Separation and crystal structures of geometric isomers of *cis*-$(-)_{589}$-dicyanobis(*d*-propylenediamine)chromium(III) chloride

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Abstract

Three geometric isomers, which result from the differences in relative position of the methyl groups of propylenediamine ligands of Λ-*cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-pn})_2]Cl$ (pn = propylenediamine = 1,2-diaminopropane), have been separated by liquid column chromatography on ion-exchange Sephadex C-25. Structural differences and Λ absolute configuration of the two geometric isomers **A** and **B**, which could be obtained as crystals, have been determined by single crystal X-ray analyses for the first time for this kind of isomer. Isomer **A** crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 9.854(4)$, $b = 22.762(9)$, $c = 6.579(3)$ Å, and $Z = 4$. Isomer **B** also crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 8.555(4)$, $b = 24.254(5)$, $c = 7.374(7)$ Å, and $Z = 4$. Intensity data were collected on a four-circle computer-controlled diffractometer with use of the $\theta-2\theta$ scan technique. The structures were solved by the heavy atom method for isomer **A** and direct method for isomer **B** on 1264 and 1020 reflections, respectively. The structures were refined by the block-diagonal-matrix least-squares method for isomer **A** and full-matrix least-squares method for isomer **B** to the final R values of 0.078 and 0.089, respectively.

Introduction

Existence of the *fac* and *mer* geometric isomers of octahedral tris(propylenediamine) complexes (Fig. 1, top) has been recognized as the general concept of coordination chemistry as the descriptions about it are seen in most fundamental textbooks. But to our surprise, existence of the *mer* isomer has not been confirmed to date by any substantial experimental evidence. The first attempt to separate the *fac* and *mer* isomers was made for Δ-$[Co(l\text{-pn})_3]^{3+}$ by MacDermott [1] and then for Λ-$[Co(l\text{-pn})_3]^{3+}$ by Kojima *et al.* [2] but crystallographic characterization has not been made, except for the *fac* isomer of Δ-$[Co(l\text{-pn})_3]^{3+}$ by Iwasaki and Saito [3]. It is necessary to characterize these kinds of geometric isomers by single crystal X-ray analyses because other effective analytical techniques, which could elucidate the quantitative structural features of these isomers, have not been found.

While the two geometric isomers exist in tris(propylenediamine) complexes as mentioned above, the formation of three isomers is theoretically possible in *cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-pn})_2]Cl$ (Fig. 1, bottom). As a result of the strong stereoselectivity of *d*-propylenediamine ligands, our bis(*d*-propylenediamine) complex is obtained in a state of high optical purity [4] but it is still composed of a mixture of the three geometric isomers. We separated these three geometric isomers by liquid column chromatography and made an attempt at crystallization. X-ray structure analysis including determination of the absolute configuration has been carried out for the two isomers which were obtained as single crystals. The existence of the geometric isomers corresponding to **I** and **II** (Fig. 1) has been confirmed as the answer to the long-pending question,

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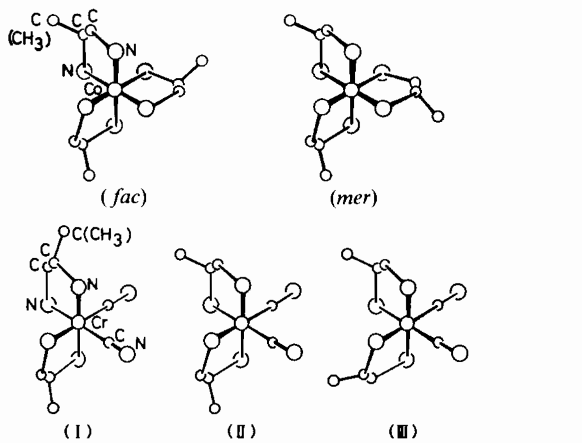


Fig. 1. *mer* and *fac* geometric isomers of the Λ-[Co(*d*-pn)$_3$]$^{3+}$ ion (top) and three isomers considered for the Λ-*cis*-($-$)$_{589}$-[Cr(CN)$_2$*d*-pn)$_2$]$^+$ ion (bottom).

whether the isomers differing in the relative position of the methyl group of the propylenediamine ligands exist or not.

Experimental

cis-($-$)$_{589}$-[Cr(CN)$_2$(*d*-pn)$_2$]Cl·H$_2$O was obtained according to our earlier work [4]. Potassium bis(μ-*d*-tartrato)diantimonate(III), K$_2$[Sb$_2$(*d*-tart)$_2$], (high-purity grade) was supplied by Waco Chemical Co.; ammonium-3-bromo-(+)$_{589}$-camphor-8-sulfonate was supplied by Aldrich Chemical Co. and they were used without further treatment. UV–Vis spectra were recorded on a Hitachi 330 spectrophotometer at room temperature, IR spectra were obtained on a Perkin-Elmer 983 spectrophotometer at 20 °C, CD spectra were recorded on a JAS.CO J-500C spectropolarimeter at 20 °C and optical rotation measurements were performed on a JAS.CO DIP-140 polarimeter at 20 °C.

