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PREPARATION AND CHARACTERIZATION OF *MER* AND *FAC* ISOMERS OF TRIS(*MESO*-2,4-PENTANEDIAMINE)COBALT(III) COMPLEX

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The *mer* and *fac* isomers of $[Co(meso\text{-}ptn)_3]^{3+}$ (*meso*-ptn = *meso*-2,4-pentanediamine) have been separated and resolved by column chromatography on SP-Sephadex. The structures of these isomers have been assigned on the basis of the electronic, circular dichroism, ^1H- and ^{13}C-NMR spectra.

Tris(*meso*-2,4-pentanediamine)cobalt(III) complex can have two geometric isomers, *mer* and *fac* as shown in Fig. 1. In the previous paper$^{1)}$, we obtained this complex and assigned it tentatively to the *fac* isomer based on the spectral pattern of ^1H-NMR (60 MHz) and the examination of molecular models. As Figure 1 shows, the two chelate rings in the *mer* isomer approach very close to each other, when they adopt a chair conformation in which both methyl groups of the *meso*-2,4-pentanediamine(*meso*-ptn) are in equatorial orientations to the average plane of the chelate ring. Since this conformation is known to be very stable$^{2)}$, the *mer* isomer is expected to be

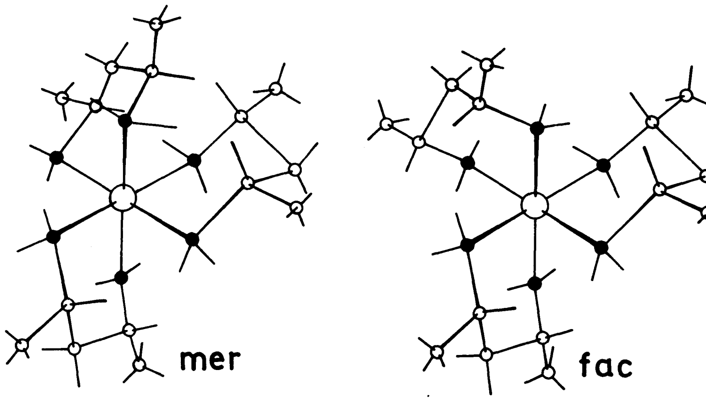

Fig. 1. *mer*(C_1) and *fac*(C_3) isomers of Λ-$[Co(meso\text{-}ptn)_3]^{3+}$ viewed along the pseudo 3-fold axis.

particularly unstable compared with the *fac* isomer. However, we have obtained both *mer* and *fac* isomers of [Co(*meso*-ptn)$_3$]$^{3+}$ and resolved each isomer into a pair of enantiomers.

A solution of *meso*-ptn·2HCl$^{1)}$ (0.55 g, 3 mmol) and sodium methoxide(0.25 g, 4.6 mmol) in methanol(2 ml) was added to a solution of *trans*-[CoCl$_2$(*meso*-ptn)$_2$]Cl$^{1)}$ (0.7 g, 1.9 mmol) in methanol(30 ml). The mixture was stirred for three days at room temperature. The resulting reddish brown solution was diluted to *1* l with water, poured on an SP-Sephadex column($^{\phi}$2.7 x 120 cm) and the adsorbed band was eluted with a 0.16 M sodium (+)$_{589}$-tartratoantimonate(III) solution. The column gave two separate bands, A and B in the order of elution. From these bands, the isomers, A and B were isolated as the perchlorate salts. Neither of them showed optical activity. The formation ratio of the A(*mer*) isomer to the B(*fac*) isomer was 3 : 2. A isomer, Found: C, 25.58; H, 6.58; N, 11.97 %. B isomer, Found: C, 25.64; H, 6.01; N, 11.82 %. Calcd for $C_{15}H_{46}N_6O_{14}CoCl_3$=[Co(*meso*-ptn)$_3$](ClO$_4$)$_3$·2H$_2$O; C, 25.74; H, 6.62; N, 12.01 %.

Each isomer was resolved by SP-Sephadex column($^{\phi}$2.7 x 120 cm) chromatography$^{3)}$ using the same eluent used above. For the B isomer, the separation of bands was incomplete and the chromatography was repeated to obtain optically pure isomers. Thus, two pairs of enantiomers, A-I and A-II, and B-I and B-II, were isolated as the perchlorate salts, I and II denoting the order of elution on each column.

