CHEMISTRY LETTERS, pp. 141-144, 1983. © The Chemical Society of Japan 1983

SYNTHESIS AND STEREOCHEMISTRY OF 2-PYRIDINETHIOLATO ETHYLENEDIAMINE MIXED COMPLEXES OF COBALT(III)

Masakazu KITA,* Kazuaki YAMANARI, and Yoichi SHIMURA
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560

A series of mixed complexes $[Co(pyt)_{3-n}(en)_n]^{n+}$ (n = 0, 1, and 2) have been newly prepared and characterized by their visible and ultraviolet absorption, circular dichroism, and magnetic circular dichroism spectra (pyt = 2-pyridinethiolato-*N,S* ligand). In $[Co(pyt)_3]$ or $[Co(pyt)_2(en)]^+$ complex, only one geometrical isomer, *mer(S)* or *trans(S)*, has been obtained, respectively.

2-Pyridinethiolato (= pyt) is a potentially bidentate-*N,S* ligand, forming 4-membered chelate ring on coordination. To examine the ability of this mode of coordination in mononuclear complexes,[1)] we attempted to prepare a series of cobalt(III) complexes, $[Co(pyt)_{3-n}(en)_n]^{n+}$ (n = 0, 1, and 2). The mixed complexes obtained were characterized from their absorption, circular dichroism (CD), magnetic circular dichroism (MCD),[2)] and ^{13}C NMR spectra.

To a stirred solution of $Co(ClO_4)_2\cdot 6H_2O$ (17.0 g, 0.046 mol) in 30 cm^3 of ethanol was added a solution of ethylenediamine (6.0 g, 0.1 mol) in 40 cm^3 of ethanol. To the solution was immediately added a solution of bis(2-pyridyl) disulfide (5.0 g, 0.023 mol) in 100 cm^3 of ethanol and the mixture was stirred at *ca.* 50°C for 2h. 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, and cooling to *ca.* 5°C. At this stage, orthorhombic brown crystals of $[Co(pyt)(en)_2](ClO_4)_2$ were obtained as a spontaneously resolved racemate: the yield was 18.0 g (80 %). Found: C, 22.27; H, 4.20; N, 14.41%. Calcd for $[Co(pyt)(en)_2](ClO_4)_2$ = $C_9H_{20}N_5O_8SCl_2Co$: C, 22.14; H, 4.13, N, 14.35%. For optical resolution, to a solution of $[Co(pyt)(en)_2](ClO_4)_2$ (2.0 g, 0.004 mol) in 30 cm^3 of water was added a solution of $K_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot H_2O$ (1.4 g, 0.002 mol) in 30 cm^3 of water. Immediately, Λ-$[Co(pyt)(en)_2]\cdot[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$ began to deposit and was filtered off. $NaClO_4$ (10 g) was added to the filtrate and the mixture was cooled to induce crystallization. The crystals of Δ-$[Co(pyt)(en)_2](ClO_4)_2$ were collected and recrystallized from hot water. Found for the less-soluble diastereomeric salt: C, 22.38; H, 3.65; N, 7.61%. Calcd for Λ-$[Co(pyt)(en)_2]\cdot[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 5H_2O$ = $C_{17}H_{34}N_5O_{17}SCoSb_2$: C, 22.32; H, 3.75; N, 7.65 %. Found for the Δ-isomer: C, 22.30; H, 4.13; N, 14.32 %. Calcd for Δ-$[Co(pyt)(en)_2](ClO_4)_2$ = $C_9H_{20}N_5O_8Cl_2SCo$: C, 22.14; H, 4.13; N, 14.35 %.

A green complex $[Co(pyt)_2(en)]ClO_4$ was obtained as a by-product (1.0 g, 5 %) from the mother liquor in the above preparation. But, this complex was prepared in a higher yield by the following method. Bis(2-pyridyl) disulfide (1.5 g, 0.0068 mol) was added to a stirred solution of $Co(ClO_4)_2 \cdot 6H_2O$ (5.0 g, 0.0135 mol) in 50 cm^3 of ethanol. To the solution was 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, the green precipitate began to deposit. The mixture was stirred at *ca.* 50°C for 2h. The resulting green precipitate was filtered and washed with cold water (below 5°C) until the washings became no longer brown. The precipitate was recrystallized by dissolving it in hot water (*ca.* 70°C) and cooling to room temperature. The columnar green crystals with metallic luster were 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%.