Separation of geometric isomers of cis-($-$)$_{589}$-[Cr(CN)$_2$(d-pn)$_2$]Cl·H$_2$O

A solution of 0.2 g of sample in 1.5 ml 0.09 M K$_2$[Sb$_2$(*d*-tart)$_2$] was poured on the top of a SP-Sepahadex C-25 (potassium form) column (22 x 870 mm) producing about 0.5 cm of adsorbed band which was eluted with 0.09 M K$_2$[Sb$_2$(*d*-tart)$_2$] solution at a rate of 0.5 ml/min. The absorbances at 340 nm of the eluate were measured and plotted against the elution volume (Fig. 2, a solid line) and the eluate was fractionated into 5 ml portions. The fractionated eluate was classified into three bands which were provisionally named 'isomer **A**, isomer **B**, and isomer **C**' in eluted order, then each band was concentrated to near dryness and 30 ml of ethanol was added to each band. The deposited white crystals of K$_2$[Sb$_2$(*d*-tart)$_2$] were filtered off and each of the filtrates was concentrated to dryness. The three dried crude isomers were subjected twice to the same column chromatography separation. Each elution curve of isomers **A**, **B** and **C** at their last separation is illustrated as a broken line (Fig. 2).

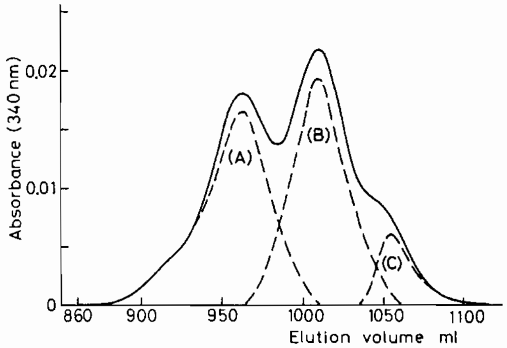


Fig. 2. Elution curves observed at the separation of isomers of *cis*-($-$)$_{589}$-[Cr(CN)$_2$(*d*-pn)$_2$]Cl: first separation (——) and last separation of isomers of **A**, **B** and **C**, respectively (– – –).

To remove the trace amount of K$_2$[Sb$_2$(*d*-tart)$_2$] eluent from the chromatographically separated water soluble isomers, slightly soluble diastereomers were formed and washed with a small amount of cold water. That is, each isomer was dissolved in a minimum amount of water, and ammonium-3-bromo-(+)$_{589}$-camphor-8-sulfonate was added with stirring in a 1:1.2 mol fraction. Then the deposited diastereomers were washed with water and converted again into the chloride form by passing the aqueous solutions of the diastereomer through the anion exchange resin (chloride form Amberlite IRA-400) column. The eluates from the column were evaporated to dryness. The yield of isomer **A** was 0.02 g, isomer **B** was 0.015 g and isomer **C** was 0.004 g. The optical activities ($[\alpha]^{20}_{589}$) were measured to be $-57.81°$ for isomer **A**, $-51.64°$ for isomer **B** and $-41.59°$ for isomer **C**. *Anal.* Found: C, 32.09; H, 7.05; N, 28.25; Cr, 17.31. Calc. for isomer **A** ([Cr(CN)$_2$(pn)$_2$]Cl·0.5H$_2$O): C, 32.38; H, 7.13; N, 28.32; Cr, 17.52%. Found: C, 31.40; H, 7.25; N, 27.25; Cr, 17.15. Calc. for isomer **B** ([Cr(CN)$_2$(pn)$_2$]Cl·H$_2$O): C, 31.43; H, 7.25; N, 27.49; Cr, 17.01%. Found: C, 28.47; H, 7.23; N, 25.36. Calc. for isomer **C** ([Cr(CN)$_2$(pn)$_2$]Cl·2.5H$_2$O): C, 28.87; H, 7.57; N, 25.25%. Depending upon the conditions of crystallization and drying, the crystallization water of isomer **A** varies between 0.5 and 1H$_2$O.

X-ray diffraction analysis

The light yellow crystals of isomer **A** suitable for X-ray diffraction analysis were grown by slow evaporation of nearly saturated 75% ethanol solution placed in a CaO desiccator. The yellow crystals of isomer **B** were also grown in the same way but from an aqueous solution. In both cases, the crystal was mounted on a glass fiber with epoxy cement put on a rotation-free goniometer head for data collection at room temperature. The diffraction intensities were measured on Philips PW-1100 (for analysis of isomer **A**) and Rigaku AFC-4 (for isomer **B**) automatic four-circle diffractometers using graphite-monochromated Cu Kα radiation. The unit cell parameters of both isomers were derived by least-squares refinement of the setting angles of 25 reflections with $15° \leqslant \theta \leqslant 45°$. The systematic extinction revealed that each isomer crystallizes in the orthorhombic system, space group $P2_12_12_1$. The crystal data and data collection parameters are displayed in Table 1.