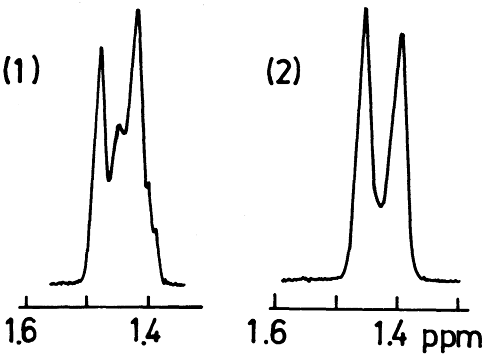

Fig. 2. 100 MHz ^{1}H-NMR spectra of (1)A isomer and (2)B isomer in D$_2$O with TSP-deuterated as an internal reference.

Figure 2 shows the 100 MHz ^{1}H-NMR spectra of the isomers A and B in D$_2$O in the methyl proton region. The *fac*(C$_3$ symmetry) and the *mer*(C$_1$ symmetry) isomer should show two and six kinds of doublet signal due to the methyl protons, respectively. However, the B isomer gives only one doublet signal, while the A isomer complicated signals. The latter isomer at 60 MHz spectrum shows only one broad doublet signal. Nevertheless, these results suggest that the isomers A and B can be assigned to *mer* and *fac* configuration, respectively.

In Figure 3, the ^{13}C-NMR(15.04 MHz) spectra distinguish more clearly between the *fac* and the *mer* isomer. Tentative assignments for the signals are given in the Figure. The B(*fac*) isomer shows two, one and two resonances for the methyl, the methylene and the methine carbons, respectively. These numbers of the resonances agree with those expected from symmetry argument. On the other hand, the A(*mer*) isomer gives a rather

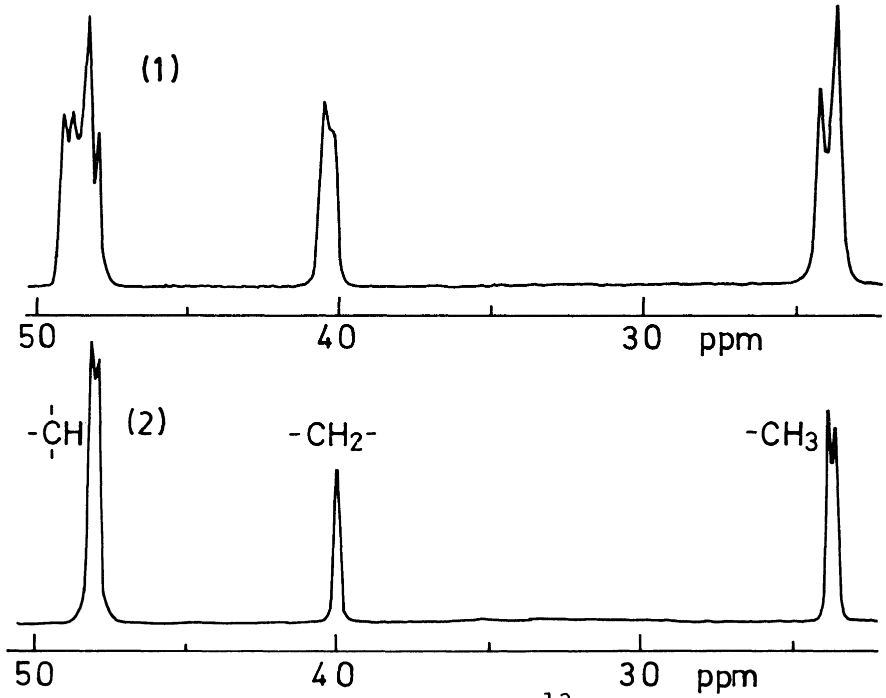

Fig. 3. Proton-decoupled 15.04 MHz ^{13}C-NMR spectra (JEOL FX-60) of (1) A isomer and (2) B isomer in D_2O. Dioxane (δ = 67.69 ppm) was used as an internal reference.

complicated spectrum. Although the spectrum is not enough resolved to exhibit all the nonequivalent carbon signals, the appearance of the multiplet due to the methine carbons clearly indicates the *mer* configuration.

Tris(propylenediamine)-cobalt(III) complex exists in similar *mer* and *fac* isomers. However, neither ^{1}H(100 MHz)- nor ^{13}C-NMR spectroscopy is useful for assigning the structures of these isomers.4,5)

