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Metal Complexes Coordinating Pyridine Derivatives. I. Preparation and Circular Dichroism Spectra of *cis*-*α* Isomers of [(*S*)-*N*,*N*′-Bis(2-pyridylmethyl)propylenediamine]dihalogenochromium(III) and -cobalt(III) Complexes

Yukihiro Yamamoto* and Yoichi Shimura

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Several chromium(III) and cobalt(III) complexes with (*S*)-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine (*S*-picpn) were prepared and their structures assigned. The $[CoCl_2(S\text{-picpn})]^+$ complex was reassigned to have *cis*-α configuration. The Δ and Λ diastereomers of $[CrX_2(S\text{-picpn})]^+$ of *cis*-α configuration were obtained ($X=Cl^-$ and Br^-) and their absorption and circular dichroism spectra were discussed.

The structural assignment of $[CoX_2(S\text{-picpn})]^+$ complexes, where *S*-picpn is the abbreviation for (*S*)-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine and X^- stands for an aniono ligand such as Cl^- or Br^- has been the subject of controversy. In 1967 Bosnich prepared several complexes and discussed their circular dichroism (CD) spectra in terms of *cis*-*α* configuration (Fig. 1).[1] Cragel and Brubaker[2] studied the stereospecific formation of such complexes from racemic or resolved picpn ligand, and concluded that in contrast most of the cobalt(III) complexes have *cis*-*β* configuration. Studies on strain energy minimization and conformational analysis[3] of six possible isomers of $[Co(ox)(S\text{-picpn})]^+$ have shown that the strain energy of a *cis*-*α* isomer is the lowest of the six isomers, although the strain energy of some *cis*-*β* isomers differs from that of the lowest *α*-isomer by only a few percent.

The corresponding ethylenediamine analogue ligand, *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (abbrev. picen), also forms several cobalt(III) complexes.[4] The structures of two isomers of dichloro complex $[CoCl_2(picen)]^+$, a purple and a cherry-red one, were definitely assigned by Gibson and McKenzie to *cis*-*α* and *cis*-*β* configurations, respectively, from their PMR spectra.[4a] Michelsen[5] prepared the *cis*-*α* and *cis*-*β* isomers of dichloro chromium(III) complexes, and also studied chromium(III) complexes of some analogous bidentate ligands, *i.e.*, 2-pyridylmethylamine[6] and 1-(2-pyridyl)ethylamine.[7]

The present paper deals with the preparation of several dianiono *S*-picpn chromium(III) and cobalt(III) complexes, their structures being discussed along with the absorption and CD spectra.

Experimental

Ligands. The ligands *S*-picpn and picen were prepared from (*S*)-propylenediamine or ethylenediamine and 2-pyridinecarbaldehyde by the method of Goodwin and Lions.[8]

Cobalt(III) Complexes. $(+)^{\rm CD}_{600}$-$[CoCl_2(S\text{-}picpn)]Cl\cdot H_2O$: A portion of $Na_3[Co(NO_2)_6]$ was dissolved in water, and an equimolar amount of *S*-picpn was added with stirring. A yellowish orange precipitate was formed. This is supposed to be $[Co(NO_2)_2(S\text{-picpn})]NO_2$. After cooling in an ice bath, the product was collected and washed with ether; this was suspended in a small amount of concd hydrochloric acid and evaporated to dryness on a steam bath. The violet residue was dissolved in warm dilute hydrochloric acid (*ca.* 6 M (1 M= 1 mol dm^{-3})) and cooled in an ice bath. Violet crystals were obtained; $\Delta\varepsilon_{600}=+1.67$. Found: C, 41.29; H, 4.84; N, 12.85%. Calcd for $CoC_{15}H_{20}N_4Cl_3\cdot H_2O$: C, 40.98; H, 5.04; N, 12.74%. The CD spectrum in the region of 15000—50000 cm^{-1} was the same as that of a $[CoCl_2(S\text{-picpn})]^+$ complex which was erroneously assigned to *cis*-*β* configuration by Cragel and Brubaker.[2]

$(+)^{\rm CD}_{600}$-$[CoCl_2(S\text{-}picpn)]ClO_4$: The violet residue mentioned above was dissolved in water to which was added sodium perchlorate. After the solution had been left to stand overnight in a refrigerator, violet crystals were obtained. Recrystallization was performed from a small amount of warm dilute hydrochloric acid; $\Delta\varepsilon_{600}=+1.67$. Found: C, 36.89; H, 4.20; N, 11.55%. Calcd for $CoC_{15}H_{20}N_4O_4Cl_3$: C, 37.10; H, 4.15; N, 11.54%.

