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The Preparation, Stereochemistry, and Oxidation of 2-Pyridinethiolato Cobalt(III) Complexes, and the Crystal Structure of $[Co(2\text{-pyridinethiolato})(en)_2](ClO_4)_2$

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A series of mixed complexes $[Co(pyt)_{3-n}(diamine)_n]^{n+}$ (n=0, 1, and 2; pyt=2-pyridinethiolate(1−) and diamine=ethylenediamine, (*R*)-propylenediamine, or 2,2′-bipyridine) have been prepared and characterized by means of their visible and ultraviolet absorption, circular dichroism, and magnetic circular dichroism spectra. In the $[Co(pyt)_3]$ or $[Co(pyt)_2(diamine)]^+$ complex, only one geometrical isomer, *mer(S)* or *trans(S)* respectively, has been obtained. The $[Co(pyt)(en)_2](ClO_4)_2$ complex, which was spontaneously resolved, had an orthorhombic space group of $P2_12_12_1$, with a=12.406(1), b=12.754(1), c=11.621(4) Å, V=1838.7(6) Å^3, and Z=4. The refinement of 2276 reflections (Mo $K\alpha$ radiation) led to R=0.049. The Co-N bond trans to the pyt sulfur atom was longer by 0.023(11) Å than the cis one. The novel oxidation product $[Co(2\text{-pyridinesulfenato-}N,S)(en)_2]^{2+}$ was photochemically converted into the *N,O*-chelated linkage-isomer $[Co(2\text{-pyridinesulfenato-}N,O)(en)_2]^{2+}$ in the solid state, accompanied by ring-expansion from a four- to a five-membered chelate ring.

We have long been interested in the synthesis and stereochemistry of cobalt(III)[1)] and rhodium(III)[2)] complexes containing various kinds of bidentate-*N,S* ligands, such as 2-aminoethanethiol (=Haet), L-cysteine, L-cysteine methyl ester, and their oxidation derivatives. We previously prepared only *fac*(*S*) isomers of the [M(III)(bidentate-*N,S*)$_3$] (M=Co(III) and Rh(III)) type complexes. On the other hand, 2-pyridinethiolate(1−)(=pyt), which is an aromatic bidentate-*N,S* ligand and which forms a 4-membered chelate ring on coordination, showed a different stereochemical preference, as was reported in our preliminary papers.[3,4)]

This paper will describe the preparation and characterization of a series of cobalt(III) complexes containing pyt $[Co(pyt)_{3-n}(diamine)_n]^{n+}$ (diamine= ethylenediamine(=en), (*R*)-propylenediamine(=R-pn), or 2,2′-bipyridine(=bpy); n=0, 1, or 2) by means of their electronic absorption, circular dichroism (CD), magnetic circular dichroism (MCD), and ^{13}C NMR spectra. In the complexes of $[Co(pyt)_3]$ or $[Co(pyt)_2(diamine)]^+$, one geometrical isomer, *mer*(*S*) or *trans*(*S*) respectively, was obtained. These results are quite different from those obtained from complexes with aliphatic *N,S*-ligands. The crystal structure of $[Co(pyt)(en)_2](ClO_4)_2$ revealed the trans influence (trans lengthening) induced by the pyt sulfur donor atom. The difference in the electronic structures of the pyt and aet complexes is discussed on the basis of the X-ray crystal data. The orange sulfenato complex, which is the oxidation product of $[Co(pyt)(en)_2](ClO_4)_2$, changed photochemically into a green one in the solid state. These complexes were characterized as novel linkage isomers with a *N,S*- and *N,O*-chelate as the basis of the X-ray photoelectron spectra (XPS).

Experimental

Preparation, Separation, and Optical Resolution of 2-Pyridinethiolato Complexes. Most of the complexes were prepared by a redox reaction between di-2-pyridyl disulfide and the cobalt(II) ion.

(1) $[Co(pyt)(en)_2](ClO_4)_2$: Into a solution of $Co(ClO_4)_2\cdot 6H_2O)$ (17.0 g, 0.046 mol) in 30 cm^3 of ethanol we stirred a solution of ethylenediamine (6.0 g, 0.1 mol) in 40 cm^3 of ethanol. To the resulting solution we then immediately added a solution of di-2-pyridyl disulfide (5.0 g, 0.023 mol) in 100 cm^3 of ethanol, after which the mixture was stirred at ca. 50 °C for 2 h. The resulting brown precipitate was filtered and washed with ethanol (100 cm^3) and diethyl ether (100 cm^3). The precipitate was recrystallized by dissolving it in hot water (ca. 70 °C), filtering it, and cooling it to ca. 5 °C. At this stage, the orthorhombic brown crystals of $[Co(pyt)(en)_2](ClO_4)_2$ obtained were spontaneously resolved, as was confirmed by the CD spectrum of the aqueous solution, which contained one crystal, and by the following X-ray crystallographic data with a chiral space group. The yield was 18.0 g (80%). Found: C, 22.27; H, 4.20; N, 14.41%. Calcd for $[Co(pyt)(en)_2](ClO_4)_2=C_9H_{20}\text{-}N_5O_8SCl_2Co$: C, 22.14; H, 4.13; N, 14.35%.

For optical resolution, a solution of $K_2[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]\cdot 3H_2O$ (1.4 g, 0.002 mol) in 30 cm^3 of water was added to a solution of $[Co(pyt)(en)_2](ClO_4)_2$ (2.0 g, 0.004 mol) in 30 cm^3 of water. Immediately, crystals of $\Lambda[Co(pyt)(en)_2][Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]\cdot 5H_2O$ which showed a positive CD peak at 588 nm began to deposit, they were filtered off. Ten grams of $NaClO_4$ were then added to the filtrate, and the solution was cooled to induce crystallization. The crystals of $\Delta\text{-}[Co(pyt)(en)_2](ClO_4)_2$ were collected and recrystallized from hot water. Found for the Λ-diastereomer: C, 22.38; H, 3.65; N, 7.61%. Calcd for $\Lambda\text{-}[Co(pyt)(en)_2][Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]\cdot 5H_2O=C_{17}H_{34}N_5O_{17}SCoSb_2$: C, 22.32; H, 3.75; N, 7.65%. Found for the Δ-complex: C, 22.30; H, 4.13; N, 14.32%. Calcd for $\Delta\text{-}[Co(pyt)(en)_2](ClO_4)_2=C_9H_{20}N_5O_8SCl_2Co$: C, 22.14; H, 4.13; N, 14.35%.

