Isomers of the Diamminebis(trimethylenediamine)cobalt(III) Complex

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Synopsis. The isomers of $[Co(NH_3)_2(tn)_2]^{3+}$ were separated by recycling chromatography. The CD spectra of cis isomers were obtained and are compared with the spectra of the corresponding tris complexes. The magnitude of CD intensity of bisdiamine complex is roughly one-third of the corresponding trisdiamine complex.

A number of studies have been made on the stereochemistry of cobalt(III) complexes with five-membered diamine chelate rings. However, this has not been the case for those complexes including six-membered diamine chelate rings, probably because many of their isomers can be hardly separated and/or resolved.

The circular dichroism (CD) intensity of cobalt(III) complexes with six-membered diamine chelate rings is known to be much weaker than the corresponding cobalt(III) complexes with five-membered rings. The purpose of the present work was to separate *cis*-$[Co(NH_3)_2(tn)_2]^{3+}$, which had not yet been separated, to resolve it into antipodes, and to assign the configuration by comparing their CD spectra with those of known $[Co(NH_3)_2(diamine)_2]^{3+}$- and $[Co(diamine)_3]^{3+}$-type complexes (diamine=en, tn, and RR-ptn**).

Experimental

To about 10 ml of liquid ammonia cooled in a Dry Ice–acetone bath was added 350 mg of *trans*-$[CoCl_2(tn)_2]Cl$ prepared according to the literature.[1)] The mixture was stirred for one hour and allowed to stand overnight, while the temperature of the solution gradually increased up to room temperature and finally all the solvent ammonia evaporated.

The orange-red product obtained as residue was subjected to recycling chromatography[2,3)] on an SP-Sephadex column (4.1 dia.×96 cm) using an aqueous 0.18 M (1 M= 1 mol dm^{-3}) sodium $(+)_{589}$-tartrate solution as eluent. The flow rate of elution was about 2.0 ml per minute. The elution after the sixth recycling gave two well-separated bands, which are denoted by A and B in the order of effluence (Fig. 1a).

The CD spectral measurements of each fraction of the effluent showed that the complex contained in the B band was partially resolved. The combined solution of B-band fractions was rechromatographed on the same column with a different eluent, 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solution. The elution after the tenth recycling resulted in two well-separated bands, B-I and B-II, with an area ratio of about 1:1 (Fig. 1b). The notations, A, B-I, and B-II, will hereafter be used to designate the isomer contained in each band.

The chlorides of A, B-I, and B-II were obtained from the eluates of the corresponding bands with the method described previously.[4)] Found for the isomer A: C, 19.62; H, 7.65; N, 22.61%. Found for the isomer B-I: C, 19.32; H, 7.65; N, 22.61%. Calcd for $[Co(NH_3)_2(tn)_2]Cl_3 \cdot H_2O$: C, 19.72; H, 7.72; N, 22.99%.

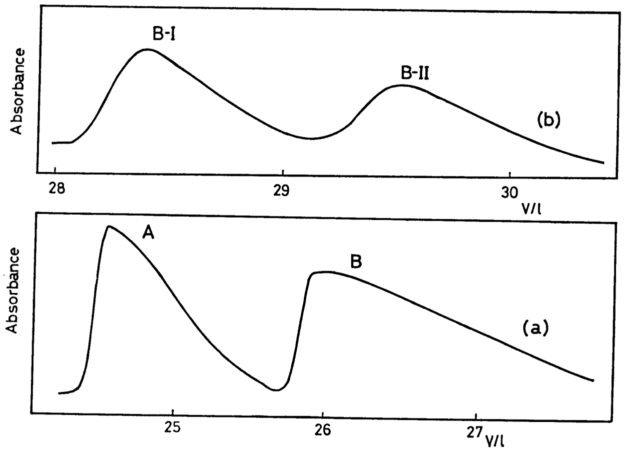

Fig. 1. The elution curves of the recycling chromatography of (a) $[Co(NH_3)_2(tn)_2]^{3+}$ by the 0.18 M sodium $(+)_{589}$-tartrate and (b) *cis*-$[Co(NH_3)_2(tn)_2]^{3+}$ by the 0.15 M sodium $(+)_{589}$-tartratoantimonate(III).