cis-*α*-$[CoCl_2(picen)]Cl$: The complex, prepared by the method of Michelsen[5] and for which the *cis*-*α* configuration has been confirmed,[4a] was partially resolved on an SP-Sephadex C-25 column when eluted with a 0.25 M sodium antimony(III) $(+)_{589}$-tartrate aqueous solution. The CD spectrum of the former fractions of the eluted band is opposite in the sign to that of $(+)^{\rm CD}_{600}$-$[CoCl_2(S\text{-picpn})]Cl$, showing a negative band at 16670, positive ones at 19230 and 23810, and a negative one at 30300 cm^{-1} (Fig. 3). The latter fractions exhibited the same CD pattern of opposite sign.

Chromium(III) Complexes. $(-)^{\rm CD}_{600}$-$[CrF_2(S\text{-}picpn)]Br\cdot LiBr\cdot 3H_2O$: *S*-picpn (2.5 g, 9.9 mmol) was dissolved in a solution of *trans*-$[CrF_2(py)_4]Br\cdot 2H_2O$[9] (5.17 g, 9.9 mmol) and 20 cm^3 of 2-methoxyethanol. The solution was heated on a water bath with occasional stirring until it became sticky. To the resulting solution were added a small amount of water, an ethanol solution (20 cm^3) of 10 g LiBr, and then 50 cm^3 of an ethanol–ether mixture (1 : 1). After standing the solution overnight in a refrigerator, a violet precipitate was filtered, the precipitate mainly consisting of the starting complex, *trans*-$[CrF_2(py)_4]Br$. To the filtrate were added 20 cm^3 of methanol and 400 cm^3 of acetone, and an oily material obtained by decantation was dissolved in 10 cm^3 of water; then an ethanol solution (20 cm^3) of 10 g LiBr and 150 cm^3 of acetone were added. By scratching with a glass rod and cooling, the desired violet crystals were precipitated, the precipitate showing a CD spectrum. The violet crystals were washed with acetone and dried in the air. The substance was adsorbed on an SP-Sephadex C-25 column (ϕ10× 200 mm) and eluted with a 0.1 M sodium chloride aqueous solution in order to confirm the purity of the complex; all fractions showed the same CD spectra: $\Delta\varepsilon_{600}=-1.61$. Found: C, 31.78; H, 4.71; N, 9.84%. Calcd for $CrC_{15}H_{20}N_4F_2Br\cdot LiBr\cdot 3H_2O$: C, 31.77; H, 4.62; N, 9.88%.

$(-)^{\rm CD}_{600}$-$[CrCl_2(S\text{-}picpn)]Cl\cdot 0.5NaCl$: In dimethyl sulfoxide

(10 cm^3) was suspended anhydrous chromium(III) chloride (3.2 g, 20 mmol), and *S*-picpn (5.07 g, 20 mmol) was added to it with stirring at room temperature. After 1 h, the unreacted chromium(III) chloride was filtered off and washed with a small amount of water. The filtrate and washings were adsorbed on an SP-Sephadex C-25 column ($\phi 45\times 600$ mm) and eluted with a 0.1 M sodium chloride aqueous solution acidified with hydrochloric acid (0.12 M). Four colored bands, (i) violet, (ii) red-violet, (iii) blue-violet, and (iv) dirty violet, were eluted in this order. A dark green band appearing between bands (i) and (ii) turned red after being eluted from the column. Eluate (i) was condensed to a small volume with a vacuum rotary evaporator below 40 °C, red-violet crystals being separated. They were filtered and washed with cold water and ether: $\Delta\varepsilon_{600}=-1.26$. Found: C, 40.13; H, 4.54; N, 12.54%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Cl_3\cdot 0.5NaCl}$: C, 40.58; H, 4.54; N, 12.62%. The CD spectrum of the latter half of eluate (i) showed the opposite sign to that of the former half, indicating that the band contains two diastereomers. However, the crystals obtained above showed the same CD spectrum as that of the former half of eluate (i). Eluate (ii) was condensed to a small volume. The crystals obtained were collected but no pure crystals obtained in spite of repeated recrystallization. Their absorption spectrum indicates that band (ii) contains $[\mathrm{Cr(OH)(H_2O)}(S\text{-picpn})]^{2+}$ ions. Eluate (iii) and (iv) were adsorbed so tightly to the Sephadex column that they could not be eluted with a 0.1 M sodium chloride aqueous solution. They were eluted with a 0.25 M sodium chloride aqueous solution, but broadened through the column. They may be some polynuclear complexes.