(2) $[Co(pyt)_2(en)]ClO_4$: This complex was obtained as a by-product (1.0 g, 5%) from the mother liquor in the above preparation, but was prepared in a higher yield by the following method. Di-2-pyridyl disulfide (1.5 g, 0.0068

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mol) was stirred into a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (5.0 g, 0.0135 mol) in 50 cm^3 of ethanol. To this solution we then added a mixed solution of 2-pyridinethiol (1.5 g, 0.0135 mol) and ethylenediamine (1.0 g, 0.0166 mol) in 50 cm^3 of ethanol. After a few minutes, a green precipitate began to deposit. The mixture was stirred at ca. 50 °C for 2 h. The resulting green precipitate was filtered and washed with cold water (below 5 °C) until the washings were no longer brown. The precipitate was then recrystallized from water (ca. 70 °C). Columnar green crystals with a metallic luster were thus collected (4.3 g, 72%). Found: C, 32.98; H, 3.69; N, 12.81%. Calcd for $[Co(pyt)_2(en)]ClO_4 = C_{12}H_{16}N_4O_4S_2ClCo$: C, 32.85; H, 3.67; N, 12.77%.

(3) $[Co(pyt)_3]$: This nonelectrolyte complex was effectively prepared by the reaction of freshly prepared CoO(OH) (0.015 mol) with 2-pyridinethiol (5.0 g, 0.045 mol) in 200 cm^3 of ethanol–water (1 : 1). The dark brown orthorhombic crystals of $[Co(pyt)_3]$ (5.0 g, 90%) were collected by filtration and recrystallized by dissolving them in dimethyl silfoxide (DMSO) and by then adding water. The yield was 4.7 g (80%). Found: C, 46.27; H, 3.18; N, 10.92%. Calcd for $[Co(pyt)_3] = C_{15}H_{12}N_3S_3Co$: C, 46.27; H, 3.18; N, 10.79%.

(4) $[Co(pyt)_2(R\text{-}pn)]ClO_4$: A bis(2-pyridinethiolato) complex containing (*R*)-propylenediamine $[Co(pyt)_2(R\text{-}pn)]ClO_4$ was prepared by the same procedure as that used for $[Co(pyt)_2(en)]ClO_4$ except for the use of R-pn instead of en. A pair of green diastereomers, Λ-$[Co(pyt)_2(R\text{-}pn)]ClO_4$ (more soluble in ethanol) and Δ-$[Co(pyt)_2(R\text{-}pn)]ClO_4$ (less soluble in ethanol), was obtained. Found for the Λ-diastereomer: C, 34.34; H, 4.00; N, 12.17%. Found for the Δ-diastereomer: C, 34.74; H, 4.04; N, 12.47%. Calcd for Λ- or Δ-$[Co(pyt)_2(R\text{-}pn)]ClO_4 = C_{13}H_{18}N_4O_4S_2ClCo$: C, 34.48; H, 4.01; N, 12.37%.

(5) $[Co(pyt)(bpy)_2](ClO_4)_2$: Into a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (7.3 g, 0.020 mol) in 30 cm^3 of water we stirred a solution of 2,2′-bipyridine (6.2 g, 0.040 mol) in 40 cm^3 of hot ethanol. To the solution we then immediately added a solution of di-2-pyridyl disulfide (2.2 g, 0.010 mol) in 100 cm^3 of ethanol, after which the mixture was stirred at ca. 70 °C for 2 h. The resulting brown precipitate was filtered and washed with ethanol (100 cm^3) and diethyl ether (100 cm^3). The precipitate was recrystallized from water (ca. 70 °C). The yield was 12 g (85%). Found: C, 42.22; H, 3.22; N, 9.66%. Calcd for $[Co(pyt)(bpy)_2](ClO_4)_2 \cdot 1.5H_2O = C_{25}H_{23}N_5O_{9.5}SCl_2Co$: C, 42.45; H, 3.28; N, 9.90%.

(6) $[Co(pyt)_2(bpy)]ClO_4$: Di-2-pyridyl disulfide (2.0 g, 0.0091 mol) was stirred into a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (7.3 g, 0.020 mol) in 60 cm^3 of water–ethanol (1 : 3). To this solution we then added a mixed solution of 2-pyridinethiol (2.0 g, 0.0182 mol) and 2,2′-bipyridine (4.0 g, 0.0256 mol) in 50 cm^3 of ethanol. The mixture was stirred at ca. 70 °C for 2 h. The resulting brown-green precipitate was filtered and washed with hot water until the washings were no longer brown. The precipitate was recrystallized from methanol. Needle-like yellow-green crystals were collected (5.0 g, 47%). Found: C, 44.85; H, 3.09; N, 10.42%. Calcd for $[Co(pyt)_2(bpy)]ClO_4 = C_{20}H_{16}N_4O_4S_2ClCo$: C, 44.91; H, 3.01; N, 10.47%.

Oxidation of $[Co(pyt)(en)_2](ClO_4)_2$ and Photoisomerization of the Oxidation Product. A solution of 30% aqueous H_2O_2 (10 g) and 60% aqueous $HClO_4$ (10 g) was stirred into a solution of Δ-$[Co(pyt)(en)_2](ClO_4)_2$ (5 g) in 50 cm^3 of DMSO below 5 °C to give an orange solution instantly. To the resulting solution we immediately added a mixture of diethyl ether (700 cm^3) and ethanol (300 cm^3). Orange crystals appeared on the inside wall of a beaker in a few minutes; they were filtered. The yield was ca. 1 g. Found: C, 21.44; H, 3.93; N, 13.53%. Calcd for $(-)^{CD}_{507}$-$[Co(pyse)(en)_2](ClO_4)_2 = C_9H_{20}N_5O_9SCl_2Co$: C, 21.44; H, 4.00; N, 13.89% (Hpyse=2-pyridinesulfenic acid).