The structure of isomer **A** was solved by the heavy atom method and refined by the block-diagonal-matrix least-squares method, and isomer **B** was solved by the direct method and refined by the full-matrix least-squares method. The hydrogen atoms were located on the difference electron-density map, and their positions were at first regularized by the standard bond lengths and bond angles and then included in the least-squares refinement with isotropic temperature factors. The final R values for isomers **A** and **B** are 0.078 and 0.089, respectively. The positional and isotropic thermal parameters are given in Tables 2 and 3.

The X-ray diffraction analysis of isomer **C** was not attempted because of the difficulty in preparing a single crystal.

TABLE 2. Final fractional coordinates (× 10^4) and equivalent isotropic temperature factors for isomer **A** with e.s.d.s in parentheses

Atom	x	y	z	B_{eq} ($Å^2$)
Cr	−258(1.7)	−877(0.7)	−886(2.5)	2.66(0.02)
N(1)	1408(8)	−656(4)	−2690(13)	2.8(0.1)
N(2)	735(9)	−1688(4)	−787(15)	3.4(0.1)
C(3)	2168(12)	−1612(5)	−1428(19)	4.0(0.2)
C(4)	2178(11)	−1205(5)	−3244(18)	3.4(0.2)
N(5)	−1517(9)	−1157(4)	−3267(13)	3.5(0.1)
N(6)	−1787(9)	−1224(3)	911(14)	3.1(0.1)
C(7)	−2725(12)	−1593(5)	−336(18)	3.9(0.2)
C(8)	−2882(13)	−1292(5)	−2388(19)	4.0(0.2)
C(9)	−1201(10)	−70(4)	−1141(15)	2.8(0.1)
C(10)	744(11)	−567(5)	−1674(18)	3.4(0.2)
N(11)	−1766(11)	359(4)	−1305(15)	4.4(0.2)
N(12)	1280(13)	−334(5)	2979(16)	5.5(0.2)
C(13)	3608(12)	−1064(6)	−3986(24)	5.0(0.2)
C(14)	−4063(14)	−1697(6)	717(25)	5.4(0.2)
O(W)	2939(24)	−2238(9)	−7152(28)	6.8(0.4)
Cl	−252(4)	−2211(1)	−6135(5)	5.1(0.0)

TABLE 1. Crystal data and summary of structure determination

	Isomer **A**	Isomer **B**
Formula	$C_8H_{20}N_6CrCl \cdot H_2O$	$C_8H_{20}N_6CrCl \cdot H_2O$
M_r	305.8	305.8
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions		
a (Å)	9.854(4)	8.555(4)
b (Å)	22.762(9)	24.254(5)
c (Å)	6.579(3)	7.374(1)
V ($Å^3$)	1476	1530
Z	4	4
Density (calc.) (g cm^{-3})	1.375	1.327
Color of crystal	light yellow	yellow
Crystal dimensions (mm)	0.20 × 0.15 × 0.25	0.2 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54178 Å graphite monochromated)	
μ (cm^{-1})	9.395	9.395
2θ range (°)	6–150	6–150
Scan speed (° min^{-1})	4	8
Phasing	heavy atom method	direct method
No. measured reflections	1497	1152
No. independent reflections ($I > 2\sigma(I)$)	1264	1020
Refinement	block-diagonal-matrix least-squares method	full-matrix least-squares method
Final R	0.078	0.089
No. refined atoms	17 (anisotropic) + 20 H (isotropic)	

TABLE 3. Final fractional coordinates (× 10^4) and equivalent isotropic temperature factors for isomer **B** with e.s.d.s in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Cr	569(3)	4179(1)	−464(4)	1.7
N(1)	1679(15)	3850(6)	−2704(21)	2.6
N(2)	2566(16)	3881(6)	812(21)	2.7
C(3)	3110(22)	3530(7)	−2195(25)	3.0
C(4)	3781(17)	3799(6)	−566(30)	2.8
N(5)	−702(15)	3463(5)	119(17)	2.0
N(6)	−428(16)	4440(5)	1950(19)	2.4
C(7)	−1984(19)	3616(8)	1404(26)	3.3
C(8)	−1196(26)	3973(8)	2844(30)	3.7
C(9)	−1283(22)	4462(6)	−2054(24)	2.7
C(10)	1759(19)	4922(6)	−747(21)	2.3
N(11)	−2238(25)	4660(8)	−2874(28)	6.3
N(12)	2425(18)	5331(6)	−854(20)	3.5
C(13)	4291(32)	3484(11)	−3760(35)	5.6
C(14)	−2825(22)	3110(9)	2199(35)	4.3
O(W)	−53(14)	2910(5)	−4058(20)	4.3
Cl	1917(6)	2650(2)	2336(8)	4.5

Results and discussion

Absolute configuration

For isomer **A**, the intensities of 12 Friedel pairs (*hkl* and $\bar{h}\bar{k}\bar{l}$) having the largest calculated intensity differences were measured on the diffractometer using graphite-monochromated Cu Kα ($\lambda = 1.54178$ Å) radiation. The structure factors were calculated for the Δ configuration by use of the values of anomalous scattering terms of chromium given in the literature [5]. All the relations between $|F_c(hkl)|$ and $|F_c(\bar{h}\bar{k}\bar{l})|$ are inconsistent with those between $|F_o(hkl)|$ and $|F_o(\bar{h}\bar{k}\bar{l})|$, indicating that isomer **A** is in the Λ configuration. These relationships are presented in Table 4.