On recrystallization of $[Co(pyt)_2(en)]ClO_4$ from a hot aqueous solution, a crop of tris complex $[Co(pyt)_3]$ was obtained as an insoluble dark brown precipitate (0.6 g, 10%). This nonelectrolyte complex was more effectively prepared by the reaction of freshly prepared CoO(OH) (0.015 mol) and 2-pyridinethiol (5.0 g, 0.045 mol) in 200 cm^3 of ethanol-water (1:1). The dark brown orthorhombic crystals of $[Co(pyt)_3]$ (5.3 g, 90%) were collected and recrystallized by dissolving them in dimethyl sulfoxide, and adding water to induce crystallization. The yield was 4.7 g (80%). Found: C, 46.38; 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%.

Neither complex $[Co(pyt)_2(en)]ClO_4$ nor $[Co(pyt)_3]$ could be optically resolved to date. A bis(2-pyridinethiolato) complex containing (*R*)-propylenediamine $[Co(pyt)_2\{(R)\text{-pn}\}]ClO_4$ was prepared by the same procedure as that for $[Co(pyt)_2(en)]ClO_4$ except for the use of (*R*)-pn instead of en. A pair of green diastereomers was obtained, 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). Found for Λ-diastereomer: C, 34.34; H, 4.00; N, 12.17%. Found for 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%.

The absorption, CD, and MCD spectra of $[Co(pyt)(en)_2](ClO_4)_2$ (Fig. 1) are quite similar to those of $[Co(aet)(en)_2](ClO_4)_2$ 3,4) (aet = 2-aminoethanethiolato-*N,S*) in the spin-allowed first d-d transition band region ($^1T_{1g} \leftarrow {}^1A_{1g}$ in O_h symmetry), in spite of the fairly different characters of pyt and en, the aromatic former forming 4-membered chelate ring and the aliphatic latter 5-membered. The shoulder at *ca.* 17000 cm^{-1} in the CD band (or the positive MCD extreme at 17330 cm^{-1}) and the negative CD extreme at 19800 cm^{-1} are assigned to the two nondegenerate components generated from the $^1E \leftarrow {}^1A_1$ transition in C_{4v} symmetry of the present complex. The similar splitting has been ascribed to the perturbation of p-like lone pair on the sulfur atom after Houlding *et al.* 4) The positive CD band and the negative MCD one at *ca.* 22000 cm^{-1} are assigned to $^1A_2 \leftarrow {}^1A_1$ (C_{4v}) transition. The lowest energy band at *ca.* 11000 cm^{-1} in the absorption or the CD spectrum is assigned to the spin-forbidden d-d transition, $^3T_{1g} \leftarrow {}^1A_{1g}$ (O_h). The bands at 30000 and 35000 cm^{-1} in the absorption spectra (in H_2O) can be assigned to the transitions $\pi^*(py) \leftarrow n(S)$, $\sigma^*(Co) \leftarrow \sigma(S)$, respectively (py means pyridine ring). The absorption band at 39000 cm^{-1} is due to a $\pi^*(py) \leftarrow \pi(py)$ transition.

The absorption and MCD spectra of $[Co(pyt)_2(en)]ClO_4$ and the CD spectrum of Δ-

