N (4)	2832(3)	6500(3)	2500(4)	2.5
N (5)	6643(4)	5218(3)	2598(4)	3.0
C (1)	4062(6)	4599(4)	−153(5)	4.0
C (2)	4297(5)	3869(4)	1113(6)	3.7
C (3)	4214(5)	3861(4)	3907(6)	3.6
C (4)	4000(5)	4581(4)	5162(5)	3.6
C (5)	3236(5)	6375(4)	5112(5)	3.3
C (6)	2095(4)	6304(4)	3917(5)	3.3
C (7)	2089(5)	6312(4)	1041(5)	3.4
C (8)	3257(5)	6396(5)	−103(5)	3.8
C (9)	7765(5)	5981(4)	2972(7)	4.4
C(10)	7502(5)	6933(4)	2146(6)	3.8
C(11)	8512(5)	7777(5)	2572(7)	5.0
O(W) 1†	88(1)	360(1)	209(1)	8.1
O(W) 2	69(2)	383(2)	329(3)	7.9
O(W) 3	82(4)	411(3)	145(4)	8.8
O(W) 4	102(4)	320(4)	127(4)	9.4

* This parameter was used to define the origin of b and listed without e.s.d. † Population parameters of the disordered hydrate O atoms: O(W)1, 0.40; O(W)2, 0.26; both O(W)3 and O(W)4, 0.17.

Table 3. Bond Lengths (l/Å) and Bond Angles (ϕ/°)

Zn -Cl (1)	2.293(1)	Cl(1)-Zn -Cl (2)	108.3(1)
Zn -Cl (2)	2.277(2)	Cl(1)-Zn -Cl (3)	108.5(1)
Zn -Cl (3)	2.200(2)	Cl(1)-Zn -Cl (4)	108.5(1)
Zn -Cl (4)	2.265(2)	Cl(2)-Zn -Cl (3)	112.6(1)
Co -S	2.235(1)	Cl(2)-Zn -Cl (4)	106.2(1)
Co -N (1)	1.968(4)	Cl(3)-Zn -Cl (4)	112.6(1)
Co -N (2)	1.982(4)	S -Co -N (1)	95.3(1)
Co -N (3)	1.976(4)	S -Co -N (2)	177.6(1)
Co -N (4)	1.959(3)	S -Co -N (3)	96.9(1)
Co -N (5)	2.004(4)	S -Co -N (4)	85.9(1)
S -C(10)	1.820(5)	S -Co -N (5)	85.4(1)
N (1)-C (1)	1.519(7)	N(1)-Co -N (2)	84.2(2)
N (1)-C (8)	1.487(7)	N(1)-Co -N (3)	164.8(2)
N (2)-C (2)	1.483(6)	N(1)-Co -N (4)	86.3(1)
N (2)-C (3)	1.470(6)	N(1)-Co -N (5)	95.5(2)
N (3)-C (4)	1.518(6)	N(2)-Co -N (3)	83.9(2)
N (3)-C (5)	1.481(6)	N(2)-Co -N (4)	96.4(1)
N (4)-C (6)	1.476(6)	N(2)-Co -N (5)	92.3(2)
N (4)-C (7)	1.487(6)	N(3)-Co -N (4)	85.6(1)
N (5)-C (9)	1.486(6)	N(3)-Co -N (5)	94.4(2)
C (1)-C (2)	1.495(7)	N(4)-Co -N (5)	171.3(1)
C (3)-C (4)	1.483(7)	Co -S -C(10)	99.7(2)
C (5)-C (6)	1.500(6)	Co -N (1)-C (1)	111.0(3)
C (7)-C (8)	1.516(7)	Co -C (1)-C (8)	107.1(3)
C (9)-C(10)	1.470(8)	C(1)-N (1)-C (8)	111.0(4)
C(10)-C(11)	1.502(8)	Co -N (2)-C (2)	107.2(3)
		Co -N (2)-C (3)	108.5(3)
		C(2)-N (2)-C (3)	115.6(4)
		Co -N (3)-C (4)	111.1(3)
		Co -N (3)-C (5)	107.4(3)
		C(4)-N (3)-C (5)	110.3(3)
		Co -N (4)-C (6)	108.9(3)
		Co -N (4)-C (7)	108.8(3)
		C(6)-N (4)-C (7)	120.2(3)
		Co -N (5)-C (9)	115.1(3)
		N(1)-C (1)-C (2)	110.5(4)
		N(2)-C (2)-C (1)	107.6(4)
		N(2)-C (3)-C (4)	108.6(4)
		N(3)-C (4)-C (3)	111.0(4)
		N(3)-C (5)-C (6)	107.7(4)
		N(4)-C (6)-C (5)	105.1(3)
		N(4)-C (7)-C (8)	104.2(4)
		N(1)-C (8)-C (7)	108.1(4)
		N(5)-C (9)-C(10)	110.4(4)
		S -C(10)-C (9)	106.2(4)
		S -C(10)-C(11)	110.4(4)
		C(9)-C(10)-C(11)	113.6(4)