Figure 4 shows the absorption and CD spectra of the A-II and B-II isomers. In the previous paper1), we could not give any plausible assignment on the absolute configuration of $[\mathrm{Co}(\textit{meso}\text{-}\mathrm{ptn})_3]^{3+}$. However, the present isomers can be assigned to Λ configuration on the basis of the CD sign in the charge transfer region.6) Mason and his coworkers7) assigned the A-II(or B-II) isomer to the opposite configuration Δ by the fact that its CD pattern in the first absorption band region resembles that of the solid state Δ-$[\mathrm{Co(tn)}_3]\mathrm{Br}_3\cdot\mathrm{H_2O}$ (tn = trimethylenediamine) of the known absolute configuration.8) Since the six-membered chelate rings in this complex take the same chair conformation in crystals as those expected in the *meso*-ptn complexes, the Δ-$[\mathrm{Co(tn)}_3]\mathrm{Br}_3\cdot\mathrm{H_2O}$ would be a good reference complex for assigning the absolute configuration of the present isomers. However, it is known that the CD signs in the first absorption band region of tris(diamine)-cobalt(III) complexes with six-membered chelates depend often on the measuring conditions, solid or solution, solution with or without the presence of excess counter ions and so on.9) On the other hand, no such a dependence is seen for the CD in the charge transfer region; a tris(diamine)cobalt(III) complex of which the sign of the lowest frequency CD band in the charge transfer region is negative has Λ configuration. Thus, we assigned the isomers A-II and B-II to Λ configuration.

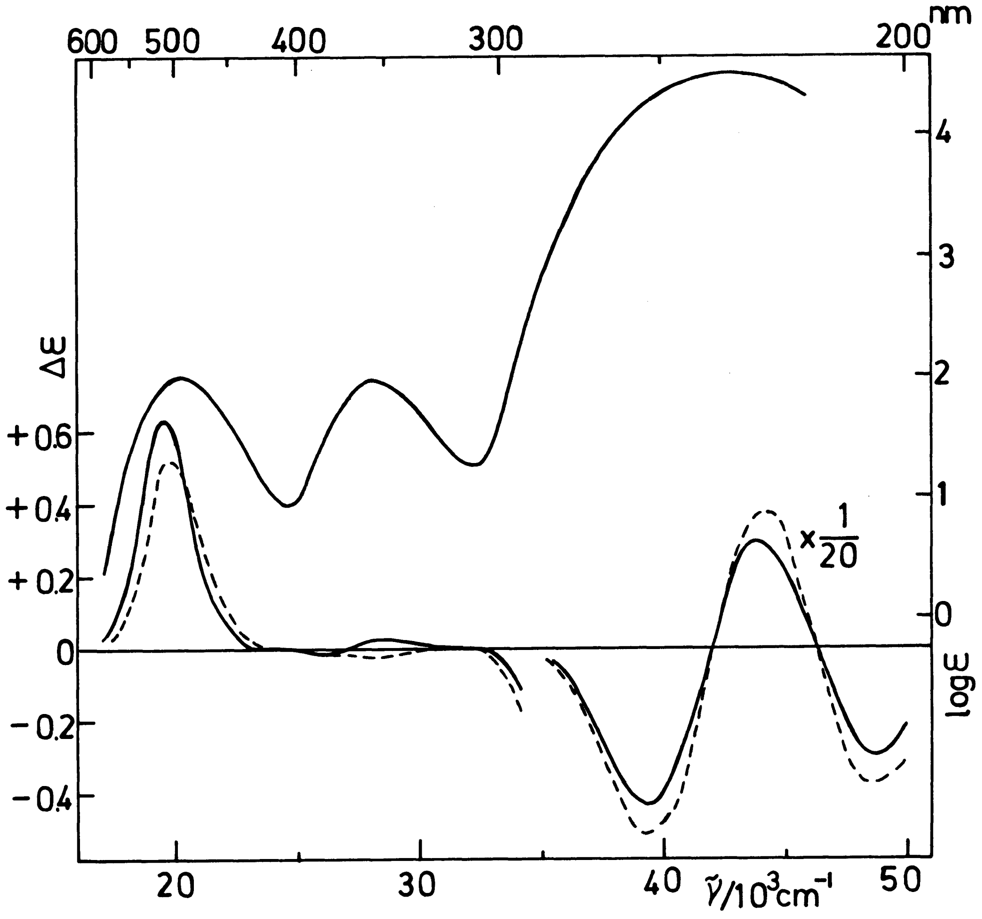

Fig. 4. AB and CD spectra of A-II: *mer*-Λ-[Co(*meso*-ptn)$_3$](ClO$_4$)$_3$·2H$_2$O (——) in water. CD spectrum of B-II: *fac*-Λ-[Co(*meso*-ptn)$_3$](ClO$_4$)$_3$·2H$_2$O (- - -) in water.

As stated previously, the A(*mer*) isomer might involve larger steric interactions among the chelate rings than the B(*fac*) isomer. However, the first absorption band of the former is at the longer wavelength side by only 2 nm than that of the latter, and both isomers show the CD curves very similar to each other.

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