For isomer **B**, the final R value 0.089 calculated by the full-matrix least-squares refinement including anomalous dispersion terms on a supposition of the Λ configuration of isomer **B** was raised to 0.114 when all the resulting atomic coordinates were inverted and used as input data. So Λ was recognized as the true absolute configuration for isomer **B** [6].

TABLE 4. Determination of the absolute configuration of isomer **A**: relations of $|F|$ of Friedel pairs for the Δ configuration

h	k	l	$\lvert F_c(hkl)\rvert$	Observed relations	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$
3	1	1	26.4	<	20.3
1	6	1	39.2	<	31.9
1	7	1	10.8	>	16.9
4	15	1	17.1	<	11.7
5	3	2	18.7	<	11.6
6	10	2	8.6	>	12.8
5	17	2	10.4	<	8.3
5	10	3	8.5	>	12.4
2	2	4	15.0	<	11.0
3	1	5	10.4	>	19.0
1	4	6	25.2	<	18.9
2	3	7	12.6	<	9.4

Structures of geometric isomers

The crystal unit cells for both the isomers are shown in Fig. 3. The c axis projections of the crystal structures are illustrated in Figs. 4 and 5, and intermolecular distances, which are expected to be hydrogen bonds, are listed in Table 5. The perspective views of the isomers showing the coordination of the Cr^{3+} ions are given by ORTEP drawings with 30% probability thermal ellipsoids (Fig. 6). Selected intramolecular interatomic distances and valency angles are listed in Tables 6 and 7.

Even though reported data are limited, Co–N and Co–C bond distances of 1.94–2.00 and 1.85–1.88 Å, respectively and N–Co–N angles of 85–86° in Λ-$(+)_{589}$-$[Co(CN)_2(en)_2]Cl$ [7] or Cr–N

TABLE 5. Important intermolecular distances (Å) in isomers of *cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-}pn)_2]Cl{\cdot}H_2O$

Isomer A	Distance	Isomer B	Distance
Cl–O(W)^{a}	3.215(24)	Cl–O(W)^{e}	3.211(15)
Cl–O(W)^{b}	3.071(21)	Cl–O(W)^{h}	3.191(13)
N(1)–N(12)^{c}	2.945(13)	N(1)–N(12)^{i}	3.150(20)
N(1)–N(12)^{d}	3.234(15)	N(2)–N(12)^{j}	3.114(21)
N(5)–N(11)^{f}	3.186(13)	N(6)–N(11)^{k}	2.962(24)
N(6)–N(11)^{g}	3.043(13)	N(6)–N(12)^{i}	3.087(21)

Some of them are expected to be hydrogen bonds. Key to the symmetry operations: $^{a}x, y, z$; $^{b}\frac{1}{2}+x, -\frac{1}{2}-y, -1-z$; $^{c}x, y, z-1$; $^{d}\frac{1}{2}-x, -y, z-\frac{1}{2}$; $^{e}x, y, z+1$; $^{f}-\frac{1}{2}-x, -y, z-\frac{1}{2}$; $^{g}-\frac{1}{2}-x, -y, \frac{1}{2}+z$; $^{h}\frac{1}{2}+x, \frac{1}{2}-y, -z$; $^{i}\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; $^{j}\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; $^{k}-\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.

TABLE 6. Bond distances (Å) for isomers **A** and **B** with e.s.d.s in parentheses

	Isomer A	Isomer B
Cr–N(1)	2.088(8)	2.066(14)
Cr–N(2)	2.090(9)	2.081(14)
Cr–N(5)	2.097(9)	2.093(11)
Cr–N(6)	2.071(9)	2.072(13)
Cr–C(9)	2.065(10)	2.087(18)
Cr–C(10)	2.076(12)	2.081(15)
N(1)–C(3)	1.507(14)	1.497(22)
N(2)–C(4)	1.484(15)	1.467(23)
N(5)–C(7)	1.496(15)	1.496(21)
N(6)–C(8)	1.495(15)	1.465(23)
N(11)–C(9)	1.131(14)	1.125(27)
N(12)–C(10)	1.139(16)	1.148(20)
C(3)–C(4)	1.511(17)	1.482(26)
C(3)–C(13)	1.525(17)	1.538(32)
C(4)–N(2)	1.484(15)	1.467(23)
C(7)–N(5)	1.496(15)	1.496(21)
C(7)–C(8)	1.522(17)	1.527(28)
C(8)–C(14)	1.508(18)	
C(7)–C(14)		1.538(29)

