# Syntheses and Stereochemistry of Optical Isomers of tris(2,4-Pentanediamine)cobalt(III) Complex

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Tris(trimethylenediamine)-cobalt(III) ion has been found to have chair form chelates in its bromide crystal.[1] The conformation of 2,4-pentanediamine (ptn) metal chelate was studied by PMR spectra.

We have synthesized a diastereomeric pair of $[Co(R,R\text{-}ptn)_3]^{3+}$ and an opticaly active $[Co(R,S\text{-}ptn)_3]^{3+}$. Racemic and meso-ptn were prepared by the known method.[2,3] The $(-)_D$-ptn was assigned to R,R (D,D)-configuration.[3]

Perchlorate and chloride of *trans*-$[CoCl_2(ptn)_2]^+$ were synthesized with R,R- and R,S-ptn, respectively.[4] The former was warmed with R,R-ptn and activated charcoal to give orange diastereomeric mixture of $[Co(R,R\text{-}ptn)_3](ClO_4)_3$. The filtered solution was cooled together with 60% perchloric acid, and the orange prismatic crystals were recrystallized from water. $(-)_{546}$-$[Co(R,R\text{-}ptn)_3]\cdot(ClO_4)_3\cdot H_2O$: Found: C, 26.35; H, 6.51; N, 12.07%. Calcd for $CoC_{15}H_{44}N_6Cl_3O_{13}$: C, 26.42; H, 6.50; N, 12.33%.

*trans*-$[CoCl_2(R,R\text{-}ptn)_2]ClO_4$ was converted into chloride, and warmed with R,R-ptn in 50% aqueous ethanol. The orange needles were recrystallized in a similar way. $(+)_{546}$-$[Co(R,R\text{-}ptn)_3]Cl_3\cdot 2H_2O$: Found: C, 36.08; H, 9.09; N, 16.12%. Calcd for $CoC_{15}H_{46}N_6Cl_3O_2$: C, 35.47; H, 9.13; N, 16.55%.

*trans*-$[CoCl_2(R,S\text{-}ptn)_2]Cl$ was warmed with R,S-ptn and activated charcoal. The filtered solution was treated with perchloric acid. The reddish orange product was recrystallized from water, resolved with silver *d*-tartrate and converted into needle-like perchlorate. $(-)_{546}$-$[Co(R,S\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$: Found: C, 25.31; H, 6.30; N, 11.72%. Calcd for $CoC_{15}H_{48}N_6Cl_3O_{15}$: C, 25.10; H, 6.74; N, 11.71%. Both isomers of $[Co(R,R\text{-}ptn)_3]^{3+}$ give a sharp doublet of methyl signal in its 60 MHz PMR spectrum in $D_2O$. This suggests that the complex has $D_3$ symmetry with twist-form six-membered chelate rings and the two methyls have equatorial orientation. On the other hand, the PMR spectrum of $[Co(R,S\text{-}ptn)_3]^{3+}$ gives a broader methyl signal, which seems to be due to overlapped two signals. This complex can have two geometrical isomers with respect to the mer and fac coordination of the amino groups near R- and S-$\alpha$-carbon. Study of molecular models disclosed that the stable chair form has the two methyls equatorial and only the fac isomer is formed without large steric hindrance. The apparent two kinds of methyl signal seem to be due to $C_3$ symmetry of this fac complex. From the CD sign in the first *d-d* transition region, the prismatic and the needlelike $[Co(R,R\text{-}ptn)_3]^{3+}$ are tentatively assigned to absolute configurations $\Delta$ and $\Lambda$, respectively. $(-)_{546}$-$[Co(R,S\text{-}ptn)_3]^{5+}$ seems to have absolute configuration $\Delta$.

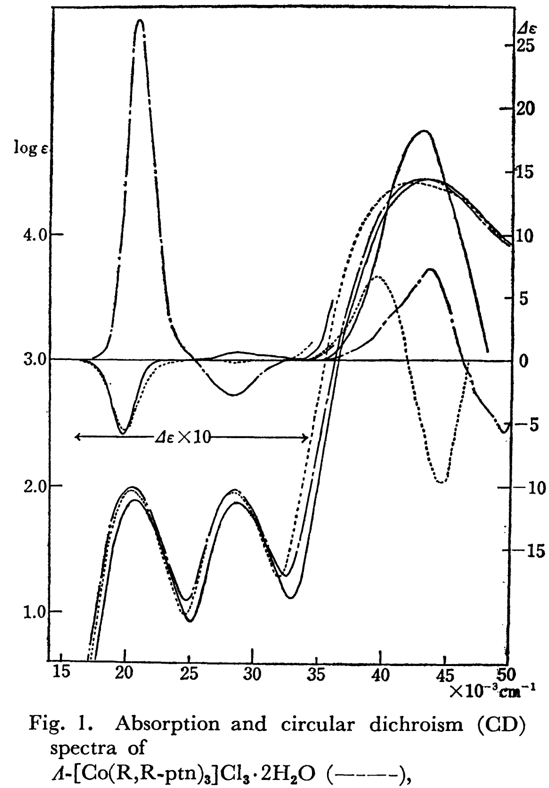

Fig. 1. Absorption and circular dichroism (CD) spectra of
$\Lambda$-$[Co(R,R\text{-}ptn)_3]Cl_3\cdot 2H_2O$ (——-—-),
$\Delta$-$[Co(R,R\text{-}ptn)_3](ClO_4)_3\cdot H_2O$ (——) and
$\Delta$-$[Co(R,S\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$ (-----) in water.

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[1] Y. Saito, T. Nomura and F. Marumo, This Bulletin, **41**, 530 (1968).

[2] T. G. Appleton, and J. R. Hall, *Inorg. Chem.*, **9**, 1800 (1970).

[3] F. Mizukami, H. Ito, J. Fujita and K. Saito, This Bulletin, **43**, 3633 (1970).

[4] C. J. Dippel and F. M. Jaeger, *Rec. Trav. Chim. Pays-Bas*, **50**, 547 (1931).