The orange pyse complex immediately turned a green one in the solid state upon exposure to the sun or a fluorescence lamp. The results of an elemental analysis of the photoproduct were identical with the original formula $[Co(pyse)(en)_2](ClO_4)_2$. The DMSO or aqueous solution of the orange complex became dark brownish within several tens minutes, even in the dark. Such a color change in solution was caused probably by redox decomposition and/or solvolysis. However, the green pyse complex was stable in an aqueous or DMSO solution at room temperature.

Measurements. 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 1.5 T magnetic field. The absorption, CD, and MCD measurements were carried out in DMSO and H_2O solutions at the low- and high-energy regions respectively. The XPS data were recorded on a Shimadzu HIPS 70 apparatus. The binding energies relative to the Fermi level were determined by referring to the Na-2s (64.0 eV) and S-$2p_{3/2}$ (169.5 eV) values of Na_2SO_4 mixed with an appropriate amount of each sample. All the measurements were done at room temperature.

X-Ray Study of $[Co(pyt)(en)_2](ClO_4)_2$. A brown crystal (0.40×0.39×0.33 mm) of the title compound was used for the data collection. Crystal data: orthorhombic, $P2_12_12_1$, $a=12.406(1)$, $b=12.754(1)$, $c=11.621(4)$ Å, and $V=1838.7(6)$ Å^3, $D_{calcd}=1.76$, $D_{obsd}=1.80$ g cm^{-3}, and $Z=4$. It is very interesting that this complex is spontaneously resolvable, for in the corresponding aet complex the perchlorate forms a conglomerate.[5] The diffraction intensities were measured using a Rigaku four-circle diffractometer, with graphite monochromatized Mo$K\alpha$ radiation ($\lambda=0.71069$ Å). $\mu(\mathrm{Mo}K\alpha)=13.80$ cm^{-1} and no absorption correction was applied. Within the range of $24° < 2\theta < 55°$, 2276 independent reflections ($I < 3\sigma(I)$) were obtained. All the computations were performed on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III.[6] The structure was solved by the usual heavy-atom method. The positions of ten hydrogen atoms were identified in subsequent difference Fourier maps, but the others could not be determined. The positional parameters of the hydrogen atoms, the anisotropic thermal parameters for all the non-hydrogen atoms, and the complete list of $|F_o|$ and $|F_c|$ values are deposited as Document No. 8892 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Results and Discussion

Characterization and Stereochemistry of 2-Pyridinethiolato Complexes. The electronic strucutre of the Hpyt compound in acidic conditions is considered to be comparable to that of the pyt-*N,S* ligand in a metal complex. In a 0.1 mol dm^{-3} $HClO_4$ solution, the absorption spectrum of the Hpyt compound showed

Table 1. Absorption Spectral Data

Complex/Solvent	σ_{max} ($\log \varepsilon$)[a)]
Hpyt	
0.1 mol dm^{-3} $HClO_4$	29.20(3.89), 37.00(4.03)
$[Co(pyt)(en)_2](ClO_4)_2$	
DMSO	12.66(0.31)^{sh}, 17.00(1.58)^{sh}, 20.20(2.06), 25.00(2.16)^{sh}, 29.85(3.43), 33.90(4.05)
H_2O	17.00(1.51)^{sh}, 20.35(2.05), 25.11(2.11)^{sh}, 30.50(3.43), 34.48(4.04), 39.22(4.25), 46.51(4.38)
trans(*S*)-$[Co(pyt)_2(en)]ClO_4$	
DMSO	11.49(0.06), 16.31(2.16), 21.74(2.42)^{sh}, 27.78(3.96), 30.81(4.19)
H_2O	16.59(2.08), 22.00(2.47)^{sh}, 28.34(3.99), 31.61(4.19), 38.00(4.34), 45.05(4.42), 49.50(4.49)
mer(*S*)-$[Co(pyt)_3]$	
DMSO	10.00(0.54)^{sh}, 14.93(2.17)^{sh}, 18.00(2.54)^{sh}, 21.00(2.91)^{sh}, 23.53(3.15)^{sh}, 27.40(3.92)^{sh}, 30.77(4.24)^{sh}, 32.79(4.36)^{sh}, 36.36(4.53)
CH_3OH	18.00(2.50)^{sh}, 21.00(2.85)^{sh}, 23.50(3.15)^{sh}, 27.40(3.87)^{sh}, 31.00(4.25)^{sh}, 33.00(4.30)^{sh}, 36.70(4.54)
trans(*S*)-$[Co(pyt)_2(R\text{-}pn)]ClO_4$	
Δ-diastereomer/DMSO	11.49(0.17)^{sh}, 16.31(2.17), 21.54(2.50)^{sh}, 27.78(3.96) 30.81(4.20)
H_2O	16.69(2.14), 22.00(2.49)^{sh}, 28.17(3.99), 31.70(2.18), 38.00(4.32), 45.10(4.42), 49.50(4.47)
Λ-diastereomer/DMSO	11.49(0.13)^{sh}, 16.39(2.16), 21.54(2.50)^{sh}, 27.78(3.94), 30.80(4.19)
H_2O	16.69(2.20), 22.01(2.57)^{sh}, 28.17(3.96), 31.70(4.16), 38.00(4.30), 45.00(4.42)
$[Co(pyt)(bpy)_2](ClO_4)_2$	
DMSO	12.20(0.36)^{sh}, 16.39(1.52), 20.78(2.10), 25.00(2.34)^{sh}, 33.38(3.45)
Δ-[Co(pyse-*N*,*S*)(en)$_2$](ClO$_4$)$_2$	
DMSO	16.13(1.26)^{sh}, 20.00(2.37)^{sh}, 25.64(3.28), 31.25(3.47)
Δ-[Co(pyse-*N*,*O*)(en)$_2$](ClO$_4$)$_2$	
DMSO	16.53(2.30), 20.00(2.43)^{sh}, 26.30(3.47), 31.25(3.57)
trans(*S*)-$[Co(pyt)_2(bpy)]ClO_4$	
DMSO	11.49(0.19)^{sh}, 16.39(1.52), 20.78(2.10), 33.38(3.45)

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

two intense absorption bands, at ca. 27000 and ca. 36000 cm^{-1} (Table 1). The energetically lower and higher bands can be assigned to the $\pi^*(py) \leftarrow n(s)$ and $\pi^*(py) \leftarrow \pi(py)$ transitions respectively (py=pyridine). Such bands can also be expected to appear in the spectra of the pyt complexes.