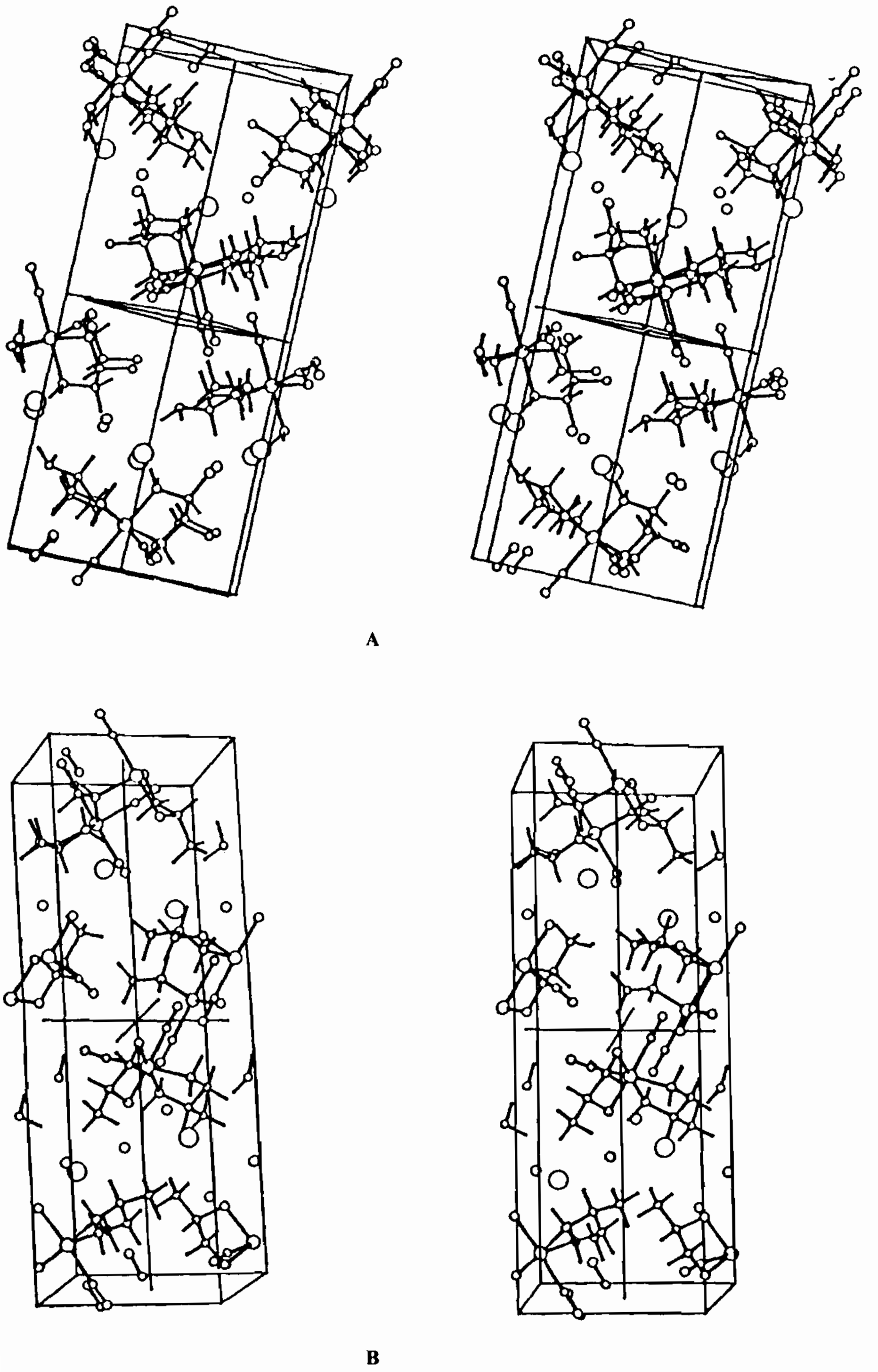


Fig. 3. Stereo drawings of the crystal unit cell of Λ-*cis*-(−)$_{589}$-[Cr(CN)$_2$(*d*-pn)$_2$]Cl·H$_2$O.

bond distances of 2.01–2.11 Å and N–Cr–N angles of 80.0–83.3° in Λ-(+)$_{589}$-[Cr(en)$_3$]Cl$_3$, [8] may be compared with the results of the present study and it is shown that all the distances and angles within the chelate rings of isomers **A** and **B** are regarded as normal. The CH–CH$_2$ bond axis of both chelate rings configurates nearly parallel to the dummy three-fold axis of the complex ion and the CH$_3$ group in both cases orients equatorially with respect to the five-membered metal–