$(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{ClO_4}$: $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl\cdot 0.5NaCl}$ was dissolved in water, and sodium perchlorate was added to the solution. A dark violet precipitate was soon formed. After filtering and washing with ethanol and ether, the product was air-dried: $\Delta\varepsilon_{600}=-1.26$. Found: C, 37.44; H, 4.21; N, 11.61%. Calcd for $\mathrm{CrC_{15}H_{20}N_4O_4Cl_3}$: C, 37.64; H, 4.21; N, 11.70%.

$(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{I}$: $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrF_2}(S\text{-picpn})]\mathrm{Br\cdot LiBr\cdot 3H_2O}$ was dissolved in a small volume of concd hydrochloric acid in a flask (50 cm^3). The mixture was saturated with gaseous hydrogen chloride below −13 °C, and the flask was stoppered tightly and left to stand at room temperature for 3 d. After cooling, the flask was opened. Sodium iodide was added to the red-violet solution with stirring, the violet precipitate being filtered promptly and washed with acetone. Recrystallization was carried out by dissolving it in hot water (70 °C): $\Delta\varepsilon_{600}=-1.26$. Found: C, 35.31; H, 3.94; N, 11.08%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Cl_2I}$: C, 35.59; H, 3.98; N, 11.07%.

$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{I\cdot 0.5H_2O}$: One gram of chromium shot (19.2 mmol) was dissolved in a 50 cm^3 flask containing 15 cm^3 of concd hydrochloric acid under a current of nitrogen. The resulting solution was evaporated and heated to dryness in a vacuum rotary evaporator to obtain chronium(II) chloride. To the flask was added *S*-picpn (4.9 g, 19.4 mmol, in 20 cm^3 pyridine) and the mixture was heated, a solution of iodine (2.4 g, 9.5 mmol, in 8 cm^3 pyridine) being added. The reaction was carried out by refluxing for 20 min. After cooling, the violet precipitate was filtered and washed with ethanol. The crude product (0.78 g) was suspended in 10 cm^3 of water, and 0.2 g of freshly prepared silver chloride was added with stirring. The silver salt precipitated was filtered off. The filtrate was adsorbed on an SP-Sephadex C-25 column ($\phi 20\times 300$ mm) and eluted with a 0.1 M sodium chloride aqueous solution acidified with hydrochloric acid (0.1 M), only one band being eluted. The band was collected in 15 fractions, all fractions except for the last two showing the same CD pattern. The first 13 fractions were combined and condensed with a rotary evaporator below 40 °C. To the concentrated solution was added sodium iodide. On cooling, violet crystals were obtained. They were recrystallized from water: $\Delta\varepsilon_{600}=+0.89$. Found: C, 33.87; H, 3.94; N, 10.55%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Cl_2I\cdot 0.5H_2O}$: C, 34.97; H, 4.11; N, 10.88%.

$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl\cdot 0.5H_2O}$: The dichloro iodide, $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{I}$, was suspended in water and silver chloride was added to it. The silver salt was filtered. Concd hydrochloric acid was added to the filtrate and the solution was cooled in an ice bath. Violet crystals were obtained. $\Delta\varepsilon_{600}=+0.89$. Found: C, 42.61; H, 4.87; N, 13.12%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Cl_3\cdot 0.5H_2O}$: C, 42.52; H, 5.00; N, 13.22%.

$(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrBr_2}(S\text{-picpn})]\mathrm{Br\cdot 0.5LiBr\cdot 0.5H_2O}$: The difluoro bromide, $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrF_2}(S\text{-picpn})]\mathrm{Br\cdot LiBr\cdot 3H_2O}$ (1.15 g), was suspended in a small amount of 47% hydrobromic acid in a flask. Gaseous hydrogen bromide was bubbled into the mixture below −13 °C for 5 min, and the flask was stoppered tightly and left to stand at room temperature for 3 d. After cooling, the violet precipitate was filtered and washed with ethanol and ether. By adding a mixture of ethanol–ether (1:1) to the filtrate, more crystals were obtained. Recrystallization was carried out by dissolving the combined precipitate in hot water (70 °C) acidified with 47% hydrobromic acid (1 M). The bromide salt was sparingly soluble in water: $\Delta\varepsilon_{600}=-1.10$. Found: C, 29.94; H, 3.48; N, 9.22%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Br_3\cdot 0.5\,LiBr\cdot 0.5H_2O}$: C, 30.00; H, 3.52; N, 9.33%.

