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CIRCULAR DICHROISM OF COBALT(III) COMPLEXES CONTAINING OPTICALLY ACTIVE 1,3-DIPHENYL-1,3-PROPANEDIAMINE

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Four optical isomers of $[Co(en)_2(rac\text{-}dppn)]^{3+}$(en = ethylenediamine, rac-dppn = (R,R)- or (S,S)-1,3-diphenyl-1,3-propanediamine) and a pair of enantiomers of $[Co(NH_3)_4(rac\text{-}dppn)]^{3+}$ were prepared and circular dichroism (CD) spectra obtained. The calculated vicinal effect curve for the dppn in $[Co(en)_2(dppn)]^{3+}$ differs greatly from that in $[Co(NH_3)_4(dppn)]^{3+}$. Such a difference was not observed between those of the corresponding new stilbenediamine (stien) complexes, $[Co(en)_2(\ell\text{-stien})]^{3+}$ and $[Co(NH_3)_4(\ell\text{-stien})]^{3+}$.

Recently, an interest has been taken in the stereochemistry of six-membered chelate rings of 1,3-diamines in metal complexes.[1-3] In previous papers,[2] it was observed that the CD spectra of mono and trans-bis(R,R-2,4-pentanediamine)-cobalt(III) complexes resemble those of the corresponding R-propylenediamine complexes in the first absorption band region. Here we report a significant difference in the vicinal effects of the dppn in $[Co(en)_2(dppn)]^{3+}$ and $[Co(NH_3)_4(dppn)]^{3+}$ complexes, which has not been observed for the complexes with five-membered chelate rings, e.g., propylenediamine.[4] The corresponding ℓ-stien and (R,R)-2,4-pentanediamine(R,R-2,4-ptn)complexes were also prepared and the CD spectra compared.

Experimental: Ligand dppn was prepared from benzacetophenone by treating with hydroxylamine and then reducing with sodium, and separated into meso and racemic forms by fractional crystallization of its dihydrochloride in ethanol. Their purities were confirmed by PMR spectra. A solution obtained by the reaction of rac-dppn with cis-$[CoCl_2(en)_2]Cl$ in dimethyl sulfoxide (DMSO) was poured on an SP-Sephadex C-25 ion exchange column, and eluted with 2M aqueous sodium perchlorate solution to obtain two orange bands of $[Co(en)_2(dppn)]^{3+}$. Neither of them showed optical activity. Each product (BI and BII) from these two bands was adsorbed again on an SP-Sephadex C-25 ion exchange column and the adsorbed band was eluted with 0.3M aqueous sodium $(+)_D$-tartratoantimonate(III) solution. Two bands (BI_1 and BI_2 from BI, and BII_1 and BII_2 from BII) were observed on each column and the four optical isomers, Δ- and Λ-$[Co(en)_2$(R,R- or S,S-dppn)$]Br_3$, were isolated by eluting with

0.5M aqueous potassium bromide solution after the complete separation of the two bands. $[Co(NH_3)_4(dppn)]Br_3 \cdot H_2O$ was obtained from the reaction of rac-dppn with $[Co(H_2O)(NH_3)_5](ClO_4)_3$ in DMSO and resolved (T_1 and T_2) by an SP-Sephadex C-25 ion exchange column chromatography with a 0.15M aqueous sodium $(+)_D$-tartratoantimonate(III) solution as an eluent. The corresponding three ℓ-stien complexes, Δ- and Λ-$[Co(en)_2(\ell\text{-stien})]^{3+}$ and $[Co(NH_3)_4(\ell\text{-stien})]^{3+}$, and two (R,R)-2,4-ptn complexes, Δ- and Λ-$[Co(en)_2(R,R\text{-}2,4\text{-ptn})]^{3+}$, were prepared by the same method as for the dppn complexes. All these new compounds gave satisfactory elemental analyses.

Results and Discussion: Absorption and CD spectra of the separated isomers disclosed that both BI and BII consist of enantiomers, i.e. Δ-$[Co(en)_2(R,R\text{-dppn})]^{3+}$ and Λ-$[Co(en)_2(S,S\text{-dppn})]^{3+}$, and Δ-$[Co(en)_2(S,S\text{-dppn})]^{3+}$ and Λ-$[Co(en)_2(R,R\text{-dppn})]^{3+}$, respectively. PMR spectra supported that the dppn ligands in these complexes take a skew boat form.

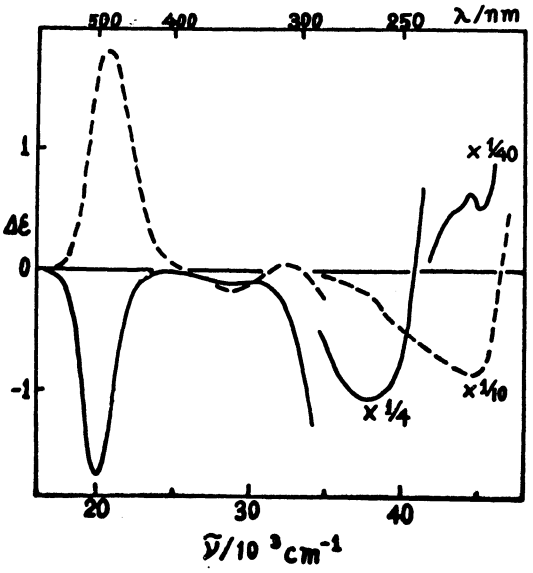

Fig. 1 The CD spectra of $[Co(en)_2(S,S\text{-dppn})]^{3+}$ in H_2O, BI_1 (----) and BII_2 (——).