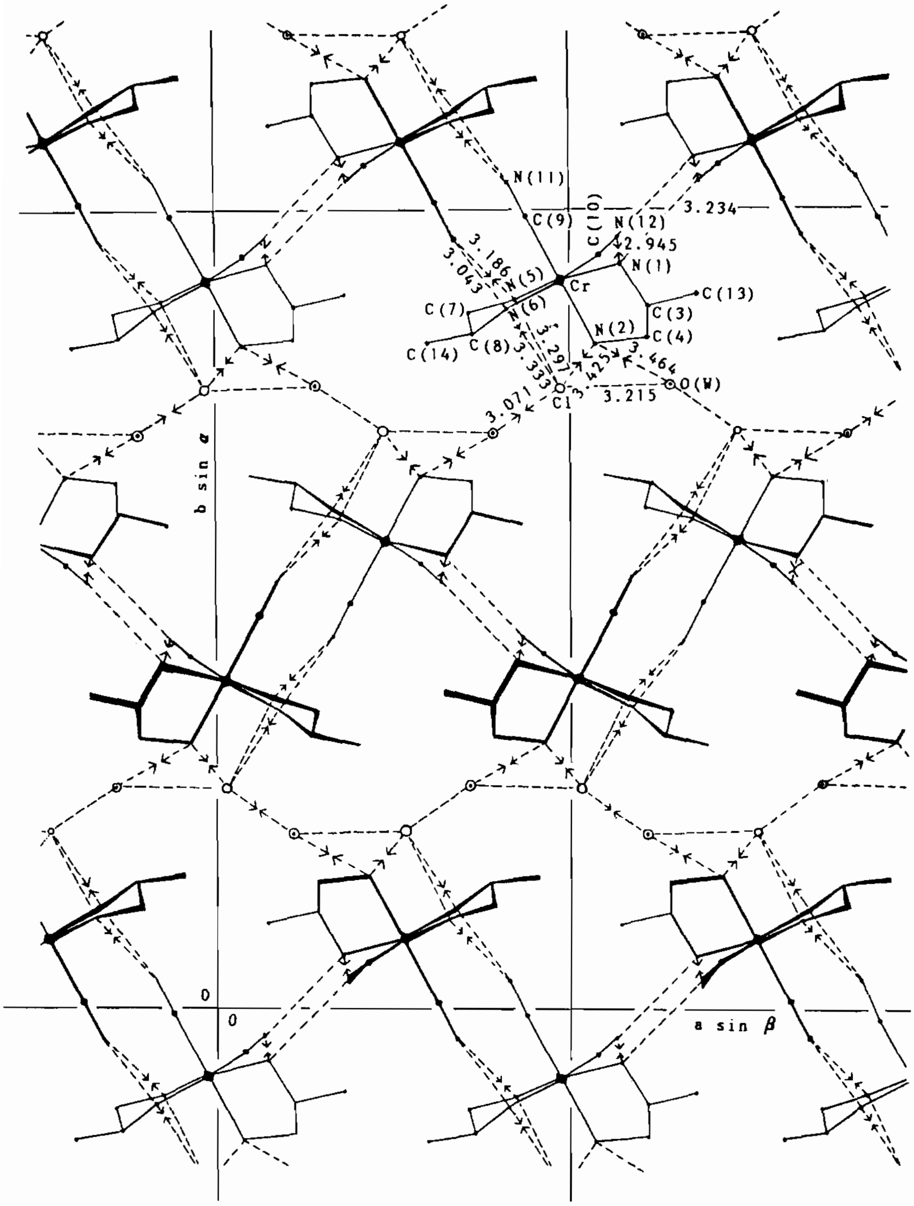


Fig. 4. Projection of the crystal structure along the *c* axis of Λ-*cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-pn})_2]Cl{\cdot}H_2O$ (isomer **A**). Broken lines indicate the evaluated intermolecular distances (Å) and arrows indicate that the atoms concerned are not in the same level.

ligand ring to which it is attached. Both stereoviews of the isomers (Fig. 6) can be suitably described as the most stable Λ-*lel*,*lel*-*e*,*e* conformation (*lel* = parallel, *e* = equatorial), respectively.

As seen from the ORTEP drawings of both isomers, the methyl group, C(13) is bonded to C(3) of the five-membered ring in the equatorial direction. On the other hand, in isomer **A**, the methy group, C(14) is bonded to C(8) of the five-membered ring while in isomer **B** C(14) is bonded to C(7) but not to C(8). The coordination geometry of both isomers **A** and **B** is now clearly shown as follows: isomer **A** corresponds to isomer **I** and isomer **B** corresponds to isomer **II** (Fig. 1).

