Circular dichroism studies for absolute configuration determination of 1,2-diaminopropane chromium(III) complexes, and synthesis of tetracyano(1,2-diaminopropane)chromate(III)

Yuzuru Sakabe*

School of Hygienic Sciences, Kitasato University 1-15-1, Kitasato, Sagamihara, Kanagawa 228 (Japan)

and Haruo Ogura

School of Pharmaceutical Sciences, Kitasato University, Minato-ku, Tokyo 108 (Japan)

Abstract

This is the first study of the absolute configuration determinations for metal complexes coordinated by chiral propylenediamine ligands, using CD spectra. The CD (circular dichroism) spectra of analogous Cr(III) complexes represented by $[Cr(CN)_{2n}(A)_{3-n}]^{3-2n}$ (A = pn or en, $n = 0$ or 1, pn = d-pn or ℓ-pn and pn = 1,2-diaminopropane = propylenediamine, en = ethylenediamine) have been systematically measured, and they have been compared with that of the Λ-cis-$(-)_{589}$-$[Cr(CN)_2(d$-pn$)_2]Cl$ standard, of which an absolute configuration has been confirmed by X-ray analysis, and absolute configurations of the seven complexes have been collectively determined. In this study the two new complexes of tetracyano(d- or ℓ-1,2-diaminopropane)chromate(III) are synthesized to learn the contribution of the chiral configurations, localized upon the propylenediamine ligands, to CD spectra of complexes, because CD peaks, depending on the chiral propylenediamine, are liable to interfere with correct absolute configuration determinations. We have elucidated the effectiveness of using CD spectra as the absolute configuration determination method. The superiority of this method is particularly obvious when complexes cannot answer to X-ray analysis — as was the case with several complexes in this study — due to the difficulty in preparing single crystals.

Introduction

Utilizing CD spectra for absolute configuration determination of metal complexes would be the second best method, after X-ray analysis [1–3], but when difficulties arise in X-ray analysis of these complexes CD spectra become the more dependable method. Moreover, this simple method is even more reasonable than X-ray crystallographic methods as a method for determining collected absolute configuration of similar complexes [1, 4]. Further application of this method can be expected.

The absolute configuration determination method using CD spectra is entirely dependent on experimentally observed CD spectra, because theoretical attempts to explain CD spectra have failed to illuminate anything but the fundamentals [5, 6]. The rationale of this method is that when similar complexes have an identical symmetry around a central metal and an identical absolute configuration, their

CD peaks, based on the chiral configuration around a central metal, will resemble one another [1–3]. If the complexes are made up of the same species of a central metal, the above relationship becomes surer. For these reasons, appropriate standard complexes are required in this determination method. We have employed Λ-cis-$(-)_{589}$-$[Cr(CN)_2(d$-pn$)_2]Cl$ for this purpose. For the Λ-cis-$(-)_{589}$-$[Cr(CN)_2(d$-pn$)_2]Cl$ standard, three geometric isomers exist according to differences in the relative position of the methyl groups of propylenediamine ligands (Fig. 1). In this study, the CD spectrum of the geometric isomer I of Λ-cis-$(-)_{589}$-$[Cr(CN)_2(d$-pn$)_2]Cl$ has been used as the standard, since its crystal structure and Λ absolute configuration have been confirmed by single crystal X-ray analysis in our previous work [7].

In this paper, we present results of absolute configuration determinations of a series of complexes represented by $[Cr(CN)_{2n}(A)_{3-n}]^{3-2n}$ (A = pn or en; $n = 0$ or 1), which include several species whose configurations have been difficult to determine using X-ray crystallography.

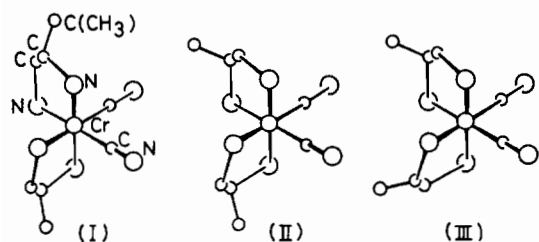*Author to whom correspondence should be addressed.