The absorption, CD, and MCD spectra of $[Co(pyt)(en)_2](ClO_4)_2$ (Fig. 1 and Tables 1, 2, and 3) are quite similar to those of $[Co(aet)(en)_2](ClO_4)_2$[7,8] (aet=2-aminoethanethiolato) in the spin-allowed first d-d transition band region. The shoulder at ca. 17000 cm^{-1} in the CD spectrum (or the positive MCD peak at 17330 cm^{-1}) and the negative CD peak at 19800 cm^{-1} are assigned to the components generated from the $^1E \leftarrow {}^1A_1$ transition in the C_{4v} symmetry on the CoN_5S geometry. These splittings have been ascribed by Houlding et al.[8,9] to the perturbation of the p-like lone pair of the two remaining lone-pairs on the sulfur atom. The positive CD band and the negative MCD one at ca. 22000 cm^{-1} are assigned to the $^1A_2 \leftarrow {}^1A_1$ (C_{4v}) transition. The energy peaks at ca. 12000 and 14000 cm^{-1} in the CD and MCD spectra are assigned to the spin-forbidden d-d transition, $^3T_{1g} \leftarrow {}^1A_{1g}$ and $^3T_{2g} \leftarrow {}^1A_{1g}(O_h)$ respectively. The bands at 30000, 35000, and 39000 cm^{-1} in the absorption spectra (in H_2O) can be assigned to $\pi^*(py) \leftarrow n(S)$, $\sigma^*(Co) \leftarrow \sigma(S)$, and $\pi^*(py) \leftarrow \pi(py)$ transitions respectively on the basis of the spectrum-pattern similarity of the Hpyt compound under acidic conditions.

The absorption and MCD spectra of $[Co(pyt)(bpy)_2](ClO_4)_2$ (Tables 1 and 3) are quite similar to those of $[Co(aet)(en)_2](ClO_4)_2$ and $[Co(pyt)(en)_2](ClO_4)_2$ in the spin-allowed first d-d transition region. The positive MCD peak at 15900 cm^{-1} and the negative one at 20400 cm^{-1} of $[Co(pyt)(bpy)_2]$-$(ClO_4)_2$ are energetically lower by ca. 1400 and ca. 1900 cm^{-1} respectively, than the corresponding peaks of $[Co(pyt)(en)_2](ClO_4)_2$; tentatively, the difference can be attributed to the destabilization of the Co dπ orbitals by the pi-donor character of bpy ligand.

The absorption and MCD spectra of $[Co(pyt)_2(en)]ClO_4$, and the absortion and CD spectra of *Λ*- and *Δ*-$[Co(pyt)_2(R\text{-}pn)]ClO_4$, are shown in Figs. 2 and 3 respectively. For the former en complex, three geometrical isomers, *C₂-cis*(*S*), *C₁-cis*(*S*), and *trans*(*S*), are possible. However, only one green isomer was obtained for $[Co(pyt)_2(en)]^+$, as for $[Co(pyt)_2(R\text{-}pn)]^+$. The bis(pyt) complexes are assigned to a *trans*(*S*) isomer on the basis of the fair agreement of the absorption spectra of the *trans*(S)-$[Co(thiolato)_2(amine)_4]^+$-type complexes[10] in the spin allowed first d-d transition region. The intense transitions, $\pi^*(py) \leftarrow n(S)$ at 28000 cm^{-1} and $\sigma^*(Co) \leftarrow \sigma(S)$ at 32000 cm^{-1}, were considerably red-shifted compared with those of

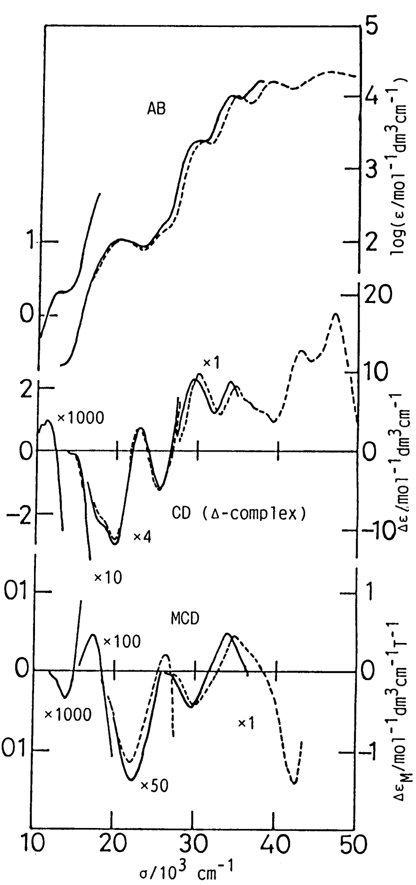

Fig. 1. Absorption, CD (for Δ-complex), and MCD spectra of (Co(pyt)(en)$_2$](ClO$_4$)$_2$ (—— in DMSO and ----in H$_2$O).

[Co(pyt)(en)$_2$](ClO$_4$)$_2$; tentatively, this may be attributed to the destabilizations of the sulfur nonbonding and sigma-donor orbitals by the mutual 'trans-influence' of the *trans-S* donors, whereas the π^*(py)$\leftarrow$$\pi$(py) transition (38000 cm^{-1}) does not shift.