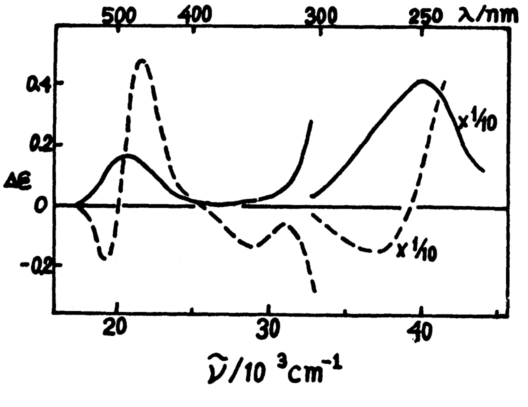

Fig. 2 Vicinal effect curve of (S,S)-dppn in $[Co(en)_2(S,S\text{-dppn})]^{3+}$ (----), and the CD spectrum of $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ in H_2O (——).

In Fig. 1, the CD spectrum of BI_1 in the first absorption band region suggests Λ configuration around the cobalt ion, and that of BII_2 Δ on the basis of the empirical rule.[5] The CD spectra at 43-45 × 10^3 cm^{-1} also support this assignment.[4] In Fig. 2, the CD spectrum of the tetraammine complex (T_2, $(+)_D$) is similar to that of $[Co(NH_3)_4(R,R\text{-}2,4\text{-ptn})]^{3+}$ in the first absorption band region (Fig. 6), indicating that the dppn takes a λ skew boat form with (S,S)-configuration of the asymmetric carbons. This designation (S,S) is opposite to that of 2,4-ptn with the same λ skew boat, on the basis of the numbering in sequence rule.[6] The absolute conformations of the ring moiety of (S,S)-dppn and (R,R)-2,4-ptn with the skew boat form are the same upon coordination. It has been confirmed by X-ray diffraction method that the (R,R)-2,4-ptn in $(+)_{546}$-$[Co(R,R\text{-}2,4\text{-ptn})_3]Cl_3 \cdot H_2O$ takes a λ skew boat form.[7] Assuming the additivity of CD due to the configurational effect around the cobalt ion and the vicinal effect of ligands, we can calculate the vicinal effect curve of the dppn in $[Co(en)_2(dppn)]^{3+}$ according to the equation of $\Delta\varepsilon(BI_1 + BII_2)/2$ (Fig. 2). The main CD component of the vicinal effect curve is positive in the first absorption band region, and therefore the conformation of dppn in these complexes would be assigned to a λ skew boat form. It is interesting that the vicinal effect curve for the $[Co(en)_2(dppn)]^{3+}$ complex is very different from that for $[Co(NH_3)_4(dppn)]^{3+}$ in the spectral pattern and the CD strength.

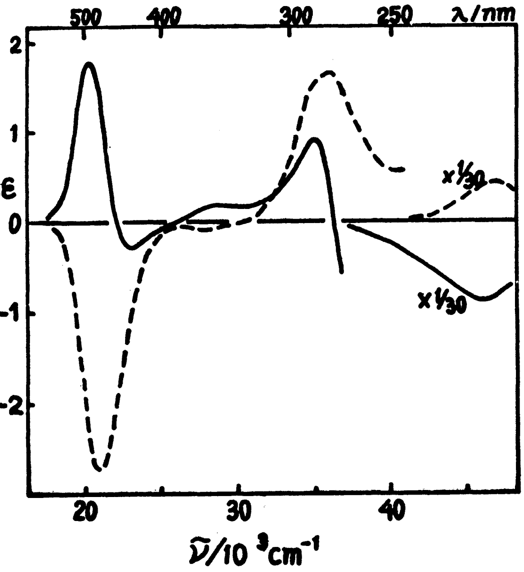

Fig. 3 The CD spectra of $[Co(en)_2(\ell\text{-stien})]^{3+}$ in H_2O, Fraction I (——) and Fraction II (----).

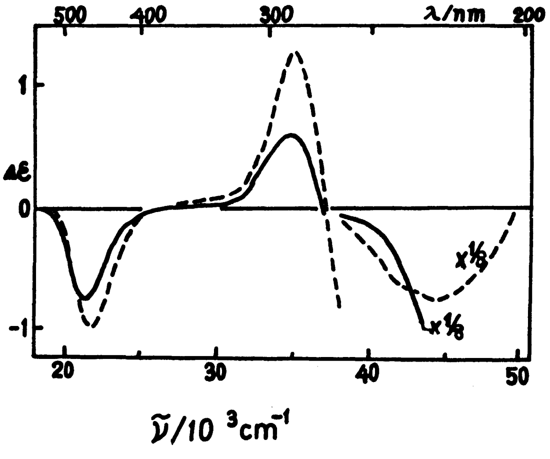

Fig. 4 Vicinal effect curve of ℓ-stien in $[Co(en)_2(\ell\text{-stien})]^{3+}$ (----), and the CD spectrum of $[Co(NH_3)_4(\ell\text{-stien})]^{3+}$ in H_2O (——).