Fig. 1. The geometric isomers of Λ-cis-$(-)_{589}$-[Cr(CN)$_2$(d-pn)$_2$]$^+$ion; the CD spectrum of isomer I served as the standard.

Experimental

Preparation of complexes and instrumentation

Mg[Cr(CN)$_4$(d-pn)]$_2 \cdot$2H$_2$O and Na[Cr(CN)$_4$(ℓ-pn)]$\cdot$2H$_2$O were separated from the reaction mixture of chromic sulfate, 1,2-diaminopropane and KCN, in analogy with the previous separation of cis-[Cr(CN)$_2$(pn)$_2$]$^+$ [8]. Namely, 35 g (0.049 ~ 0.047 mol) of violet chromic sulfate [Cr(OH$_2$)$_6$]$_2$(SO$_4$)$_3 \cdot n$H$_2$O (n = 6 ~ 8) were mixed with 24 ml (0.28 mol) of d-pn or ℓ-pn, then 15 g (0.28 mol) of KCN powder was added and heated (about 130 °C) for 1 h while being stirred. An aqueous solution of the reaction mixture was charged into a column of Sephadex G-10 resin (65 × 400 mm) and developed with water. The light yellow band of the desired tetracyano complex was eluted from the column lastly and at a distance from other bands. For removal of trace amounts of by-products, the collected light yellow eluate was charged on top of a DEAE-Sephadex A-25 (anion exchange) resin (Cl$^-$ form) column (35 × 400 mm) producing an adsorbed band. The column was washed with water and the adsorbed band was eluted with 0.1 M MgCl$_2$ aqueous solution (for Mg[Cr(CN)$_4$ (d-pn)]$_2$) or 0.2 M NaClO$_4$ aqueous solution (for Na[Cr(CN)$_4$(ℓ-pn)]). In both cases, the eluates from the DEAE-Sephadex column were evaporated to dryness, and they were offered for the separation of the MgCl$_2$ or NaClO$_4$ eluent. The MgCl$_2$ eluent was separated from Mg[Cr(CN)$_4$(d-pn)]$_2$ by repeated separation using a Sephadex G-10 column chromatography, because the first eluted band of the desired complex overlapped with part of secondly eluted MgCl$_2$ band. But, in the case of Na[Cr(CN)$_4$(ℓ-pn)], when the dried mixture was dissolved in 99% ethanol, the desired pure complex was immediately obtained as fine crystals, and NaClO$_4$ remained in the filtrate. Anal. Found: C, 32.01; H, 4.81; N, 31.98. Calc. for Mg[Cr(CN)$_4$(d-pn)]$_2 \cdot$2H$_2$O: C, 32.29; H, 4.58; N, 32.28%. Anal. Found: C, 29.06; H, 5.01; N, 29.01. Calc. for Na[Cr(CN)$_4$(ℓ-pn)]$\cdot$2H$_2$O: C, 29.07; H, 4.88; N, 29.06%.

The complexes of cis-[Cr(CN)$_2$(pn)$_2$]Cl and cis-[Cr(CN)$_2$(en)$_2$]Cl were prepared, isolated into iso-

mers, and optically resoluted according to our reported methods [7–9]. The complexes of [Cr(en)$_3$]Cl$_3$ and [Cr(pn)$_3$]Cl$_3$ were prepared by almost the same methods as those reported previously [10, 11], except for the use of violet chromic sulfate as a source of chromium. Then, they were optically resoluted by a conventional method [12].

Violet chromic sulfate was prepared by a reported conventional method. Optically resoluted d-pn ($[\alpha]_{589}^{20}$ = + 34.2°) and ℓ-pn ($[\alpha]_{589}^{20}$ = − 34.8°) were obtained by resolution of reagent grade $d\ell$-pn [13], and other reagents used in the preparation were of reagent grade and used without further purification. CD spectra were measured on a JAS.CO J-500C spectropolarimeter in 0.5 cm cells using $4 \sim 7 \times 10^{-3}$ mol/l aqueous solutions in the vicinity of 20 °C. UV–Vis spectra were measured on a Hitachi 330 spectrophotometer.