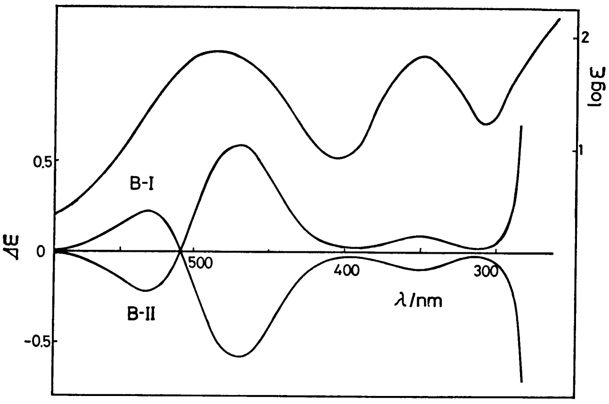

Fig. 2. Visible absorption and CD spectra of isomers of *cis*-$[Co(NH_3)_2(tn)_2]^{3+}$.

The ^{13}C NMR spectra were obtained with a JEOL JNM FX-60 spectrometer, using dioxane as an external reference. Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer and CD curves on a JASCO J-20 spectrophotometer.

Results and Discussion

The ^{13}C NMR spectra of $[Co(NH_3)_2(tn)_2]Cl_3$ isomers have a broader signal at 25.5 ppm and a more intense signal at 39—40 ppm, the latter being split into two peaks for the B isomer. The signals, in the order mentioned, are assigned to β- and α-methylene carbons according to the literature.[5)]

The α-methylene carbon atoms are all equivalent in the trans complex, but are divided into two groups in the *cis* complex. Therefore, the A and B isomers

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** Ethylenediamine, trimethylenediamine, and (2*R*,4*R*)-2,4-pentanediamine, respectively.

Table 1. CD intensities of bis- and tris-diamine complexes

Diamine	Λ-$[Co(NH_3)_2(diamine)_2]^{3+}$		Λ-$[Co(diamine)_3]^{3+}$		$\frac{\Delta\varepsilon_{bis}}{\Delta\varepsilon_{tris}}$
	$\Delta\varepsilon_{bis}$	(λ/nm)	$\Delta\varepsilon_{tris}$	(λ/nm)	
en	+0.42	(492)[a]	+1.89	(493)[a]	0.22
	−0.04	(430)	−0.166	(428)	0.24
	+0.056	(356)	+0.25	(351)	
tn	+0.024	(531)[b]	+0.081	(535)[c]	0.30
	−0.064	(473)	−0.0165	(478.5)	0.39
	−0.011	(352)	−0.020	(357)	
RR-ptn[e]	+1.01	(482)[d]	+3.22	(482)[d]	0.31
	+0.031	(362)	−0.31	(352)	

a) Ref. 8. b) Present work. c) Ref. 6. d) Ref. 9. e) This ligand holds the *ob* form of chelate rings in both the bis and tris complexes.

are assigned to the trans and cis isomers of $[Co(NH_3)_2(tn)_2]^{3+}$, respectively. These assignments are supported also from the fact that the B isomer has been resolved into catoptromers, as described below.

The CD spectra of the B-I and B-II isomers are shown in Fig. 2 with the absorption spectrum of *cis* (B) isomer. Their CD spectra are enantiomeric to each other and resemble those of Λ- and Δ-$[Co(en)_3]^{3+}$, respectively, in their Cotton effects and their shapes.[6] Thus, the B-I and B-II isomers are the optical antipodes of pure *cis*-$[Co(NH_3)_2(tn)_2]^{3+}$, and were assigned to the Λ and Δ forms, respectively.

Table 1 shows the maximum CD intensities and positions in the first and second absorption region of the Λ-$[Co(NH_3)_2(diamine)_2]^{3+}$ and $[Co(diamine)_3]^{3+}$ spectra. The CD spectra of each bisdiamine and the corresponding trisdiamine complex are similar to each other with respect to peak positions and signs, as mentioned above for the tn complexes.

If the number of chelate rings contributes to CD intensity of a bisdiamine complex, the intensity would be expected to be two-thirds of that of the corresponding trisdiamine complex. However, as seen from the last column of Table 1, the observed ratio is roughly one-third or less, particularly with regard to the dominant CD peaks in the first absorption region. Therefore, the number of asymmetric pairs of chelate rings is considered to be more important in determining the CD intensity at least in the first absorption region of the spectra of $[Co(NH_3)_2(diamine)_2]^{3+}$ and $[Co(diamine)_3]^{3+}$, in which the diamine forms either five-membered or six-membered chelate ring. This is consistent with the previous results for the CD intensity of $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ isomers.[7]

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