The absorption and MCD spectra of [Co(pyt)$_2$(bpy)]ClO$_4$ (Tables 1 and 3) were similar to those of *trans*(*S*)-[Co(pyt)$_2$(en)]ClO$_4$ in the spin-allowed first d-d transition region. Therefore, the bpy complex is also assigned to the *trans*(*S*) isomer.

Figure 4 shows the absorption and MCD spectra of [Co(pyt)$_3$]. In this complex, only one of the two possible geometrical isomers, *fac*(*S*) and *mer*(*S*), was obtained. This dark brown complex is assigned to a *mer*(*S*) isomer on the basis of the ^{13}C NMR spectrum in the CDCl$_3$ solution, which showed eight resonances; 116.87^b, 125.48^b, 135.45, 135.94, 136.59, 147.10^b, 149.48^b, and 150.41^b ppm (b=broad), whereas only five signals are expected for the *fac*(*S*) geometry. The splitting pattern of the MCD spectrum in the first d-d transition region (14300, 17900, and 21200 cm^{-1}) also supports this assignment.

The Crystal Structure of [Co(pyt)(en)$_2$](ClO$_4$)$_2$. Figure 5 shows the numbering of the title complex ion. The atomic parameters and the bond distances and angles are listed in Tables 4 and 5. The complex has a distorted octahedral structure around Co center. The bite angle of the 4-membered pyt ligand 72.9(2)° is rather narrower than a right angle. The bond length of the Co-N(5) sited trans to pyt's sulfur is 1.993(6) Å, while the average of the Co-N(2) and Co-N(4) sited cis to the sulfur is 1.970(9) Å; that is, the difference is 0.023(11) Å. The trans-influence of the pyt thiolate is less by 0.041(10) Å than that of the aet thiolate in the corresponding complex.[11] The smaller trans influence of the pyt thiolate may be interpreted in terms of the decrease in the orbital interaction between the Co 3d and the sulfur lone pair

Table 2. CD Spectral Data

Complex/Solvent	σ_{ext} ($\Delta\varepsilon$)$^{a)}$
Δ-[Co(pyt)(en)$_2$](ClO$_4$)$_2$	
DMSO	11.36(+0.004), 18.18(−2.33)$^{\text{sh}}$, 19.80(−2.95), 22.94(+0.74), 25.32(−1.22), 29.50(+9.13), 33.90(+8.88)
H$_2$O	18.18(−2.19)$^{\text{sh}}$, 19.72(−2.83), 22.68(+0.71), 25.19(−1.25), 30.12(+9.96), 34.72(+8.42), 42.92(+12.79), 46.95(+17.61)
trans(*S*)-[Co(pyt)$_2$(R-pn)]ClO$_4$	
Δ-diastereomer/DMSO	11.43(+0.013), 16.34(−5.85), 20.00(−1.92), 22.62(+4.46), 27.40(+125.3), 30.30(−28.02)
H$_2$O	16.61(−5.13), 22.47(+3.58), 28.01(+115.9), 30.86(−31.11), 32.47(−24.16)$^{\text{sh}}$, 38.31(−27.78), 42.02(+10.57), 45.87(+9.06), 48.08(+10.12)
Λ-diastereomer/DMSO	10.31(−0.009), 16.34(+6.32), 20.20(+1.41), 22.62(−3.37), 27.17(−138.6), 30.30(27.08)$^{\text{sh}}$, 31.45(+29.45)
H$_2$O	16.67(+5.59), 19.88(+0.98), 22.47(−2.51), 24.39(+0.72), 27.86(−127.4), 31.06(32.09), 38.76(+32.25), 41.67(−3.99), 43.48(+14.69), 49.50(+7.35)
Δ-[Co(pyse-*N*,*S*)(en)$_2$](ClO$_4$)$_2$	
DMSO	10.64(−0.006), 11.36(−0.004), 19.72(−1.05), 25.51(+1.91), 34.84(+3.54)
Δ-[Co(pyse-*O*,*N*)(en)$_2$](ClO$_4$)$_2$	
DMSO	10.42(+0.004), 16.58(+2.19), 20.00(+0.23), 23.20(−3.06), 26.81(+1.57), 35.09(−7.13)

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

Table 3. MCD Spectral Data

Complex/Solvent	σ_{ext} ($\Delta\varepsilon_M$)$^{a)}$
[Co(pyt)(en)$_2$](ClO$_4$)$_2$	
DMSO	13.89(−0.0003), 17.33(+0.005), 22.32(−0.028), 29.33(−0.458), 33.76(+0.364)
H$_2$O	17.24(+0.005), 22.22(−0.023), 26.32(+0.004), 29.94(−0.414), 34.72(+0.449), 42.55(−1.42)
trans(*S*)-[Co(pyt)$_2$(en)]ClO$_4$	
DMSO	13.89(−0.00078), 15.87(−0.00084)^{sh}, 22.22(−0.26), 27.62(−0.430), 32.79(−0.430), 34.48(+0.717), 36.36(−1.698)
H$_2$O	21.74(−0.012), 28.17(−0.328), 33.33(−0.282), 35.71(+0.538), 38.46(−1.525), 42.92(+0.852), 45.45(−,1.607)
mer(*S*)-[Co(pyt)$_3$]	
DMSO	11.36(−0.0006), 12.50(−0.0011), 14.46(+0.010), 17.54(+0.021), 21.19(−0.136), 24.69(+0.042), 27.40(−0.568), 32.05(−1.147), 35.09(−2.144)
CH$_3$OH	17.86(+0.017), 21.51(−0.100), 24.69(+0.033), 27.40(−0.447), 32.79(−1.051), 35.71(−2.207), 38.17(+0.063), 41.32(−1.009)
[Co(pyt)(bpy)$_2$](ClO$_4$)$_2$	
DMSO	12.20(+0.0004), 12.66(−0.0006), 15.87(+0.0041), 20.41(−0.032), 28.17(−0.083), 30.21(+0.586), 33.11(−1.861)
H$_2$O	28.57(−0.043), 31.06(+0.547), 34.25(−1.122), 38.02(−1.642), 47.62(−1.423)
trans(*S*)-[Co(pyt)$_2$(bpy)]ClO$_4$	
DMSO	12.35(−0.0005), 20.83(−0.046), 26.67(−0.277), 28.41(−0.225), 28.99(−0.453), 31.75(−1.534)
H$_2$O	30.77(+0.144), 32.26(−0.780), 37.45(−0.990), 40.00(−0.333), 41.67(+0.130), 42.55(−0.459), 44.44(+1.216), 45.45(+0.855), 48.08(−1.306)

