Synthesis and CD Spectral Studies on Isomers of *cis*-Dicyanobis(propylenediamine)chromium(III) Chloride

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Abstract

The synthesis of *cis*-[Cr(CN)$_2$(pn)$_2$]Cl and separation of isomers with respect to a chirality of the coordinated propylenediamines (pn = 1,2-diaminopropane), i.e. *cis*-[Cr(CN)$_2$(d-pn)(l-pn)]Cl, *cis*-[Cr(CN)$_2$(d-pn)$_2$]Cl and *cis*-[Cr(CN)$_2$(l-pn)$_2$]Cl, by a liquid chromatography are reported. Identification of the separated isomers by circular dichroism (CD) and optical rotation values is discussed. Strong stereoselectivity of propylenediamine on the (d-pn)$_2$ and (l-pn)$_2$ isomers was found.

Introduction

We have worked on the synthetic and stereochemical investigation of Cr(III) complexes [1, 2]. In this report we describe an important fundamental finding in the stereochemistry. When dl-pn is used in the synthesis of six-coordinated bis(propylenediamine) complex, formation of isomers concerning the chirality of the coordinated propylenediamine is expected. However only the isolation of *trans*-[CoCl$_2$(d-pn)(l-pn)]ClO$_4$ has been reported by Wentworth and Piper [3]. Simultaneous formation of a (d-pn)$_2$ and (l-pn)$_2$ isomer was not confirmed till now.

Though complexity is unavoidable in this type of complex because of the formation of many isomers, we overcame this difficulty and clarify the simultaneous formation of isomers of *cis*-[Cr(CN)$_2$(d-pn)(l-pn)]Cl, *cis*-[Cr(CN)$_2$(d-pn)$_2$]Cl and *cis*-[Cr(CN)$_2$(l-pn)$_2$]Cl. Absolute configuration of these isomers is also deduced from the CD spectra.

Experimental

Violet chromic sulphate was prepared by a reported conventional method and other reagents were used as supplied without further purification. CD and UV–Vis spectra were recorded on JASCO J-500C and Hitachi 330 instruments, respectively. Optical rotation values were obtained on a JASCO DIP-140 machine. Elemental analysis of C, H, N, and Cl were performed by the Microanalytical Laboratory of Kitasato University, and Cr was analyzed by the reported colorimetric method [4].

Preparation of the Complexes

A total of 70 g (0.098 ~ 0.093 mol) of violet chromic sulphate, [Cr(OH$_2$)$_6$]$_2$(SO$_4$)$_3$·nH$_2$O (n = 6 ~ 8), in a 500 ml pear flask (wide mouth) was mixed with 48 ml (0.56 mol) of propylenediamine. Then 30 g (0.56 mol) of KCN powder was added and heated (130 °C) for 1 h with stirring. An aqueous solution of the reaction mixture was charged on to a column (70 X 500 mm) of a cation exchange resin (Dowex 50X4 Mg^{2+} form). After washing with a large volume of water, an aqueous solution of MgCl$_2$ (1.0 M about 1 l) was used as an eluant. A yellow eluate from the column was concentrated to one-fourth. In order to separate the complex from MgCl$_2$ a 100 ml portion of the concentrated eluate was charged on a Sephadex G-10 resin column (68 X 350 mm) and developed with water. The complex was first eluted from the column. The same procedure was needed several more times for the complete removal of MgCl$_2$. The eluate containing the complex was evaporated to dryness using a vacuum rotary evaporator. The yellow powder obtained was washed well with ethanol to remove traces of MgCl$_2$, and dried. The yield was 12 g. The analytical data and specific rotations are collected in Table 1.

Separation of Isomers

A total of 0.35 g of the mixture of isomers formed by using dl-pn was dissolved in 200 ml of water-saturated n-butanol, and put on a cellulose (Whatman CC-31) [5] column (22 X 490 mm) maintained at 35 °C. Then, the adsorbed band at the top of the column was eluted with water-saturated n-butanol at a rate of 1.5 ml/min. The eluate from the column was fractionated into 3 ml portions, and absorbances at 338 nm for each fraction were plotted against the elution volume (Fig. 1). The first and second band were collected separately and concentrated. After three more times of successive purification by the

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TABLE 1. Analytical and optical rotation data