Results and discussion

The CD spectrum of Λ-cis-$(-)_{589}$-[Cr(CN)$_2$(d-pn)$_2$]Cl standard measured over the d–d absorption region is shown in Fig. 2. It is made up of CD peaks based on the two distinct contributions of the chiral configuration around the Cr(III) central metal and the localized chiral configurations on the two d-pn
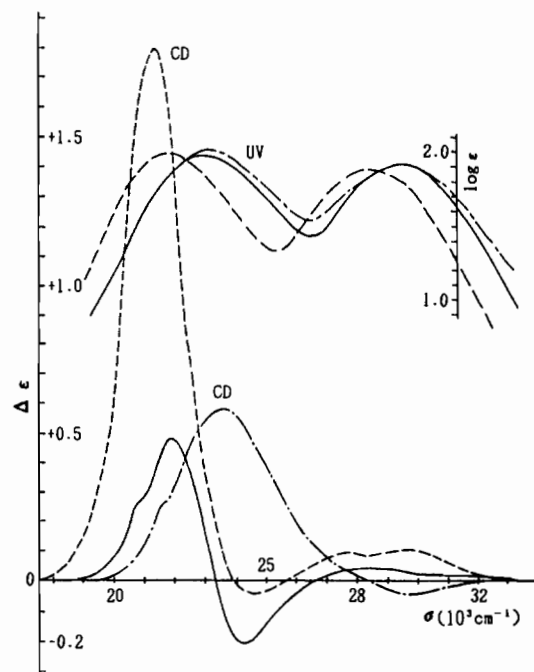

Fig. 2. CD and UV–Vis spectra of Λ-cis-$(-)_{589}$-[Cr(CN)$_2$(d-pn)$_2$]Cl$\cdot$0.5H$_2$O (——), $(+)_{589}$-[Cr(d-pn)$_3$]Cl$_3 \cdot$H$_2$O (– – – –) and cis-$(+)_{589}$-[Cr(CN)$_2$(d-pn)(l-pn)]Cl$\cdot$H$_2$O (— — —) in aqueous solutions.

ligands. Hence, identification of the main CD peaks, reflecting the Λ configuration of the standard complex, will be required for reliable absolute configuration determinations.

The CD spectra of newly synthesized $Mg[Cr(CN)_4(d\text{-pn})]_2$ and $Na[Cr(CN)_4(\ell\text{-pn})]$ are shown with their UV–Vis spectra in Fig. 3: notice that the main peaks are situated in the higher wavenumber side of the first d–d absorption band. All CD peaks observed in it can naturally be assigned to the chiral configurations localized in d-pn or ℓ-pn, i.e. the vicinal effect, since both complexes have no chiral configuration around the Cr(III) metal.

The CD spectra of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(en)_2]Cl$ and $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(d\text{-pn})(\ell\text{-pn})]Cl$ are shown in Figs. 2 and 4, both complexes bear an identical symmetry around Cr(III) to that of the $\Lambda\text{-}cis\text{-}(-)_{589}$-