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

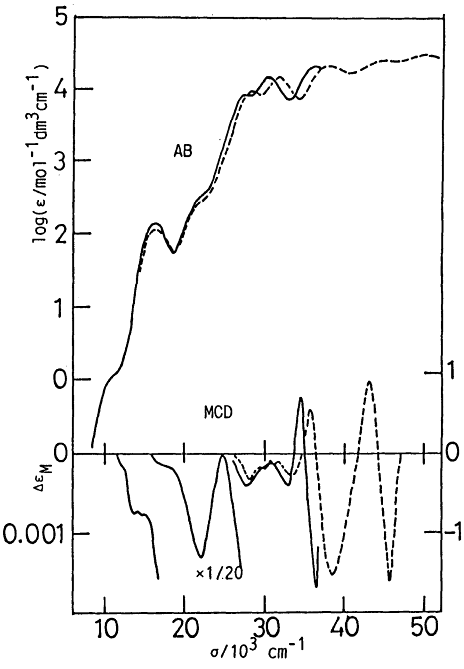

Fig. 2. Absorption and MCD spectra of [Co(pyt)$_2$(en)]ClO$_4$ in DMSO (——) and in H$_2$O (----) solutions.

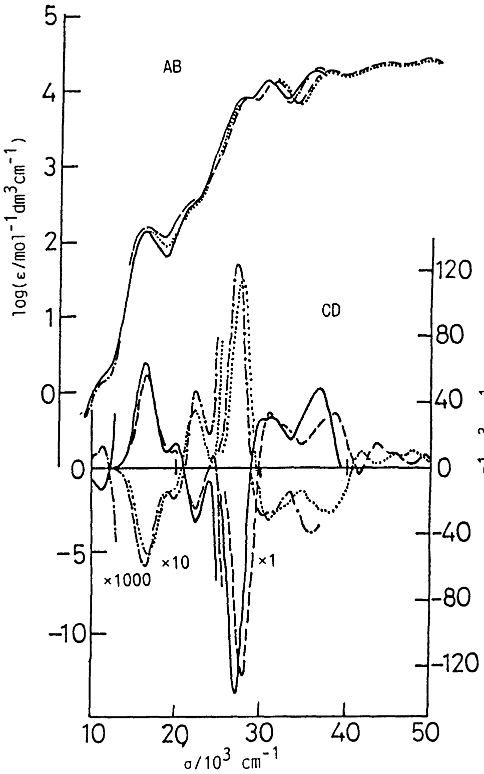

Fig. 3. Absorption and CD spectra of Λ-[Co(pyt)$_2$(R-pn)]ClO$_4$ (—— in DMSO and ---- in H$_2$O) and Δ-[Co(pyt)$_2$(R-pn)]ClO$_4$ (—·— in DMSO and ······ in H$_2$O).

orbitals, on the basis of the narrower bite angle (72.9(2)°) compared to the aet one (88.8(2)°).[11] In addition, the resonance structure **b** (anion of 2(1*H*)-pyridinethione) in Fig. 6 contributes to the pyt complex, and the sigma-donor ability of the pyt thiolate becomes weak because of the lesser electron density of the sulfur atom compared to that of the aliphatic thiolato sulfur. This resonance contribution is in good agreement with the facts that the S-C(1) bond distance (1.754(7) Å) is rather shorter than the ali-

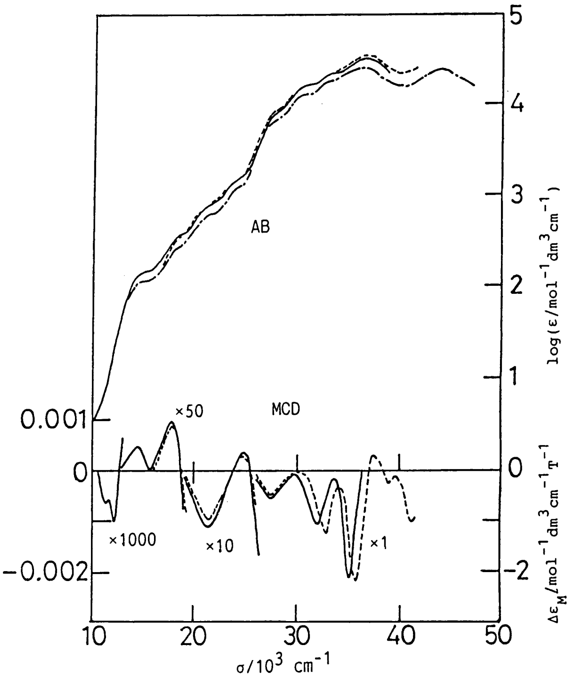

Fig. 4. Absorption and MCD spectra of $[Co(pyt)_3]$ (—— in DMSO, ---- in CH_3OH, and —·— in $(C_2H_5)_2O$).

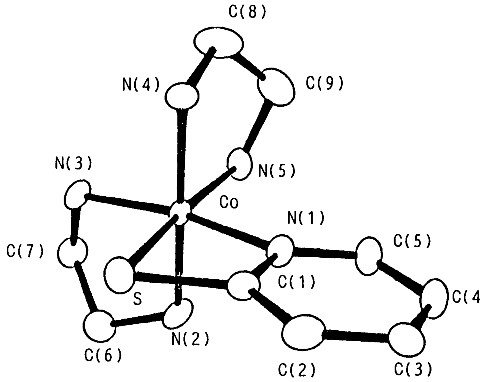

Fig. 5. The perspective view of $[Co(pyt)(en)_2](ClO_4)_2$.