Separation and properties

The detailed mechanism of the column chromatography by which Λ-*cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-pn})_2]Cl$ is separated into the component geometric isomers is not evident. However, judging from the unavailability of the same chromatography for the separation of *cis*-$(+)_{589}$-$[Cr(CN)_2(l\text{-pn})_2]Cl$ (of which Δ configuration

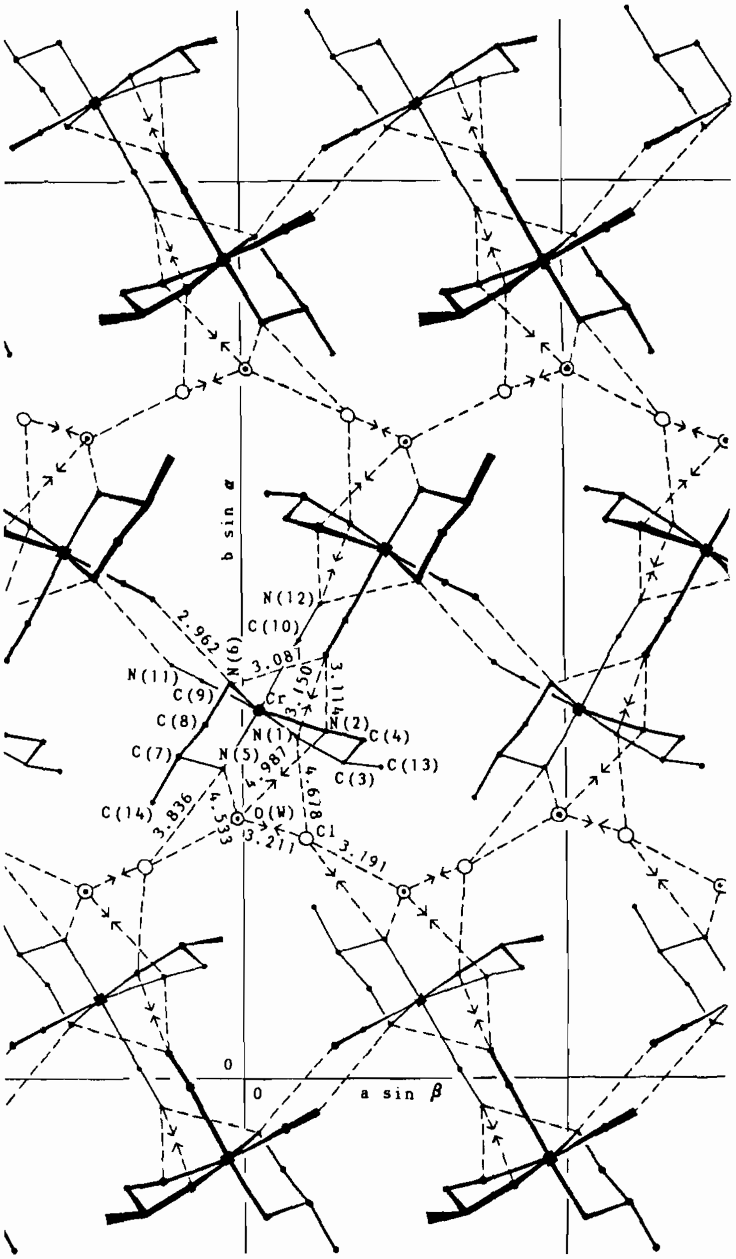
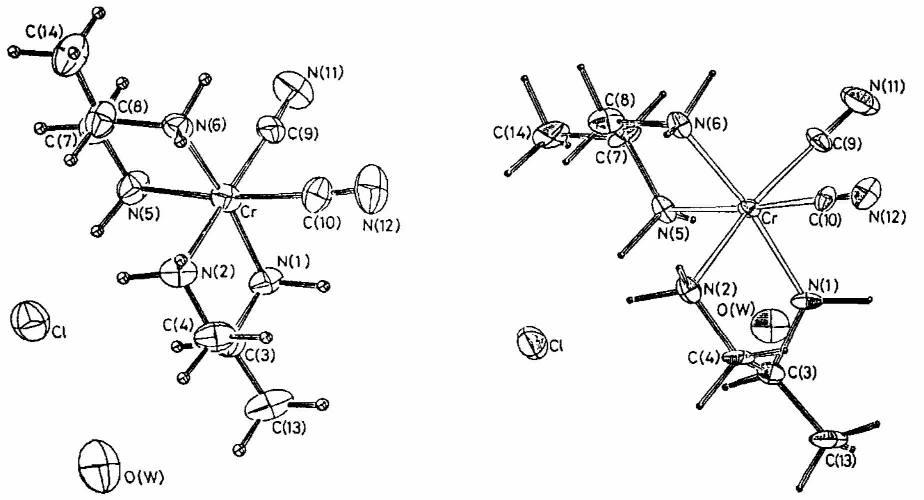


Fig. 5. Projection of the crystal structure along the *c* axis of Λ-*cis*-(−)$_{589}$-[Cr(CN)$_2$(*d*-pn)$_2$]Cl·H$_2$O (isomer **B**). Broken lines indicate the evaluated intermolecular distances (Å) and arrows indicate that the atoms concerned are not in the same level.

has been assumed from its CD spectrum [4]) into the component geometric isomers, the mechanism of separation will be closely related to that proposed by Yoneda and co-workers [9] for their optical resolution of complexes, in which separation depends on the difference in the strength of chiral interaction between the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion and optical (Δ and Λ) isomers.

