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Stereoisomers of the Bis(1,10-phenanthroline){(1*R*,2*R*)-1,2-cyclohexanediamine}cobalt(III) Complex

Akira TATEHATA* and Shigeru NATSUME
Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422

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Synopsis. The diastereomers of $[Co(R\text{-chxn})(phen)_2]^{3+}$ (R-chxn=$(-)_{589}$-(1*R*,2*R*)-1,2-cyclohexanediamine, phen=1,10-phenanthroline) were prepared and characterized by absorption, circular dichroism, and ^{1}H NMR spectra. The preference of Δ-isomer in the complex formation was observed and the degree of the stereoselectivity was greater than that of the corresponding $[Co(R\text{-pn})(phen)_2]^{3+}$ (pn=1,2-propanediamine).

Stereoselectivity in the formation of the mixed ligand Co(III) complexes of the type $[Co(aa)(phen)_2]^{n+}$ has been investigated. No remarkable stereoselectivity between Λ and Δ isomers was observed for certain complexes containing a chiral α-hydroxy carboxylate ion such as (*R*,*R*)- or (*S*,*S*)-tartrate and (*S*)-malate ions,[1] whereas fairly high stereoselectivity was observed for this type of (*S*)-α-amino acidato[2] and (*S*)- or (*R*)-pn[3] complexes. We report here the preparation, characterization, and stereoselectivity in the formation of the diastereomers of $[Co(R\text{-chxn})(phen)_2]^{3+}$.

Experimental

1,2-Cyclohexanediamine, chxn, (Aldrich Chemical Co.) was separated into cis and trans isomers by the procedure of Kidani *et al.*[4] Optically active *R*-chxn was obtained by resolving *trans*-chxn according to the method of Galsbøl *et al.*[5]

Preparation and Separation of Isomers. A methanol solution (2.3 cm^3, 10% v/v) of *R*-chxn was added to a suspension of *cis*-$[CoCl_2(phen)_2]Cl\cdot 3H_2O$ (1.0 g, 1.7 mmol) in methanol (50 cm^3). The mixture was stirred for 3 h at 40 °C, and then diluted with water. This solution was passed through an SP-Sephadex column (φ2.7×40 cm), and the adsorbed complexes were eluted with a 0.3 mol dm^{-3} NaCl solution. Yellow ($[Co(phen)_3]^{3+}$), yellowish-orange ($[Co(R\text{-chxn})(phen)_2]^{3+}$), and orange ($[Co(R\text{-chxn})_2(phen)]^{3+}$) bands were developed in this order. The effluent of the second band containing the desired complex was diluted with water and passed through an SP-Sephadex column (φ2.7×3 cm). The adsorbed complex was transferred to the top of another SP-Sephadex column (φ2.7×130 cm) and eluted with a 0.15 mol dm^{-3} $Na_2[Sb_2(d\text{-tart})_2]$ solution to separate the diastereomers. The eluted bands of diastereomers were collected, and to them the same procedure was followed as for the corresponding pn complex.[3] Two diastereomers were obtained as crystals of the perchlorate. Found for the Λ isomer: C, 40.92; H, 3.68; N, 9.66%. Calcd for $C_{30}H_{36}N_6Cl_3CoO_{15}$ (trihydrate): C, 40.67; H, 4.10; N, 9.49%. Found for the Δ isomer: C, 41.51; H, 3.79; N, 9.72%. Calcd for $C_{30}H_{34}N_6Cl_3CoO_{14}$(dihydrate): C, 41.52; H, 3.95; N, 9.68%.

Measurements. Absorption and CD spectra were obtained on a Shimadzu MPS-50L recording spectrophotometer and a JASCO J-20 spectropolarimeter, respectively. The CD magnitude was corrected by the use of that of Λ-$(+)_{589}$-$[Co(en)_3]I_3\cdot H_2O$. ^{1}H NMR spectra (90 MHz) were measured on a Varian EM-390 spectrometer in both D_2O and CD_3OD solutions using DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) and TMS(tetramethylsilane), respectively, as an internal standard reference.

Results and Discussion

The absorption and the CD spectra of $[Co(R\text{-chxn})(phen)_2]^{3+}$ are shown in Fig. 1, where their numerical data are also given. The absolute configurations of the isomers were assigned on the basis of the CD spectra in the regions of the first absorption band and the phenanthroline π-π* transitions. The configurational and vicinal effect curves under the first absorption band estimated by the conventional method are shown in Fig. 2 together with the vicinal effect curve of the corresponding *R*-pn complex for comparison.[3] The vicinal effect curves of $[Co(R\text{-chxn})(phen)_2]^{3+}$ and $[Co(R\text{-pn})(phen)_2]^{3+}$ are quite similar to each other though the former slightly shifts to longer wavelengths, indicating that the chelate ring of *R*-pn has the same λ conformation as that of *R*-chxn fixed by the cyclohexane ring. ^{1}H NMR spectra of $[Co(R\text{-chxn})(phen)_2]^{3+}$ were at first measured in D_2O solution. Since the chemical shifts of H_{2a} and H_{3e} protons of the *R*-chxn coordinated in the Λ isomer were not distinct because of overlap with the methylene protons of DSS, the ^{1}H NMR spectra of the complexes were remeasured in CD_3OD solution. The signals of each proton of the cyclohexane ring have been assigned by the use of spin-decoupling technique and by reference to the corresponding proton signals of $[Co(R\text{-chxn})(CN)_4]^-$.[6] By measuring the midpoint of the multiplets, chemical shifts of the diastereomers of $[Co(R\text{-chxn})(phen)_2]^{3+}$