Such a difference can come either from the six-membered chelate ring or from the presence of phenyl group on the ring. To distinguish these contributions, we prepared the corresponding ℓ-stien and (R,R)-2,4-ptn complexes in which ℓ-stien is a five-membered chelate with phenyl groups on asymmetric carbons and (R,R)-2,4-ptn a six-membered chelate with methyl groups.

In Fig. 3, the absolute configuration of the ℓ-stien complexes would be assigned on the basis of the CD in the first absorption and the charge transfer band region as discussed for the dppn complexes. The vicinal effect curve of ℓ-stien in $[Co(en)_2(\ell\text{-stien})]^{3+}$ was calculated by the same method as for the corresponding dppn complexes (Fig. 4). The negative CD component in the first absorption band region suggests that the conformation of ℓ-stien in these complexes seems to be δ-gauche form in which the asymmetric carbons take (S,S)-configuration.[8] The vicinal effect curve of the ℓ-stien in $[Co(en)_2(\ell\text{-stien})]^{3+}$ is similar to that in $[Co(NH_3)_4(\ell\text{-stien})]^{3+}$, in contrast to the case of the corresponding dppn complexes. This fact suggests that the difference in the vicinal effect curves of the dppn complexes is mainly brought about by the presence of the six-membered chelate ring. Figure 5 shows the CD spectra of Δ- and Λ-$[Co(en)_2(R,R\text{-}2,4\text{-ptn})]^{3+}$ in the d-d transition region. The vicinal effect curve of (R,R)-2,4-ptn calculated from these spectra differs also from that of $[Co(NH_3)_4(R,R\text{-}2,4\text{-ptn})]^{3+}$ (Fig. 6). Thus so far as the additivity rule for CD due to

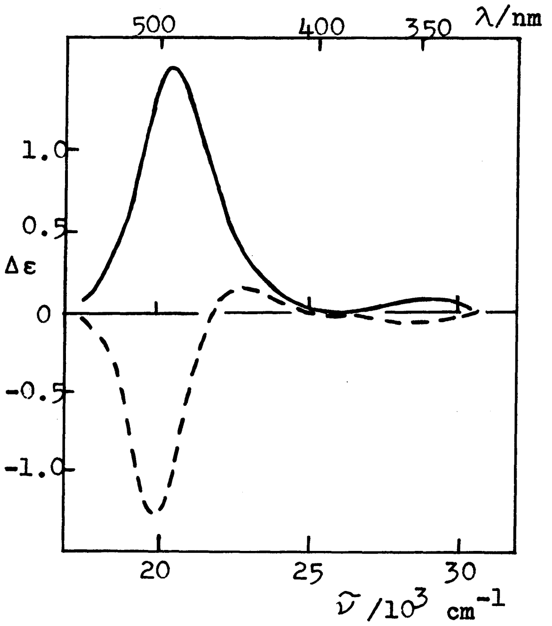

Fig. 5 The CD spectra of $[Co(en)_2(R,R\text{-}2,4\text{-}ptn)]^{3+}$ in H_2O, Fraction I (——) and Fraction II (----).

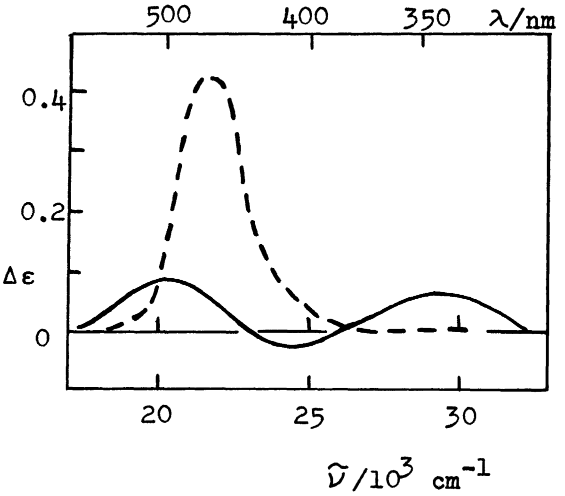

Fig. 6 Vicinal effect curve of (R,R)-2,4-ptn in $[Co(en)_2(R,R\text{-}2,4\text{-}ptn)]^{3+}$ (----), and the CD spectrum of $[Co(NH_3)_4(R,R\text{-}2,4\text{-}ptn)]^{3+}$ in H_2O (——).

the configurational and the vicinal effect can be applied to the present complexes, it is clear that the vicinal effect of a chiral six-membered chelate ring such as dppn or 2,4-ptn is different between its tetraammine and bis-ethylenediamine complexes. The interligand steric interactions in a bis-ethylenediamine complex might be different from those in a tetraammine complex, and the most stable conformations of the bulky and flexible six-membered chelate rings in these complexes might be somewhat different from each other.

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