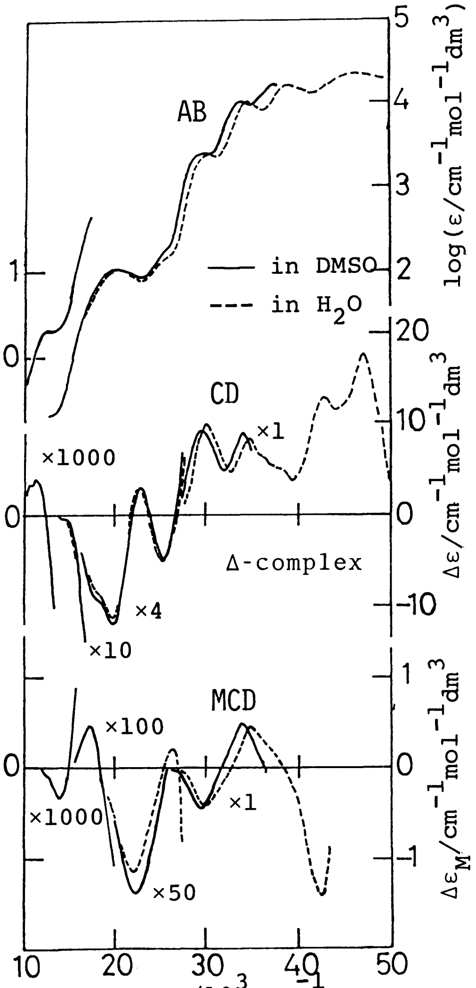

Fig. 1. Spectra of $[Co(pyt)(en)_2](ClO_4)_2$.

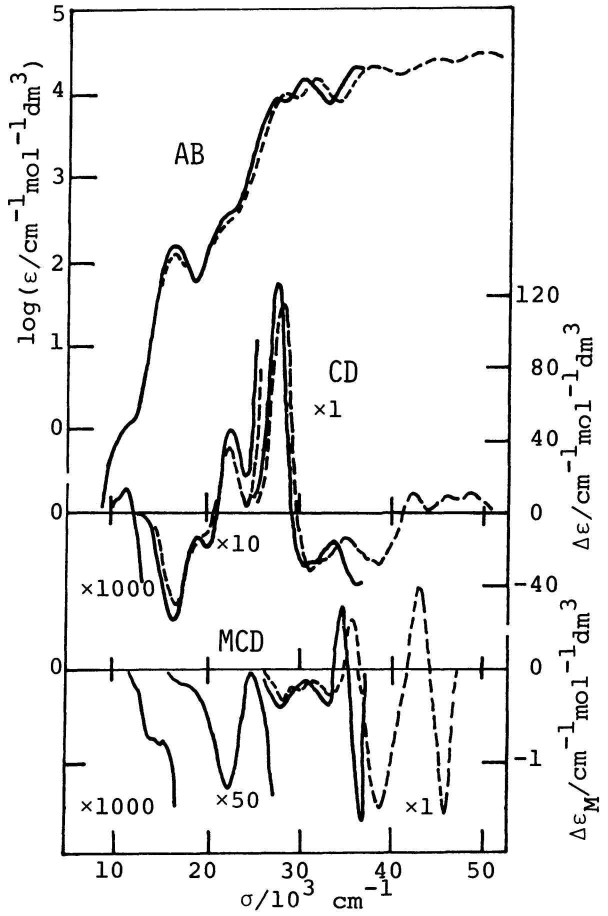

Fig. 2. Absorption and MCD spectra of *trans(S)*-$[Co(pyt)_2(en)]ClO_4$. And CD spectrum of *trans(S)*-Δ-$[Co(pyt)_2\{(R)\text{-}pn\}]ClO_4$. —— in DMSO, --- in H_2O

$[Co(pyt)_2\{(R)\text{-}pn\}]ClO_4$ are shown in Fig. 2. For the former complex three geometrical isomers, C_2-*cis(S)*, C_1-*cis(S)*, and *trans(S)*, are possible. However, only one green isomer was obtained for $[Co(pyt)_2(en)]^+$ and also a green one for $[Co(pyt)_2\{(R)\text{-}pn\}]^+$. The green complexes are assigned to a *trans(S)* isomer on the basis of fair agreement of the absorption spectra with those of the *trans(S)*-$[Co(thiolato)_2(amine)_4]^+$ type complexes[5)] in the spin-allowed first d-d transition band region. The bands at *ca.* 11000 cm^{-1} in the absorption or CD spectrum and at *ca.* 14000 cm^{-1} in the MCD spectrum are assigned to the first and second spin-forbidden d-d transitions, respectively. The $\pi^*(py) \leftarrow n(S)$ (28000 cm^{-1}) and the $\sigma^*(Co) \leftarrow \sigma(S)$ (32000 cm^{-1}) transitions locate considerably at lower energy than those of $[Co(pyt)(en)_2](ClO_4)_2$, whereas the $\pi^*(py) \leftarrow \pi(py)$ transition (38000 cm^{-1}) does not shift.

