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Preparation and Characterization of the Diastereoisomers of the (*S*)- or (*R*)-1,2-Propanediaminebis(1,10-phenanthroline)cobalt(III) Ion

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Synopsis. Four diastereoisomers of the type $[Co(S\text{- or } R\text{-pn})(phen)_2]^{3+}$ (pn=1,2-propanediamine; phen=1,10-phenanthroline) were prepared and characterized by absorption, circular dichroism (CD), and ^1H NMR spectra. High stereoselectivity in the formation of the diastereoisomers was observed and the Λ-isomer of $[Co(S\text{-pn})(phen)_2]^{3+}$ was formed in preference to the Δ-isomer.

Although some complexes of the type $[Co(aa)(phen)_2]^{n+}$ (aa=chiral α-hydroxy carboxylate ion[1] and α-amino acidate ion[2]) have been prepared and studied on the absorption and circular dichroism (CD) spectra, there is no report for this type of complex containing a chiral diamine. This Note describes the preparation and the spectroscopic properties of the optically active complexes $[Co(S\text{- or } R\text{-pn})(phen)_2]^{3+}$ and compares the formation ratio between the diastereoisomers with that of the corresponding ethylenediamine complexes $[Co(S\text{- or } R\text{-pn})(en)_2]^{3+}$. It is shown on the basis of ^1H NMR spectra that interligand interactions between 1,2-propanediamine and bis(1,10-phenanthroline) moiety lead to high stereoselectivity in this systems.

Experimental

1,2-propanediamine was resolved as described in the literature,[3] $[\alpha]_D^{25}$ +10.2° for *S*-(+)-pn and $[\alpha]_D^{25}$ −10.6° for *R*-(−)-pn (free diamine, 3—5% aqueous solution).

Preparation and Separation of Isomers. To a suspension of *cis*-$[CoCl_2(phen)_2]Cl\cdot 3H_2O$[4] (1 g, 1.7 mmol) in 50 cm³ of methanol, 1.5 cm³ of methanol solution of (*S*)- or (*R*)-1,2-propanediamine (10% v/v) was added with stirring. The solution was kept in a water bath (40 °C) for 3 h. The resulting yellow-orange solution was diluted with water and poured on a column of SP-Sephadex C-25 (ϕ2.7×50 cm) in the sodium form. Three bands were developed on the column during the elution with a 0.3 mol dm⁻³ NaCl solution. Their bands, identified as the $[Co(phen)_3]^{3+}$, $[Co(pn)(phen)_2]^{3+}$, and $[Co(pn)_2(phen)]^{3+}$, were eluted in this order from bottom of the column. The second band containing the desired complex was transfered to another SP-Sephadex column (ϕ2.7×90 cm) and was eluted with a 0.15 mol dm⁻³ $Na_2[Sb_2(d\text{-tart})_2]$ to separate into the diastereoisomers. The formation ratio between the diastereoisomers was calculated from the areas of the elution curve. In both cases of the *S*- and the *R*-pn complexes, Λ-isomer was always eluted earlier than Δ-isomer. The fractions for each band were combined and passed through an SP-Sephadex column (ϕ2.0×3 cm) after dilution with water and the adsorbed complex was eluted with a 0.5 mol dm⁻³ $NaClO_4$ solution. The solution was concentrated with a rotary evaporator under reduced pressure and was kept in a refrigerator. The specific rotations and analytical results are given in Table 1.

Measurements. Absorption and CD spectra were obtained on a Shimadzu MPS-50L recording spectrophotometer and a JASCO J-40 spectropolarimeter, respectively. ^1H NMR spectra (90 MHz) were measured on a Varian EM-390 spectrometer in D_2O solution using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard reference. For the measurement of ^1H NMR spectra, the perchlorate salts were converted into the chloride salts with an anion exchange resin (Dowex 1-X8, Cl^- form).

Results and Discussion

The absorption and the CD spectra of $[Co(S\text{-pn})(phen)_2]^{3+}$ are shown in Fig. 1, and their numerical data are given in Table 2. The absolute configurations of the isomers were assigned on the basis of the sign of dominant CD peak in the T_{1g} region and the CD spectra in the region of the phen ligand π-π* transition. The configurational and vicinal effect curves under the T_{1g} band evaluated from the CD spectra of the diastereomeric pair of *R*-pn complexes are shown in Fig. 2. The configurational effect curve for Λ-$[Co(R\text{-pn})(phen)_2]^{3+}$ is quite similar to the CD[5] for Λ-$[Co(en)(phen)_2]^{3+}$, where there is no vicinal effect. The contribution from vicinal effect exhibits a −, + CD sign pattern similar in shape to that reported for *R*-pn in Co (III) complexes containing *R*-pn and en,[6] but the relative intensities differ considerably. It is well known that the coordinated *R*-pn exists predominantly in the more stable conformation (λ gauche form) with an equatorial methyl group.[7] The above finding for the vicinal effect of the Λ-$[Co(R\text{-pn})(phen)_2]^{3+}$ may indicate that although the coordinated *R*-pn ligand keeps the λ gauche form with an equatorial methyl group, it is subjected to different degrees of distortion because of the significant difference of the interligand interactions between the pn–en systems and the pn–phen systems. This may be also reflected on the formation ratios (Λ/Δ) of the diastereoisomers in both systems. The diastereoisomeric Λ/Δ ratio was 4.8±0.2 for the $[Co(S\text{-pn})(phen)_2]^{3+}$, indicating that this stereoselectivity occurred in the phenanthroline complex is very higher than that for the corresponding ethylenedi-