Chelate rings A and B take a gauche, and C and D an envelope conformation. The geometry of cyclen is almost identical with those in cobalt(III) complexes investigated by X-ray analysis up to the present.[2,11,12] The hydrogen bonds listed in Table 4 do not seem to affect the conformation of the five-membered chelate rings of cyclen. In other Co^{III}-cyclen complexes, Co-N bond lengths involving N atoms on the pseudo-mirror plane (N(2) and N(4) atoms in the present complex) are by 0.02—0.04 Å shorter than others. However, the Co-N(2) bond is longer by 0.023(4) Å than Co-N(4) owing to the trans influence of the S atom.[16] The five-membered chelate ring formed by *S*-apS is δ-gauche to make the C(10)-C(11) bond in an equatorial position. The Co-N(5) bond is lengthened to avoid the short H···H contacts between the cyclen and *S*-apS ligands (see Fig. 6). A projection of crystal structure along *b* is shown in Fig. 7. Arrangement of the complex cation and $ZnCl_4^{2-}$ is NaCl type. There is an approximate oblate spheroidal hollow, which accomodates a disordered water molecule. The shortest interatomic distance involving the hydrate O atom is 3.03(3) Å for O(W)3···Cl(2) $(-x,\ y+\frac{1}{2},\ -z)$ and only by 0.24 Å shorter than the sum of van der Waals radii.

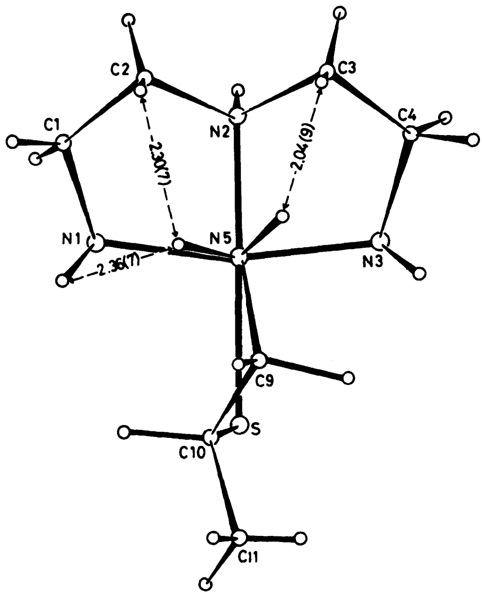


Fig. 6. The complex cation viewed along the line through the Co and N(5) atoms showing non-bonded H···H interactions between cyclen and *S*-apS ligands less than 2.4 Å, twice the van der Waals radius of the hydrogen atom.