Under equilibrium conditions, the statistical formation ratio of three geometric isomers **I**, **II** and **III** (Fig. 1) should be **I**:**II**:**III** = 1:2:1, but an actual formation ratio obtained from the elution curve (Fig. 2) is found to be about **A**:**B**:**C** = 9:10:2. We were careful to use a true equilibrium mixture of **A**, **B** and **C** isomers since they have unequal solubilities, which increase in the order of **A**, **B** and **C**. The result—the actual formation ratio disagrees with the statistical one—will suggest energy differences among the isomers. Although the methyl groups are situated fairly well apart in the propylenediamine complex, the difference of relative configuration of the



A **B**

Fig. 6. ORTEP drawings of isomers **A** and **B** of Λ-*cis*-$(-)_{589}$-$[Cr(CN)_2(d\text{-}pn)_2]Cl{\cdot}H_2O$. Atoms are drawn with 30% probability ellipsoids. H atoms are represented by spheres of arbitrary size.

TABLE 7. Bond angles (°) for isomers **A** and **B** with e.s.d.s in parentheses

	Isomer **A**	Isomer **B**
N(1)–Cr–N(2)	82.1(3)	81.4(5)
N(1)–Cr–N(5)	96.5(3)	94.8(5)
N(1)–Cr–N(6)	171.3(3)	173.6(5)
N(1)–Cr–C(9)	95.3(4)	91.5(6)
N(1)–Cr–C(10)	90.3(4)	91.7(5)
N(2)–Cr–N(5)	91.9(4)	92.6(5)
N(2)–Cr–N(6)	89.2(4)	93.2(5)
N(2)–Cr–C(9)	176.9(4)	172.7(6)
N(2)–Cr–C(10)	93.0(4)	86.8(5)
N(5)–Cr–N(6)	83.1(4)	82.1(5)
N(5)–Cr–C(9)	86.7(4)	89.6(5)
N(5)–Cr–C(10)	172.1(4)	173.4(5)
N(6)–Cr–C(9)	93.3(4)	94.0(6)
N(6)–Cr–C(10)	90.7(4)	91.3(5)
C(9)–Cr–C(10)	88.7(4)	91.8(6)
Cr–N(1)–C(3)	109.5(6)	112.1(11)
Cr–N(2)–C(4)	109.5(7)	108.4(11)
Cr–N(5)–C(7)	107.8(7)	107.8(9)
Cr–N(6)–C(8)	110.6(7)	109.6(10)
N(1)–C(3)–C(4)	108.3(9)	107.0(13)
N(1)–C(3)–C(13)	111.6(9)	112.8(16)
C(4)–C(3)–C(13)	112.8(10)	112.7(16)
N(2)–C(4)–C(3)	107.6(9)	110.3(13)
N(5)–C(7)–C(8)	110.2(10)	104.9(13)
N(6)–C(8)–C(14)	112.2(10)	
C(7)–C(8)–C(14)	112.9(10)	
N(5)–C(7)–C(14)		112.7(15)
C(8)–C(7)–C(14)		113.2(16)
N(6)–C(8)–C(7)	107.2(9)	108.8(16)
Cr–C(9)–N(11)	177.1(9)	173.9(15)
Cr–C(10)–N(12)	172.1(10)	178.2(14)

methyl groups would probably cause the large energy difference between the isomers.

The optical rotations and CD and UV–Vis spectral data for the three separated isomers are collected in Table 8. Some obvious differences in optical rotation values and $\Delta\varepsilon$ values of the main CD peak have been observed. As can be seen from Table 8, the intensity of optical properties decreases in the order of isomers **A**, **B** and **C**, but a distinct difference cannot be observed in UV–Vis spectra. Spectral differences also occur in the infrared (at C≡N stretching vibrations near 2140 cm^{-1}, CH_3 rocking near 830 cm^{-1}, Cr–N stretching (590–431 cm^{-1}), and Cr–C stretching or Cr–C–N bending vibrations (408–320 cm^{-1})).

TABLE 8. Optical rotations and CD and UV–Vis spectra of geometric isomers of Λ-*cis*-$[Cr(CN)_2(d\text{-}pn)_2]Cl$

Isomer	Optical rotations (°) $[\alpha]^{20}_{589}$ ($[M]^{20}_{589}$)	CD peaks λ (nm) ($\Delta\varepsilon$)	Absorption maxima λ (nm) (log ε)
Before separation	−55.11 (−168.50)	485(+0.448), 413(−0.204) 352(+0.048)	435(1.87) 339(1.82) 435(1.88)
A	−57.81 (−171.55)	459(+0.484), 413(−0.196) 352(+0.040)	339(1.83) 435(1.87)
B	−51.64 (−157.89)	458(+0.445), 413(−0.191) 351(+0.053)	339(1.83) 435(1.85)
C	−41.59 (−138.40)	457(+0.400), 413(−0.181) 352(+0.054)	339(1.83)

Usually in structural analyses such as in this study, NMR spectral investigations may be effective but in the case of our paramagnetic complex, a large magnetic moment originating from the unpaired 3d electrons of Cr(III) makes the NMR signals obscured.

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