Table 1. Elemental analyses and specific rotations of the isomers

No.	Complex	Found(Calcd) (%) C	H	N	$[\alpha]_{546}$
(I)	Λ-$[Co(S\text{-pn})(phen)_2](ClO_4)_3\cdot 2H_2O$	38.68(39.17)	3.27(3.66)	10.81(10.15)	+880°
(II)	Δ-$[Co(S\text{-pn})(phen)_2](ClO_4)_3\cdot 3H_2O$	38.72(38.34)	3.34(3.82)	10.03(9.94)	−681°
(III)	Λ-$[Co(R\text{-pn})(phen)_2](ClO_4)_3\cdot 3H_2O$	38.95(38.34)	3.30(3.82)	10.06(9.94)	+689°
(IV)	Δ-$[Co(R\text{-pn})(phen)_2](ClO_4)_3\cdot 2H_2O$	38.80(39.17)	3.25(3.66)	10.11(10.15)	−889°

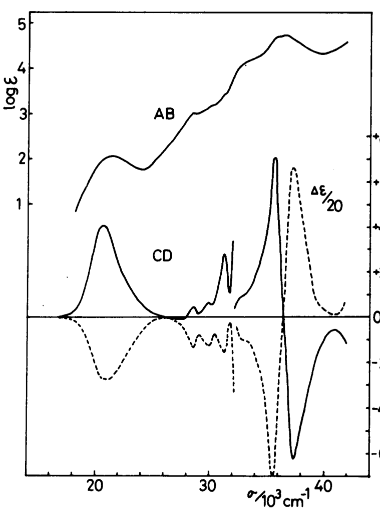

Fig. 1. Absorption and CD spectra of Λ-(+)$_{546}$-(——) and Δ-(−)$_{546}$-[Co(S-pn)(phen)$_2$]$^{3+}$(----).

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

Complex No.[a]	Absorption $\sigma/10^3$ cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})	CD $\sigma_{ext}/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
(I)	21.41 (112)	20.66(+4.08)
	35.59 sh (46500)	35.59(+141.3)
	36.50 (51500)	37.31(−125.4)
(II)	21.41 (99)	21.05(−2.78)
	35.59 sh (46900)	35.59(−140.7)
	36.50 (51700)	37.31(+132.5)

a) Complex No. is the same as those in Table 1.

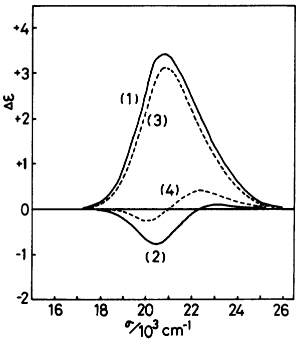

Fig. 2. Configurational effect (1) and vicinal effect curves (2) for Λ-[Co(R-pn)(phen)$_2$]$^{3+}$. CD spectrum (3) reported for Λ-[Co(en)(phen)$_2$]$^{3+}$ and vicinal effect curve (4) of R-pn reported for cobalt(III) complexes containing R-pn and en.

amine complex [Co(S-pn)(en)$_2$]$^{3+}$, for which the value of Λ/Δ=2.1 had been reported.[8] This remarkable stereoselectivity in the pn–phen systems may be attributed to intramolecular ligand-ligand interactions between the aromatic ring of the phenanthroline ligands and the S-pn ligand. Molecular model reveals that the methyl group of S-pn in the Λ-isomer is located above the aromatic ring of one phenanthroline and thus lies under the influence of the ring current (Fig. 3). Such a hydrophobic interaction (CH$\cdots\pi$ interaction) is known to function as a stabilization effect of the complexes.[9] On the other hand, the methyl group of S-pn in the Δ-isomer takes a position by the side of the phenanthroline plane, and therefore may cause some repulsive interactions with α-proton of the phenanthroline (Fig. 3), resulting in the less favored Δ-isomer. These situations were confirmed by the ^{1}H NMR spectra of the diastereoisomers (Fig. 4). The methyl protons in the Λ-S isomer (1.49 ppm) resonate at higher field than in the Δ-S isomer (1.62 ppm), as has been observed for the methyl protons in [Co(S-ala)(phen)$_2$]$^{2+}$ complexes.[2] These chemical shifts observed imply that the methyl protons in the Λ-S isomer are shielded by one phenanthroline ring to resonate at a high field and those in the Δ-S isomer are in a deshielding region near the phenanthroline plane, being in agreement with considerations from the molecular model.

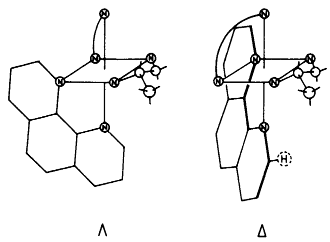

Fig. 3. Structures of Λ- and Δ-[Co(S-pn)(phen)$_2$]$^{3+}$.

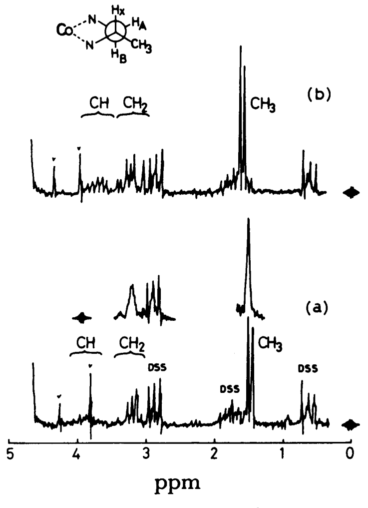

Fig. 4. ^{1}H NMR spectra of (a) Λ- and (b) Δ-[Co(S-pn)(phen)$_2$]$^{3+}$ in D_2O solutions.

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