Table 4. Intermolecular Hydrogen Bonds (Distances in Å)

A···H-B (symmetry code)	A···B	A···H	H···B
Cl(1)···H(N1)-N(1) (i)	3.268(4)	2.37(5)	1.04(5)
Cl(1)···H(N3)-N(3) (ii)	3.287(4)	2.51(4)	0.83(4)
Cl(2)···H(N5)1-N(5) (iii)	3.325(4)	2.50(5)	0.87(5)
Cl(4)···H(N5)2-N(5) (iv)	3.351(4)	2.58(6)	0.88(7)

Symmetry code: (i) $1-x,\ -1/2+y,\ -z$, (ii) $1-x,\ -1/2+y,\ 1-z$, (iii) $1-x,\ 1/2+y,\ -z$, (iv) $1-x,\ 1/2+y,\ 1-z$.

Isomerization Reactions. Figure 8 shows a typical set of absorption spectra (800—400 nm) obtained at intervals after the brown isomer had been dissolved in water at pH 6.27 and 25.4 °C. The spectra gave an isosbestic point at 597 nm and showed a large absorbance change at 480 nm, and this wavelength was used to follow the rate. In every kinetic run, the plot of $\ln(A_t-A_\infty)$ vs. time at a constant pH gave a straight line for at least three half-lives, where A_t and A_∞ represent the absorbance at time *t* and at infinite time at 480 nm, respectively. The slope gave the pseudo first-order rate constant, k_{obsd}. The $k_{obsd}/[OH^-]$ $(=k_{iso})$ values are constant at 25.4 °C in the pH range of 5.98—6.97, indicating that the reaction is first-order in $[OH^-]$. The values of k_{obsd} and k_{iso} are listed in Table 5, the average value of k_{iso} being $1.3\times10^4\ mol^{-1}\ dm^3\ s^{-1}$ at 25.4 °C. After the isomers had been equilibrated at 25.4 °C, the isomer distribution was analyzed by means of chromatography. The formation ratio of the brown to green isomer was 1.0, and no indication was observed for the formation of other isomers. The runs starting from either of the isomers gave the same result within the experimental

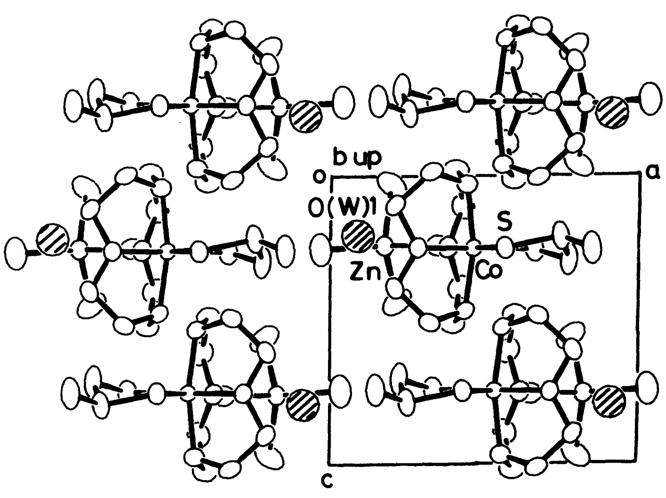


Fig. 7. A projection of the crystal structures along *b*. The hatched circles denote the O(W)1 atom. Other O(W) atoms were not drawn for simplicity.

Table 5. Rate Constants for the Isomerization of $[Co(S\text{-}apS)(cyclen)]^{2+}$ at 25.4 °C

pH	k_{obsd}/s^{-1}	$k_{iso}/mol^{-1}\ dm^3\ s^{-1}$
5.98	$(1.22\pm0.03)\times10^{-4}$	$(1.28\pm0.03)\times10^{4}$
6.27	$(2.36\pm0.05)\times10^{-4}$	$(1.27\pm0.03)\times10^{4}$
6.74	$(7.2\pm0.2)\times10^{-4}$	$(1.31\pm0.03)\times10^{4}$
6.97	$(1.25\pm0.03)\times10^{-3}$	$(1.35\pm0.03)\times10^{4}$