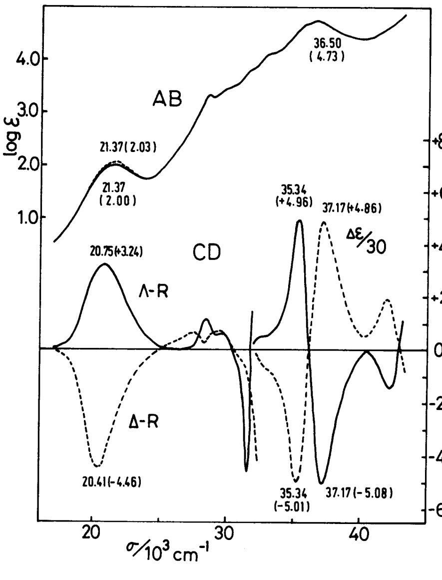

Fig. 1. Absorption and CD spectra of Λ-$(+)_{546}$-(——) and Δ-$(-)_{546}$-$[Co(R\text{-chxn})(phen)_2]^{3+}$ (----).

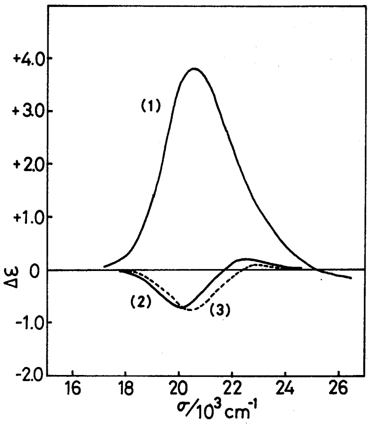

Fig. 2. Configurational effect (1) and vicinal effect (2) curves for Δ-[Co(R-chxn)(phen)$_2$]$^{3+}$ and vicinal effect curve (3) for Δ-[Co(R-pn)(phen)$_2$]$^{3+}$.

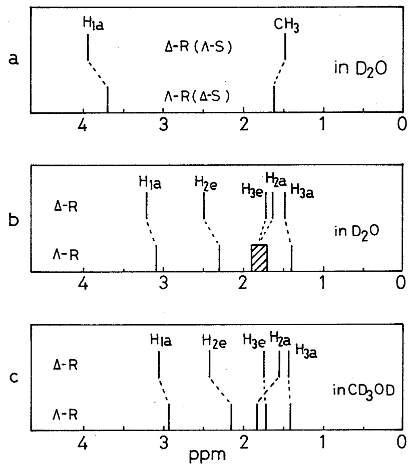

Fig. 3. The distribution of the chemical shifts of the R-pn of the [Co(R-pn)(phen)$_2$]$^{3+}$ in D_2O solution (a), and the R-chxn of the [Co(R-chxn)(phen)$_2$]$^{3+}$ in D_2O solution (b) and in CD_3OD solution (c). In each figure Δ-R isomer is shown at the upper part and Λ-R isomer at the lower part.

and [Co(R-pn)(phen)$_2$]$^{3+}$ are summerized in Fig. 3 with the assignment of the proton signals. The schematic structures and the numbering of protons of the R-chxn and R-pn complexes are shown in Fig. 4. There is a similar tendency between the spectra of the R-chxn complexes and those of the R-pn complexes owing to the ring-current effect of the aromatic phenanthroline ligand. The axial methine H_{1a} proton, the equatorial methylene H_{2e} proton, and axial and equatorial methylene H_{3a} and H_{3e} protons for the Δ-R chxn complex resonate at a lower field than the corresponding protons of the Λ-R chxn complex, as can be also seen for the axial methine H_{1a} proton of the Δ-R pn complex.[3] On the other hand, the signals due to the axial methylene H_{2a} proton of R-chxn complexes appear at a higher field by 0.28 ppm in the Δ isomer than in the Λ isomer, as observed for the methyl signals of the Δ-R pn complex. (Fig. 3) The diastereomeric ratio of the formation of [Co(R-chxn)(phen)$_2$]$^{3+}$ was Δ-R/Λ-R=5.9±0.2 in methanol at 40 °C. Although the ring-current effect may play some role in causing the stereoselectivity, it is rather difficult to explain the favored diastereomer solely in terms of ring-current effect. This stereoselectivity may come mainly from a steric factor. Molecular models suggest a sterically less favored configuration for Λ-propellor owing to the serious repulsive interactions between H_{2a} and N–H protons of R-chxn and the α-proton of phenanthroline.

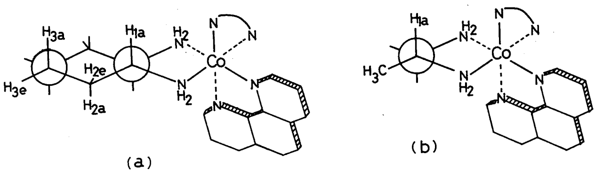

Fig. 4. Schematic structures of R-chxn moiety of Δ-[Co(R-chxn)(phen)$_2$]$^{3+}$ (a) and of R-pn moiety of Δ-[Co(R-pn)(phen)$_2$]$^{3+}$ (b) and their numbering of protons.

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