$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrBr_2}(S\text{-picpn})]\mathrm{I\cdot 0.25H_2O}$: One gram (19.2 mmol) of chromium shot was dissolved in a 50 cm^3 flask containing a mixture of 47% hydrobromic acid (3 cm^3) and water (2 cm^3) under a current of nitrogen. The resulting solution was evaporated in a vacuum rotary evaporator to give chromium(II) bromide which was heated to dryness. To the flask was added *S*-picpn (4.8 g, 19.2 mmol, in 30 cm^3 pyridine) and the mixture was heated and then a solution of iodine (2.4 g, 9.5 mmol, in 8 cm^3 pyridine) was added. The reaction was carried out by refluxing for 20 min. After cooling, the red violet precipitate was filtered. This was mainly "diol complex," $[\{\mathrm{Cr(OH)}(S\text{-picpn})\}_2]\mathrm{I_4}$, which was characterized by elemental analysis, absorption, and CD spectrum.[5] Found: C, 29.21; H, 3.84; N, 9.10%. Calcd for $\mathrm{Cr_2C_{30}H_{42}N_8O_2I_4\cdot 2.5H_2O}$: C, 29.94; H, 3.94; N, 9.31%.

To the filtrate was added *ca.* 30 cm^3 of ethanol, a small amount of violet precipitate being obtained. This was $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrBr_2}(S\text{-picpn})]\mathrm{I}$. More ethanol was added and the precipitate obtained was filtered. After standing the filtrate for a month, violet powder less soluble in water than the $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrBr_2}(S\text{-picpn})]\mathrm{I}$ complex was precipitated. The crude product was washed on a glass filter with a small amount of water (70 °C), the residue being extracted with a large amount of hot water (70 °C). To the extracted solution was added sodium iodide and the resulting solution was cooled in an ice bath. The violet crystals obtained were washed with ethanol–ether (1: 1) and then air-dried: $\Delta\varepsilon_{600}=+0.78$. Found: C, 29.48; H, 3.35; N, 9.19%. Calcd for $\mathrm{CrC_{15}H_{20}N_4Br_2I\cdot 0.25H_2O}$: C, 30.05; H, 3.45; N, 9.35%.

$(-)^{\mathrm{CD}}_{600}$-$[\mathrm{Cr(NCS)_2}(S\text{-picpn})]\mathrm{SCN}$: The dichloro chloride, $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$ (0.5 g), and an excess potassium thiocyanate were dissolved in water, and the solution was heated to boiling. The original violet solution turned red. After cooling, the precipitate was filtered and recristallized twice from water; $\Delta\varepsilon_{600}=-0.08$. Found: C, 44.97; H, 4.20; N, 20.48%. Calcd for $\mathrm{CrC_{18}H_{20}N_7S_3}$: C, 44.80; H, 4.18; N, 20.32%.

cis-α-[$CrCl_2$(picen)]Cl: The complex prepared by the method of Michelsen[5] was partially resolved by the same method as for *cis-α*-[$CoCl_2$(picen)]Cl. The CD spectrum of the former part of the eluted band showed a negative value at 17150, a positive one at 19420, a negative one at 36360, and a negative one at 37310 cm^{-1} (Fig. 4); this is similar to the spectra of $(-)_{589}$-[$CrCl_2$(picen)]ClO_4[7] and $(-)^{\mathrm{CD}}_{600}$-[$CrCl_2$(*S*-picpn)]Cl.

cis-α-[$CrCl_2$(trien)]Cl: The complex[10] was partially resolved by the same method as for *cis-α*-[$CoCl_2$(picen)]Cl. The complex was adsorbed on an SP-Sephadex C-25 column ($\phi 15\times 300$ mm) and eluted with a 0.25 M sodium antimony(III) $(+)_{589}$-tartrate aqueous solution. The CD spectrum of the former fractions was opposite in sign to that of the latter fractions (Fig. 4).