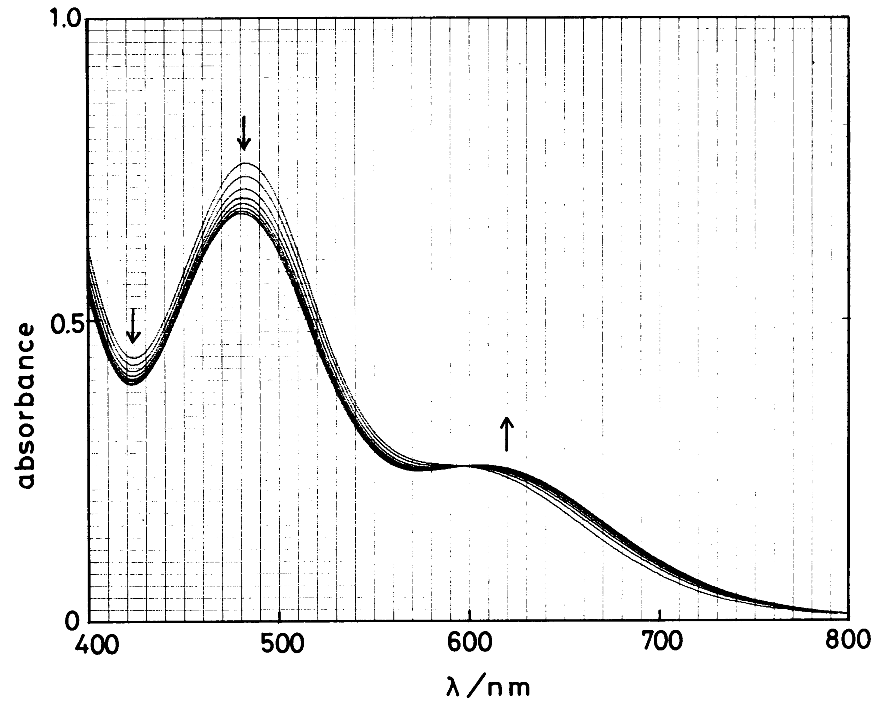


Fig. 8. Time-course changes of absorption spectrum of the brown isomer of $[\mathrm{Co}(S\text{-apS})(\text{cyclen})]^{2+}$ in an aqueous solution at pH 6.27 and 25.4 °C (recorded intervals: 20 min). Trends of spectral changes with time are shown by arrows.

error. The absorption and CD spectra of the equilibrated mixture agree well with those of an equimolar mixture of the two isomers. From these observations, the reaction can be expressed as

$$\text{brown isomer } (exo(\mathrm{S,NH})) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{green isomer } (endo(\mathrm{S,NH})).$$

The forward and reverse second-order rate constants, k_1 and k_{-1}, are related to the rate constant, k_{iso}, and to the equilibrium constant, K, as follows:

$$k_{\mathrm{iso}} = k_1 + k_{-1} \qquad K = \frac{k_1}{k_{-1}}.$$

From the k_{iso} and K values, the values k_1 and k_{-1} are calculated to be $6.5\times10^3\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ ($k_1=k_{-1}=0.5k_{\mathrm{iso}}$).

Inversion at an asymmetric nitrogen atom is known to be proportional to the hydroxide ion concentration[18] and the reversible isomerization is considered to occur between the two isomers (*exo*(S,NH) and *endo*(S,NH)) of configuration I. The observations decsribed above strongly suggest that the isomerization is resulted from the synchronous inversion at the two nitrogen atoms of the cyclen ring (N(2) and N(4) in Fig. 4). The isomerization can be compared to the racemization of *mer*-$[\mathrm{Co(dien)_2}]^{3+}$. In *mer*-$[\mathrm{Co(dien)_2}]^{3+}$, the molecular dissymmetry arises from the stereochemical relationship between the two trans NH bonds of the secondary amine nitrogen atoms in the two dien ligands. A rate constant, $2.4\times10^2\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$, for the recemization of *mer*-$[\mathrm{Co(dien)_2}]^{3+}$[19] at 35 °C is ca. 10^2 times as small as those obtained above for the isomerization of $[\mathrm{Co}(S\text{-apS})(\text{cyclen})]^{2+}$. An investigation is being undertaken to elucidate the effect of the sulfur donor atom on the rate of inversion at nitrogen.