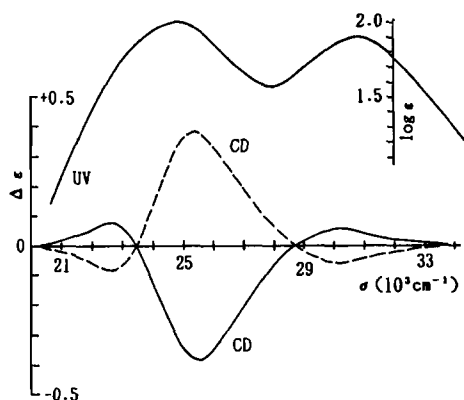Fig. 3. The vicinal effect CD spectra of $Mg[Cr(CN)_4(d\text{-pn})]_2\cdot 2H_2O$ (——) and $Na[Cr(CN)_4(\ell\text{-pn})]\cdot 2H_2O$ (– – –), and UV–Vis spectra of both complexes in aqueous solutions.
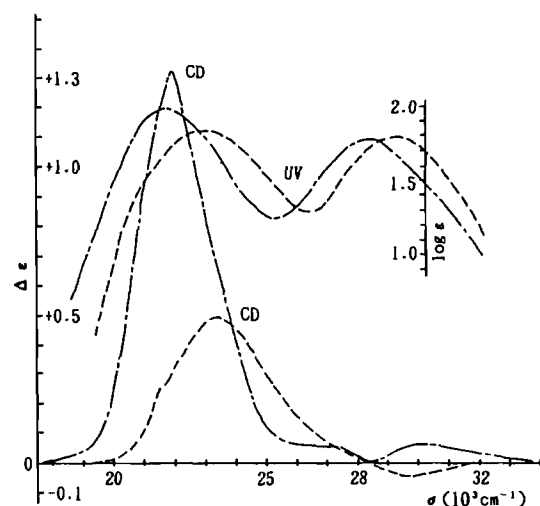
Fig. 4. CD and UV–Vis spectra of $(+)_{589}$-$[Cr(en)_3]Cl_3\cdot 2.5H_2O$ (– – – –) and $cis\text{-}(+)_{589}$-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$ (– – –) in aqueous solutions.

$[Cr(CN)_2(d\text{-pn})_2]Cl$ standard. The CD spectrum of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(en)_2]Cl$ contains no vicinal effect peak since it has no chiral ligand, thus the single large CD peak observed in the first d–d absorption band region can reasonably be assigned to the chiral configuration around the Cr(III) metal, i.e. the peak is reflecting an absolute configuration of the complex. In the case of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(d\text{-pn})(\ell\text{-pn})]Cl$, the vicinal effects of the d-pn and ℓ-pn ligands will cancel each other out. Thus, based on the vicinal effect, the appearance of the peaks cannot be expected in the CD spectrum. The disappearance of the vicinal effect can also be presumed from the similarity of the CD spectrum to that of vicinal effect free $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(en)_2]Cl$. Accordingly, the observed single main CD peak, situated in the first d–d absorption band of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(d\text{-pn})(\ell\text{-pn})]Cl$, can also be assigned to a chiral configuration around a metal. It becomes apparent from the spectral results of both of the above complexes, that the single large CD peak, reflecting the Λ absolute configuration of the standard complex, will also appear in the region of the first d–d absorption band.

As shown in Fig. 2, in the actual CD spectrum of the $\Lambda\text{-}cis\text{-}(-)_{589}\text{-}[Cr(CN)_2(d\text{-pn})_2]Cl$ standard, two large peaks, having positive and negative signs, can be observed. However, the results of the CD spectra of the foregoing tetracyano complexes show that the peak with a negative sign, situated in the higher wavenumber side of the first d–d absorption band region, can be assigned to the vicinal effect of the d-pn ligands. Thus, the residual positive main CD peak is just reflecting the Λ configuration of the standard, though its shape may be influenced by the neighboring vicinal effect peak having an opposite sign.

Consequently, by comparing the sign of the main CD peaks with that of the standard, the Λ absolute configuration of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(en)_2]Cl$ and $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(d\text{-pn})(\ell\text{-pn})]Cl$ can be determined, since both complexes exhibit positive main CD peaks, as does the $\Lambda\text{-}cis\text{-}(-)_{589}\text{-}[Cr(CN)_2(d\text{-pn})_2]Cl$ standard. The Δ configurations of $cis\text{-}(+)_{589}\text{-}[Cr(CN)_2(\ell\text{-pn})_2]Cl$ and $cis\text{-}(-)_{589}\text{-}[Cr(CN)_2(d\text{-pn})(\ell\text{-pn})Cl$, exhibiting antipodal CD spectra with a negative main peak, can also be determined. In the case of tris-diamine complexes, their symmetry around a central metal is not identical with that of the standard, but they both exhibit a single main CD peak situated in the first d–d absorption band, in analogy with the above bis-diamine complexes. Thus, Λ configuration of $(+)_{589}\text{-}[Cr(d\text{-pn})_3]Cl_3$ and $(+)_{589}\text{-}[Cr(en)_3]Cl_3$, and Δ configuration of $(-)_{589}\text{-}[Cr(\ell\text{-pn})_3]Cl_3$ are similarly determined from the sign of their main CD peaks.