	Diamine used	Obtained complex	$[\alpha]_{589}$ (°)	Analysis^a (%) C	H	N	Cr	Cl
1	dl-pn	mixture of $[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\cdot\frac{1}{2}H_2O$ $[Cr(CN)_2(d\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$ $[Cr(CN)_2(l\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	0	32.29	7.10	28.20	17.35	11.95
2		substance of band (A)	0	32.30	7.11	28.20	17.40	12.10
3		substance of band (B)	0	32.22	7.10	28.10	17.73	11.88
4	d-pn	$[Cr(CN)_2(d\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	−56.64	32.37	7.00	28.54	17.42	12.04
5	l-pn	$[Cr(CN)_2(l\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	+56.62	32.48	7.11	28.62	17.46	12.20
				(32.38)	(7.13)	(28.32)	(17.52)	(11.95)

^{a}Calculated values are given in parentheses.

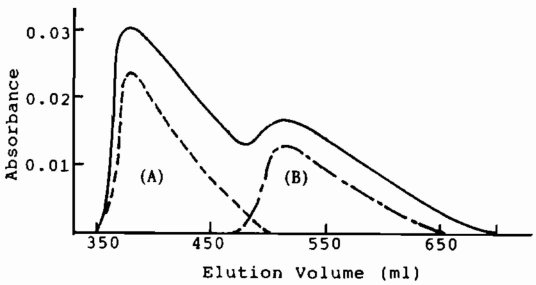

Fig. 1. Elution curve on the separation of band (A) $\{[Cr(CN)_2(d\text{-}pn)_2]Cl + [Cr(CN)_2(l\text{-}pn)_2]Cl\}$ and band (B) $\{[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\}$: mixture of (A) and (B) ——, isolated (A) – – – and (B) —·—.

same procedure, band (A) $\{[Cr(CN)_2(d\text{-}pn)_2]Cl + [Cr(CN)_2(l\text{-}pn)_2]Cl\}$ and band (B) $\{[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\}$ were completely separated as shown in Fig. 1. The yield of (A) and (B) was 0.16 g and 0.1 g, respectively. Analytical data and specific rotation data are collected in Table 1.

Optical Resolution

A 2.0 g (6.7 mmol) sample corresponding to (A) or (B) was dissolved in 10 ml of water. To this solution 1.33 g (4.1 mmol) of ammonium-3-bromo-(+)$_{589}$-camphor-8-sulfonate (d-BCS) or ammonium-3-bromo-(−)$_{589}$-camphor-8-sulfonate (l-BCS) was added with stirring. After 30 min stirring with ice cooling, precipitated yellow crystals (diastereomer) were collected by filtration, washed with a small volume of cold water and ethanol, and dried. The diastereoisomer was dissolved in water and passed through an anion exchange resin (Cl^- form Amberlite IRA-400) column. The yellow effluent was evaporated to dryness using a vacuum rotary evaporator. The solid product was washed with 95% and then absolute ethanol, and dried. The elemental analysis, specific rotation and yield data of the diastereoisomers and resoluted chloride are collected in Table 2.

Results and Discussion

$[Cr(CN)_2(pn)_2]Cl$ is synthesized by a two-step substitution reaction.

$$[Cr(OH_2)_6]^{3+} + 2pn \longrightarrow [Cr(OH_2)_2(pn)_2]^{3+}$$

$$+ 2CN^- \longrightarrow [Cr(CN)_2(pn)_2]^+$$

The final product is liable to be aquated [6] but, unless water is present the first step does not proceed at all; the presence of a small amount of water accelerates the reaction like a catalyst [7]. In this synthesis, reactive violet chromic sulphate was directly mixed with propylenediamine to form $[Cr(OH_2)_2(pn)_2](SO_4)_3$. The reaction was extremely exothermic and completed almost immediately. Most of water liberated from chromic sulphate easily escaped from the reaction vessel. Under conditions of low content of water, so realized, coordinated H_2O molecules of the first step product were substituted somewhat slowly by CN^- ions. The by-products, $[Cr(OH_2)_2(pn)_2]^{3+}$ and $[Cr(pn)_3]^{3+}$, in the reaction mixture are so strongly adsorbed to the cation exchange resin that they hardly move from the initial position, while $[Cr(CN)_2(pn)_2]^+$ effused when aqueous $MgCl_2$ solution was used as an eluant. $MgCl_2$ is removed by Sephadex column. As $MgCl_2$ is soluble in ethanol, traces of $MgCl_2$ are washed out from the product with ethanol.