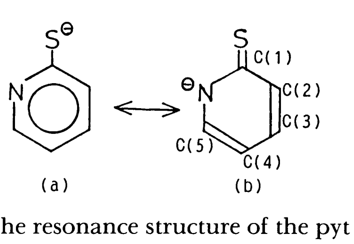

Fig. 6. The resonance structure of the pyt ligand.

Table 4. Positional Parameters (×10⁴) and Equivalent Temperature Factors (Å²) of $[Co(pyt)(en)_2](ClO_4)_2$

Atom	*x*	*y*	*z*	B_{eq}
Co	199(1)	36(1)	8525(1)	2.0
S	893(1)	−1309(1)	7464(2)	2.9
Cl(1)	−2844(1)	−2533(1)	8662(2)	3.4
Cl(2)	3429(1)	−3517(1)	5358(2)	3.6
N(1)	1730(4)	−3(5)	8811(5)	2.6
N(2)	−90(5)	−914(5)	9831(5)	3.3
N(3)	−1278(4)	−50(5)	7922(5)	2.7
N(4)	434(4)	1013(5)	7256(6)	3.2
N(5)	−183(5)	1176(5)	9625(6)	3.4
O(11)	4004(7)	−3307(6)	4415(8)	6.1
O(12)	2462(8)	−2922(9)	5612(12)	8.0
O(13)	4152(10)	−3162(15)	6386(12)	10.8
O(14)	3244(11)	−4589(7)	5597(12)	8.6
O(21)	−2192(8)	3655(5)	3717(12)	7.6
O(22)	−2786(19)	2053(15)	4643(18)	12.8
O(23)	−2707(19)	2262(10)	2664(14)	12.5
O(24)	−1117(12)	2262(9)	3851(18)	11.0
C(1)	2032(5)	−840(5)	8193(6)	2.5
C(2)	3111(6)	−1153(7)	8143(7)	3.6
C(3)	3855(6)	−565(9)	8702(7)	4.1
C(4)	3533(6)	321(7)	9333(8)	4.0
C(5)	2469(6)	579(7)	9387(8)	3.6
C(6)	−516(10)	−326(10)	10800(9)	5.6
C(7)	−77(10)	700(10)	10827(8)	5.5
C(8)	−1457(6)	801(6)	7090(7)	3.5
C(9)	−454(7)	934(6)	6418(8)	3.8

Table 5. Selected Bond Distances (*l*/Å) and Angles (*ϕ*/°) of $[Co(pyt)(en)_2](ClO_4)_2$

Co-S	2.282(2)	Co-N(1)	1.929(5)
Co-N(2)	1.975(6)	Co-N(3)	1.964(5)
Co-N(4)	1.960(6)	Co-N(5)	1.993(6)
N(1)-C(1)	1.339(9)	S-C(1)	1.754(7)
C(2)-C(3)	1.355(12)	C(1)-C(2)	1.397(10)
C(4)-C(5)	1.362(11)	C(3)-C(4)	1.405(14)
N(2)-C(6)	1.453(13)	C(5)-N(1)	1.358(10)
N(3)-C(8)	1.470(10)	N(5)-C(7)	1.528(12)
C(6)-C(7)	1.417(18)	N(4)-C(9)	1.474(11)
S-Co-N(1)	72.6(2)	C(8)-C(9)	1.479(12)
S-Co-N(3)	96.7(2)	S-Co-N(2)	91.2(2)
S-Co-N(5)	170.0(2)	S-Co-N(4)	90.9(2)
N(1)-Co-N(3)	168.0(2)	N(1)-Co-N(2)	91.8(3)
N(1)-Co-N(5)	98.2(3)	N(1)-Co-N(4)	90.0(2)
N(2)-Co-N(4)	177.6(3)	N(2)-Co-N(3)	94.1(3)
N(3)-Co-N(4)	84.6(2)	N(2)-Co-N(5)	84.9(3)
N(4)-Co-N(5)	93.2(3)	N(3)-Co-N(5)	92.8(3)
Co-N(1)-C(1)	101.8(4)	Co-S-C(1)	77.7(2)
C(1)-N(1)-C(5)	120.7(6)	Co-N(1)-C(5)	137.4(5)
Co-N(3)-C(8)	109.6(4)	Co-N(2)-C(6)	110.2(6)
Co-N(5)-C(7)	106.0(6)	Co-N(4)-C(9)	110.1(5)
C(1)-C(2)-C(3)	118.3(8)	N(1)-C(1)-C(2)	121.2(6)
C(3)-C(4)-C(5)	119.6(8)	C(2)-C(3)-C(4)	120.1(7)
N(2)-C(6)-C(7)	110.8(9)	C(4)-C(5)-N(1)	120.0(8)
N(3)-C(8)-C(9)	107.7(6)	C(6)-C(7)-N(5)	108.3(8)
C(8)-C(9)-N(4)	106.7(7)		

phatic S-C one (1.818(8) Å)[11] and that the C(1)-C(2) and C(3)-C(4) bond distances (1.397(10) and 1.405 (14) Å respectively) are considerably longer than the C(2)-C(3) and C(4)-C(5) distances (1.355(12) and 1.362(11) Å respectively). This difference of the trans influence induced by **pyt** and **aet** may be related to the geometrical isomeric preference of the $[Co(N\text{-}S)_3]$ and $[Co(N\text{-}S)_2(N\text{-}N)]^+$-type complexes. In fact, only the *fac* geometry has been obtained for the aet complexes $[Co(aet)_3]$[1] and $[Rh(aet)_3]$,[2] whereas only the *mer* geometry has been obtained for the pyt complexes $[Co(pyt)_3]$ and $[Rh(pyt)_3]$.[12] In the case of [Rh(6-

methyl-2-pyridinethiolato)$_3$],[13] only the fac geometry was isolated, but this is due to the steric effect of the 6-methyl groups. Thus, the aet thiolates with a relatively large trans-influence favor the cis disposition toward each other, but the pyt thiolates with a lesser trans influence make a trans disposition possible.