TABLE 1. CD and UV–Vis spectra results and determined absolute configurations

Complex	CD peaks $\sigma \times 10^3$ (cm^{-1}) ($\Delta\epsilon$)	Absorption maxima $\sigma \times 10^3$ (cm^{-1}) (log ϵ)	Determined absolute configuration
Mg[Cr(CN)$_4$(d-pn)]$_2 \cdot 2$H$_2$O	22.66 (+0.075), 25.54 (−0.384) 32.26 (+0.052)	24.75 (1.92) 30.86 (1.85)	
Na[Cr(CN)$_4$(ℓ-pn)]$\cdot 2$H$_2$O	22.62 (−0.081), 25.41 (+0.383) 30.17 (−0.059)	24.75 (1.90) 30.86 (1.80)	
Λ-cis-(−)$_{589}$-[Cr(CN)$_2$(d-pn)$_2$]Cl$\cdot 0.5$H$_2$O	21.81 (+0.484), 24.21 (−0.196) 28.41 (+0.040)	22.98 (1.88) 29.50 (1.83)	standard
cis-(+)$_{589}$-[Cr(CN)$_2$(ℓ-pn)$_2$]Cl$\cdot 0.5$H$_2$O	21.88 (−0.557), 24.24 (+0.219) 28.33 (−0.059)	23.00 (1.88) 29.50 (1.83)	Δ
cis-(+)$_{589}$-[Cr(CN)$_2$(d-pn)(ℓ-pn)]Cl$\cdot$H$_2$O	23.53 (+0.580) 29.59 (−0.045)	23.09 (1.92) 29.50 (1.83)	Λ
cis-(−)$_{589}$-[Cr(CN)$_2$(d-pn)(ℓ-pn)]Cl$\cdot$H$_2$O	23.53 (−0.573) 29.59 (+0.050)	23.09 (1.92) 29.50 (1.83)	Δ
(+)$_{589}$-[Cr(d-pn)$_3$]Cl$_3 \cdot$H$_2$O	21.23 (+1.805), 24.39 (−0.040) 27.40 (+0.095), 29.67 (+0.103)	21.74 (1.89) 28.41 (1.79)	Λ
(−)$_{589}$-[Cr(ℓ-pn)$_3$]Cl$_3 \cdot$H$_2$O	21.23 (−1.792), 24.39 (+0.041) 27.25 (−0.098), 29.41 (−0.112)	21.79 (1.89) 28.49 (1.79)	Δ
(+)$_{589}$-[Cr(en)$_3$]Cl$_3 \cdot 2.5$H$_2$O	21.88 (+1.321) 30.30 (+0.065)	21.74 (1.98) 28.28 (1.89)	Λ
cis-(+)$_{589}$-[Cr(CN)$_2$(en)$_2$]Cl$\cdot$H$_2$O	23.31 (+0.494) 29.76 (−0.044)	22.94 (1.84) 29.24 (1.80)	Λ

The Λ configuration of (+)$_{589}$-[Cr(en)$_3$]Cl$_3 \cdot 2$H$_2$O has also been confirmed by the single crystal X-ray analysis of Whuler et al. [14], in agreement with our result. Our results for CD and UV-Vis spectra and absolute configuration determinations are summarized in Table 1.

In conclusion, on the basis of CD spectra, absolute configurations have been collectively determined. It is noteworthy that X-ray crystallographic determination of the absolute configurations of Λ-cis-(+)$_{589}$-[Cr(CN)$_2$(d-pn)(ℓ-pn)]Cl, Δ-cis-(−)$_{589}$-[Cr(CN)$_2$(d-pn)(ℓ-pn)]Cl, Λ-(+)$_{589}$-[Cr(d-pn)$_3$]Cl$_3$ and Δ-(−)$_{589}$-[Cr(ℓ-pn)$_3$]Cl$_3$ will be impossible as a result of the difficulty of their crystallization, so the superiority of the CD spectra method in this case is clear.

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