Two peaks, (A) and (B), can be seen in the elution curve of cellose column (Fig. 1). Areal ratio (A)/(B) is calculated as 0.6. The elemental analysis of (A) and (B) resulted an identical empirical formula as seen in

TABLE 2. Analytical, optical rotation and yield data for the diastereoisomers and resoluted chlorides

	Complex	Yield (g)	$[\alpha]_{589}$ (°)	Analysis[a] (%)				
				C	H	N	Cr	Cl
3_1·d-BCS	$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]$·d-BCS	1.8	+56.84	38.33	6.06	14.81	9.10	
3_2·l-BCS	$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]$·l-BCS	1.6	−56.10	38.18	6.08	14.85	9.15	
4_1·d-BCS	$[Cr(CN)_2(d\text{-}pn)_2]$·d-BCS	2.0	+20.63	38.36	6.03	15.11	9.13	
4_2·l-BCS	$[Cr(CN)_2(d\text{-}pn)_2]$·l-BCS	1.3	−72.19	38.32	6.18	14.87	9.29	
5_1·d-BCS	$[Cr(CN)_2(l\text{-}pn)_2]$·d-BCS	1.3	+72.52	38.62	6.08	14.94	9.16	
5_2·l-BCS	$[Cr(CN)_2(l\text{-}pn)_2]$·l-BCS	2.0	−20.87	38.51	6.13	15.06	9.24	
				(38.44)	(6.09)	(14.94)	(9.24)	
3_1	*cis*-$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\cdot H_2O$	0.7	+33.84	31.32	7.10	27.22	17.01	11.62
3_2	*cis*-$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\cdot H_2O$	0.7	−34.25	31.39	7.13	27.25	16.90	11.65
				(31.43)	(7.25)	(27.49)	(17.01)	(11.60)
4_1	*cis*-$[Cr(CN)_2(d\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	1.0	−56.10	32.54	7.18	28.32	17.36	12.18
4_2	*cis*-$[Cr(CN)_2(d\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	0.6	−56.60	32.38	7.25	28.42	17.59	12.10
5_1	*cis*-$[Cr(CN)_2(l\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	0.6	+56.80	32.36	7.08	28.21	17.51	11.99
5_2	*cis*-$[Cr(CN)_2(l\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$	1.0	+56.62	32.46	7.00	28.34	17.40	11.74
				(32.38)	(7.13)	(28.32)	(17.52)	(11.95)

[a] Calculated values are given in parentheses.

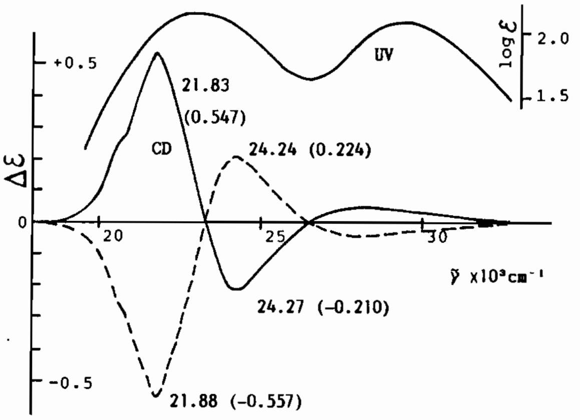

Fig. 2. CD and UV–Vis spectra of complex 4, 4_1, 4_2 and band (A) resoluted by d-BCS: $(-)_{589}$-*cis*-$[Cr(CN)_2(d\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$ (——) and complex 5, 5_1, 5_2 and band (A) resoluted by l-BCS: $(+)_{589}$-*cis*-$[Cr(CN)_2(l\text{-}pn)_2]Cl\cdot\frac{1}{2}H_2O$ (– – –) in aqueous solution.

Table 1. When the substance of band (A) is repeatedly resoluted by d-BCS and returned to the chloride form, it comes to show the same CD spectrum as that of complex 4_1 or 4_2 formed by using d-pn (Table 2). When resoluted by l-BCS, a CD spectrum the same as that of complex 5_1 or 5_2 formed from l-pn, was observed (Fig. 2). Therefore, band (A) consists of equivalent amounts of $[Cr(CN)_2(d\text{-}pn)_2]Cl$ and $[Cr(CN)_2(l\text{-}pn)_2]Cl$. Values of optical rotation and CD spectra of eluted fractions of band (A) interestingly indicate that $[Cr(CN)_2(d\text{-}pn)_2]Cl$ is eluted somewhat faster than $[Cr(CN)_2(l\text{-}pn)_2]Cl$.