Characterization of the Oxidation Product [Co(pyse-*N,S*)(en)$_2$](ClO$_4$)$_2$ and Its Photoisomerization into [Co(pyse-*N,O*)(en)$_2$](ClO$_4$)$_2$. The H_2O_2 oxidation of the [Co(pyt)(en)$_2$](ClO$_4$)$_2$ in acid media resulted in an orange complex, which was characterized as the sulfenato-*N,S* complex [Co(pyse-*N,S*)(en)$_2$](ClO$_4$)$_2$ on the basis of its elemental analysis and absorption spectrum (Fig. 7). This orange complex changed into a green one photochemically in the solid state. Since the green complex has the same chemical composition, it is reasonable to consider that the linkage isomerization from *N,S*- to *N,O*-bonded is induced by to exposure light. The green complex exhibited a ligand-field transition at 16600 cm^{-1}, as is shown in Fig. 7.[14] Though the ligand-field strength of the oxygen atom of the *O*-bonded sulfenato complex is extraordinarily weak, this may be because of the repulsion between the oxygen and adjacent sulfur lone pairs. The pyse-*S,N* and -*O,N* complexes exhibit a characteristic intense absorption band at ca. 25000 cm^{-1} and ca. 26000 cm^{-1} respectively. All the known *S*-bonded sulfenato complexes showed a similar absorption band at ca. 27000 cm^{-1}. Such an intense band has generally been observed in complexes with the Co-X-Y array, where X and Y are oxygen and/or sulfur atom with lone-pair electrons.[15] The parent complex, [Co(pyt-*S,N*)(en)$_2$]$^{2+}$, did not show such an intense band in the region below 30000 cm^{-1}. On the other hand, both sulfenato complexes showed this intense band, as is consistent with the above strucutre assignments. The optically active complexes, $(-)^{\mathrm{CD}}_{500}$-[Co(pyse-*S,N*)(en)$_2$]$^{2+}$ and its linkage isomer $(-)^{\mathrm{CD}}_{603}$-[Co(pyse-*O,N*)(en)$_2$]$^{2+}$, are assigned to the Δ absolute configuration on the basis of the dominant negative CD sign at 19700 cm^{-1} and at 16600 cm^{-1} respectively in the first d-d band region.

The XPS spectra of the S-2p binding energy region for the orange and green isomers of [Co(pyse)(en)$_2$](ClO$_4$)$_2$ are shown in Fig. 8. The orange complex exhibited a peak at 166.7 eV, with a shoulder at ca. 164 eV. The green complex showed a peak at 164.3 eV, with a shoulder at ca. 167 eV. These results indicate that the samples used for both measurements are mixtures of two species; that is, the pure orange complex should show a peak at 166.7 eV, and the pure green one, are at 164.3 eV. Since the *N,O*-coordinated pyse must show a lower sulfur binding energy because of the decrease in the partial charge on the sulfur atom as compared with the *N,S*-coordinated pyse, the orange and green isomers can be assigned to the *N,S*- and *N,O*-chelated structures respectively. Thus, the light irradiation of the 4-membered *N,S*-pyse complex caused the linkage isomerization in the solid state to give the *N,O*-chelated complex with the 5-membered ring. In general, the strain energy of a chelate ring is much eliminated in a 5-membered chelate as compared with a 4-membered one. Therefore, the present photoisomerization seems to be energetically favora-

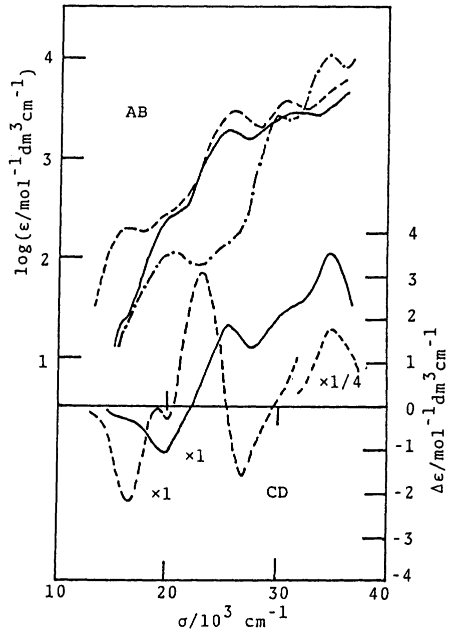

Fig. 7. Absorption and CD spectra of Δ-[Co(pyse-*N,S*)(en)$_2$](ClO$_4$)$_2$ (——), Δ-(Co(pyse-*N,O*)(en)$_2$]-(ClO$_2$)$_2$ (----), and [Co(pyt)(en)$_2$](ClO$_4$)$_2$ (—·—) in DMSO solution.

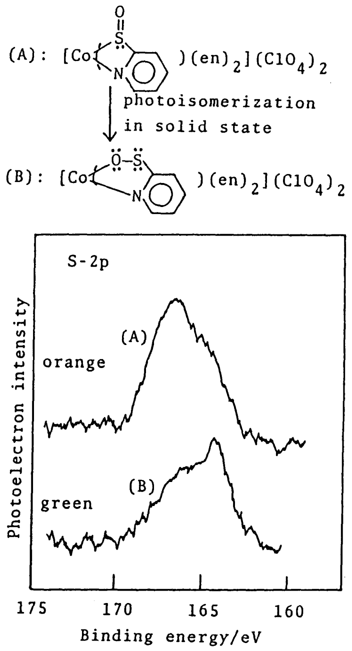

Fig. 8. The XPS spectra of S-2p binding energy region for the orange(A) and green(B) isomers of [Co(pyse)(en)$_2$](ClO$_4$)$_2$.

ble. Photoisomerization has been reported in an aqueous solution of the sulfinato complex $[Co(aesi\text{-}N,S)(en)_2]^{2+}$ (Haesi=2-aminosulfinic acid), though the corresponding sulfenato complex $[Co(aese\text{-}N,S)(en)_2]^{2+}$ (Haese=2-aminosulfenic acid) did not show any.[8)]

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