Structure of Cobalt(III) Complexes of *d*-, *l*-, and *meso*-2,4-Pentanediaminetetraacetate

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The conformation of a six-membered chelate ring of the tristrimethylenediaminecobalt(III) complex was first determined to be of chair form by X-ray diffraction by Y. Saito *et al.*[1] van Saun and Douglas, and Ogino *et al.*[2] synthesized cobalt(III) complex of trimethylenediaminetetraacetate (trdta^{4-}) and suggested that the six-membered chelate should have a twist form. We examined the influence of the methyl group on α-carbon atom of the trimethylene part upon the chelate structure, and found a stereospecific formation of 2,4-pentanediaminetetraacetatocobaltate(III) complex depending on the optical isomerism of 2,4-pentanediamine.

2,4-Pentanediamine was synthesized by the known method[3] and the racemic and meso forms were separated by utilizing the difference in solubility of their dihydrochlorides in 95% ethanol.*[1] The amine was converted into 2,4-pentanediaminetetraacetic acid (ptntaH$_4$) by Weyh and Hamm's method.[4] A violet complex was formed by heating Na$_3$[Co(NO$_2$)$_6$] and racemic ptntaH$_4$ in water at 60—70°C for 15 hr. The product was converted into diastereomers of *d*-[Co(NO$_2$)$_2$en$_2$]$^+$ salt (en=ethylenediamine) with $[\alpha]_D$ +887° and −696°. They were treated with potassium iodide to give K[Co(ptnta)]·H$_2$O. Found: $(+)_D$ isomer, C, 34.40; H, 4.55; N, 6.31: $(-)_D$ isomer, C, 34.61; H, 4.53; N, 6.27%. Calcd for $C_{13}H_{20}CoKN_2O_9$: C, 34.98; H, 4.55; N, 6.28%. When *meso*-ptntaH$_4$ was used in place of racemic ptntaH$_4$ the violet complex was not formed, and only a blue complex H[CoCl(ptntaH)] was isolated crystalline on treatment with dilute hydrochloric acid. Found: C, 36.35; H, 5.58; N, 6.55%. Calcd for $C_{13}H_{20}ClCoN_2O_8$: C, 36.59; H, 4.72; N, 6.57%.

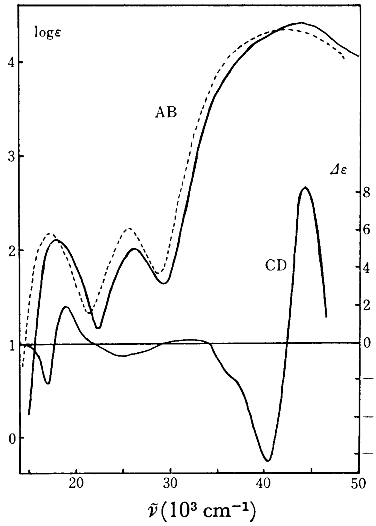

Fig. 1. AB and CD spectra of $(+)_D$-K[Co(RR-ptnta)]·H$_2$O in H$_2$O (——) and AB spectrum of H[CoCl(*meso*-ptntaH)] in dil. HCl (------).

The violet complex gives an absorption spectrum (AB) in water very similar to that of [Co(trdta)]$^-$ or [Co(edta)]$^-$. Its infrared spectrum shows no absorption of free carboxylate. Its PMR spectrum in D$_2$O gives only one methyl signal and two kinds of acetate methylene signal. The $(+)_D$ complex is assigned to be Δ, from comparison of its circular dichroism (CD) with that of Δ-[Co(trdta)]$^-$.[2] It is thus clear that the complex contains sexadentate ptnta^{4-} ligand and the trimethylenediamine chelate takes a twist form. Since methyl groups should take an equatorial position in the chelate, the ptnta^{4-} in the $(+)_D$ complex should have RR configuration.

The blue complex gives an absorption pattern similar to that of [CoCl(edta)]$^{2-}$ and the infrared absorption gives the peak of free carboxylate. The PMR spectrum gives two kinds of methyl signal, and the signals of acetate methylene are much more complicated than those of the violet complex. We consider that the ligand is quinquedentate in this blue complex. So far as the methyl groups orientate equatorially to the chelate ring, the trimethylenediamine ring should take the chair form and only three out of four acetate branches seem to be allowed to coordinate to cobalt(III).

Such a stereospecific formation of sexa- and quinquedentate complex from racemic and meso ptnta^{4-} indicates that the steric regulation coming from the methyl group on the α-carbon atom is very strong in six-membered as well as in five-membered rings.

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

2) C. W. van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969); H. Ogino, M. Takahashi and N. Tanaka, This Bulletin, **43**, 424 (1970).

3) C. Harries and T. Haga, *Ber*, **32**, 1191 (1899); C. J. Dippel, *Rec. Trav. Chim. Pays-Bas*, **50**, 525 (1931).

*[1] Dippel seems to have given a wrong identification; his *meso* was racemic and his racemic was *meso*. When $(+)_D$ violet complex was decomposed, the free ligand gave (+) normal dispersion.

4) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).