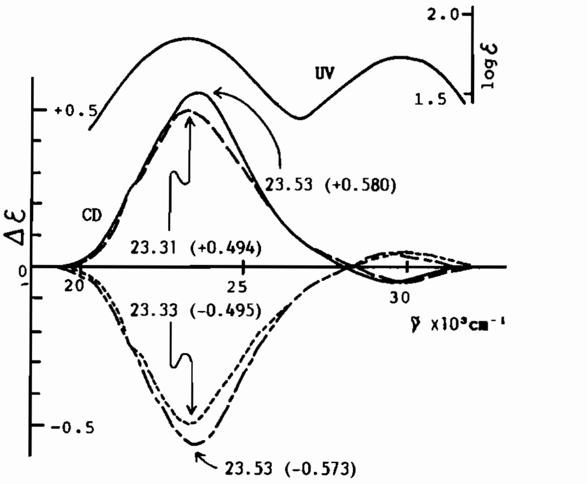

Fig. 3. CD and UV–Vis spectra of band (B) resoluted by d-BCS, 3_1: $(+)_{589}$-*cis*-$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\cdot H_2O$ (——), and band (B) resoluted by l-BCS, 3_2: $(-)_{589}$-*cis*-$[Cr(CN)_2(d\text{-}pn)(l\text{-}pn)]Cl\cdot H_2O$ (—·—) and CD spectra of $(+)_{589}$-*cis*-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$ (– – –) and $(-)_{589}$-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$ (- - -) in aqueous solution. The reported CD peaks $\nu \times 10^3$ cm^{-1} ($\Delta\epsilon$) for d-$(+)_{589}$-$[Co(CN)_2(en)_2]Cl$ are 21.67 (+0.303), 27.24 (+0.173) [11, 12] and for d-$(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ is 21.9 (+1.49) [13, 14], of which absolute configuration had been decided by X-ray analysis.

As shown in Fig. 3, the CD spectrum of 3_1, obtained by optical resolution of band (B) using d-BCS, was similar to that of Λ-$(+)_{589}$-*cis*-$[Cr(CN)_2(en)_2]Cl$, the en ligand of which was not chiral. In the case of using l-BCS, the CD spectrum of 3_2 obtained was similar to that of Δ-(−)$_{589}$-*cis*-[Cr(CN)$_2$(en)$_2$]Cl. These results can be rationally explained if we assume that both **3**$_1$ and **3**$_2$ contain equi-amounts of d- and l-pn, that optical rotation due to d- and l-pn ligands are cancelled out, and that the configurations around the metal, i.e. Δ- and Λ-configuration, induce the observed optical rotation [8, 9]. This was confirmed by the recovery of pn from **3**$_1$ or **3**$_2$ according to the method of Dwyer *et al.* [10]; neither pn recovered was optically active. In the above, assignment of Δ- and Λ-configurations to *cis*-[Cr(CN)$_2$(en)$_2$]Cl was conducted by CD spectral comparison with Λ-(+)$_{589}$-*cis*-[Co(CN)$_2$(en)$_2$]Cl and Λ-(+)$_{546}$-[Cr(en)$_3$](ClO$_4$)$_3$, absolute configurations of which were reported, determined by the X-ray diffraction method [11–14]. The configuration of **3**$_1$ and **3**$_2$ can be concluded to be Λ and Δ, respectively. Since methyl groups of pn ligands direct stable equatorial [15], the most probable forms of **3**$_1$ and **3**$_2$ correspond to Λ-δ·λ-(+)$_{589}$-*cis*-[Cr(CN)$_2$(d-pn)(l-pn)]Cl and Δ-δ·λ-(−)$_{589}$-*cis*-[Cr(CN)$_2$(d-pn)(l-pn)]Cl, respectively. Optical rotation values of *cis*-[Cr(CN)$_2$(d-pn)$_2$]Cl (**4**) and *cis*-[Cr(CN)$_2$(l-pn)$_2$]Cl (**5**) did not vary by the optical resolution procedure as seen in Tables 1 and 2, indicating that both **4** and **5** did not contain the *trans*-isomer. From this invariability of optical rotation values, it is considered that stereoselectivity of pn-ligands in **4** and **5** is as strong as it only permits formation of the isomer having the most stable configuration.

In general when dl-pn was used for the preparation of the bis(propylenediamine) complex, there should be (d-pn)(l-pn), (d-pn)$_2$ and (l-pn)$_2$ isomers There has, however, been no precise investigation of the products. Here we have clarified these products.

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