Configuration II (Fig. 1) can be a possible intermediate for the isomerization reaction. The facts that (1) during the course of isomerization the absorption spectra give an isosbestic point, (2) the equilibrated mixture gives only two bands in column chromatography, and (3) only configuration I has been found by X-ray crystallography in the cobalt(III)-cyclen complexes suggest that configuration II is not stable in $[\mathrm{Co}(S\text{-apS})(\text{cyclen})].^{2+}$ Thus we conclude that isomerization does not involve formation of any intermediate in measurable amounts.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 58470032 from the Ministry of Education, Science and Culture.

References

1) K. Nakabayashi, K. Doi, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 989 (1984). The S atoms in the p- and t-isomers are trans to the primary (p) and tertiary (t) tren amine nitrogens, respectively.

2) N. Matsumoto, A. Hirano, T. Hara, and A. Ohyoshi, *J. Chem. Soc., Dalton Trans.*, **1983**, 2405.

3) T. C. Owen, *J. Chem. Soc., C,* **1967**, 1374.

4) J. R. Piper and T. P. Johnstone, *J. Org. Chem.*, **29**, 1657 (1964).

5) Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, bond lengths and bond angles involving hydrogen atoms, and observed and calculated strucrure factors are kept as Document No. 8613 at the Chemical Society of Japan.

6) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku,* **55**, 69 (1979).

7) W. C. Hamilton, *Acta Crystallogr.,* **18**, 502 (1965).

8) D. L. Nosco and E. Deutsch, *Inorg. Synth.,* **21**, 19 (1982).

9) R. H. Lane, F. A. Sedor, M. J. Gilroy, P. F. Eisenhardt, J. P. Bennett, Jr., R. X. Ewall, and L. E. Bennett, *Inorg. Chem.,* **16**, 93 (1977).

10) Y. Yoshikawa and K. Yamasaki, *Inog. Nucl. Chem. Lett.,* **6**, 523 (1970); K. Sakakibara, Y. Yoshikawa, and H. Yamatera, *Bull. Chem. Soc. Jpn.,* **52**, 2725 (1979); K. Nakajima, M. Kojima, and J. Fujita, *Chem. Lett.,* **1982**, 925.

11) Y. Iitaka, M. Shina, and E. Kimura, *Inorg. Chem.,* **13**, 2886 (1974).

12) J. H. Loehlin and E. B. Fleischer, *Acta Crystallogr., Sect. B,* **32**, 3063 (1976).

13) M. Ciampolini, M. Micheloni, N. Nardi, P. Paoletti, P. Dapporto, and F. Zanobini, *J. Chem. Soc., Dalton Trans.,* **1984**, 1357.

14) J. Giusti, S. Chimichi, M. Ciampolini, M. Sabat, and D. Masi, *Inorg. Chim. Acta,* **88**, 51 (1984).

15) K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.,* **45**, 161 (1972).

16) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.,* **12**, 2690 (1973).

17) C. K. Johnson (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

18) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.,* **88**, 4630 (1966); W. G. Jackson and A. M. Sargeson, "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 2, p. 273.

19) F. R. Keene and G. H. Searle, *Inorg. Chem.,* **11**, 148 (1972). The second-order rate constant for the racemization of *mer*-[Co(dien)$_2$]$^{3+}$ was calculated from the half-lives for racemization at pH 7.42 and 8.10.