Figure 3 shows the absorption and MCD spectra of $[Co(pyt)_3]$. In this complex, only one geometrical isomer of the two possible ones, *fac(S)* and *mer(S)*, was obtained. The dark brown complex is assigned to a *mer(S)* isomer by ^{13}C NMR spectrum, which shows the complicated resonances in Fig. 4 (116.87^b, 125.48^b, 135.45, 135.94, 136.59, 147.10^b, 149.48^b, 149.48^b, and 150.41^b ppm in $CDCl_3$; b means broad), because

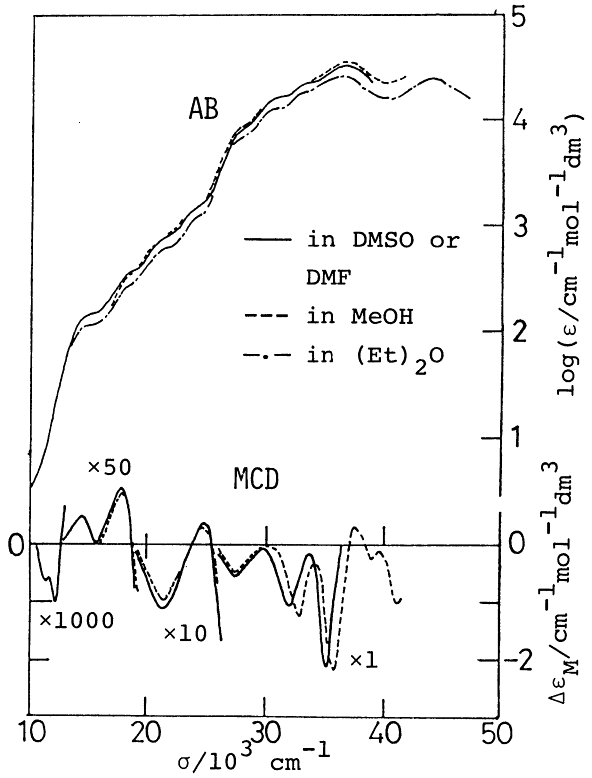

Fig. 3. Absorption and MCD spectra of *mer(S)*-$[Co(pyt)_3]$.

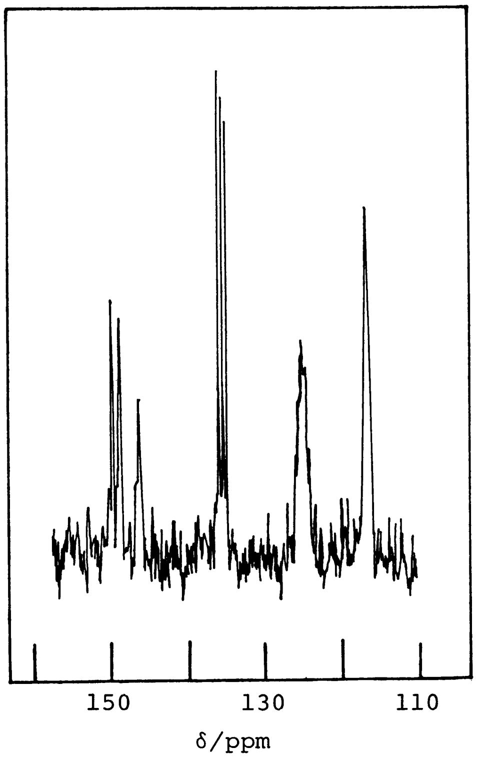

Fig. 4. ^{13}C NMR spectrum of $[Co(pyt)_3]$ in $CDCl_3$ containing TMS (δ = 0.00) as an internal standard.

only five signals are expected for the *fac(S)* geometry. The splitting pattern of the MCD spectrum in the region of the first spin-allowed d-d transition (14300, 17900, and 21200 cm^{-1}) also supports the assignment. The *mer(S)* isomer is the first example in the field of $[Co(thiolato)_3(amine)_3]$ type complexes. No *fac(S)* isomer could be obtained in contrast to several reported examples.[6]

References

1) The ligand pyt was known as a unidentate,[a] bidentate,[b] or bridging reagent.[c]
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(Received November 16, 1982)