Measurements. The visible and ultraviolet absorption spectra were obtained with a Shimadzu UV-200 spectrophotometer and the CD spectra with a JASCO MOE-1 spectropolarimeter. The absorption and CD spectra were measured in 0.1 M hydrochloric acid for the dichloro and dibromo complexes, and in water for the other complexes. The X-ray powder patterns were measured with Cu *Kα* radiation for the chromium(III) complexes and with Co *Kα* radiation for the cobalt(III) complexes. The IR spectra were run as nujol mulls on a JASCO DS-402G spectrophotometer.

Results and Discussion

Structural Assignments. *$(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(S-picpn)]$^+$*: Three geometrical configurations, *cis-α*, *cis-β*, and *trans* (Fig. 1)[11] are possible in general for an octahedral complex coordinating a linear tetradentate ligand. Both *cis-α* and *cis-β* configurations have several optically active isomers and their classifications is made in two steps. (1) In a [MX_2(picen)]$^+$ complex, Δ and Λ configurations exist for each of the *cis-α* and *cis-β* isomers. (2) Chirality of the coordinated secondary amine nitrogens should be considered for each configuration, *viz*., only one (*R*,*R*) pair of asymmetric nitrogen is possible for the Δ-*cis-α* configuration and only one (*S*,*S*) for the Λ-*cis-α*. In the *cis-β* configuration, the two nitrogen atoms differ from each other and are distinguished by numbering N_1 and N_2 for those located at the center of N–N–N moieties coordinated facially and meridionally, respectively. Thus (R^1,R^2) and (R^1,S^2) isomers exist for the Λ-*cis-β* configuration, and (S^1,S^2) and (S^1,R^2) for the Δ-*cis-β*. For the case of [$CoCl_2$(*S*-picpn)]$^+$, the number of possible isomers of the *cis-β* configuration doubles the above number because of non-symmetrical disposition of the methyl substituent. Thus two structures are possible for the *cis-α* configuration and eight for *cis-β*. It is well established that the methyl substituent of propylenediamine type moiety prefers the equatorial orientation in octahedral complexes.[12] Two of the ten possible isomers are shown in Fig. 2.

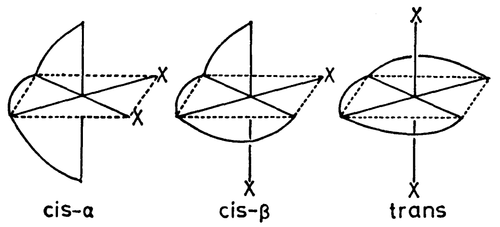

Fig. 1. Three geometrical isomers of [MX_2(linear tetradentate)]$^+$.

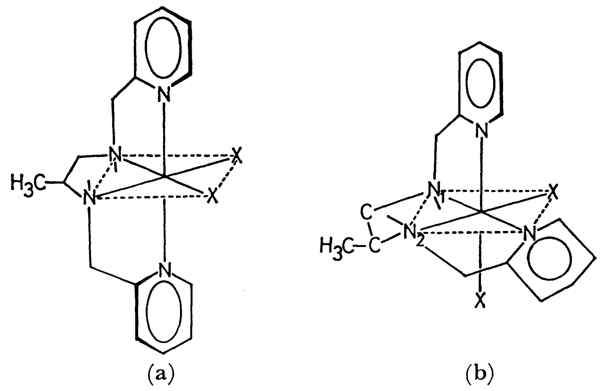

Fig. 2. Two configurations of [MX_2(*S*-picpn)]$^+$ (a) Λ-*cis-α*-(*SR*): this corresponds to the (*S*,*S*) isomer of picen complex. (b) Δ-*cis-β*-(S^1,R^2): this corresponds to the (S^1,S^2) isomer of picen complex.

The CD spectrum of $(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(*S*-picpn)]Cl prepared in the present study (Fig. 3) is in good agreement with the data of Cragel and Brubaker on their "*cis-β*" form.[2] On the other hand, the *cis-α*-[$CoCl_2$(picen)]$^+$ complex, assigned to this configuration,[4a] was resolved by SP-Sephadex column chromatography, and the CD spectrum (dotted line) is very similar in pattern to that of the $(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(*S*-picpn)]Cl complex. Thus, the $(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(*S*-picpn)]Cl complex is considered to take the *cis-α* configuration. The "*cis-β*" assignment by Cragel and Brubaker for this complex seems to be incorrect.

The CD spectrum of $(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(*S*-picpn)]Cl shows a positive (longer wavelength) and a negative (shorter wavelength) extremum in the first absorption band region. In order to assign the absolute configuration

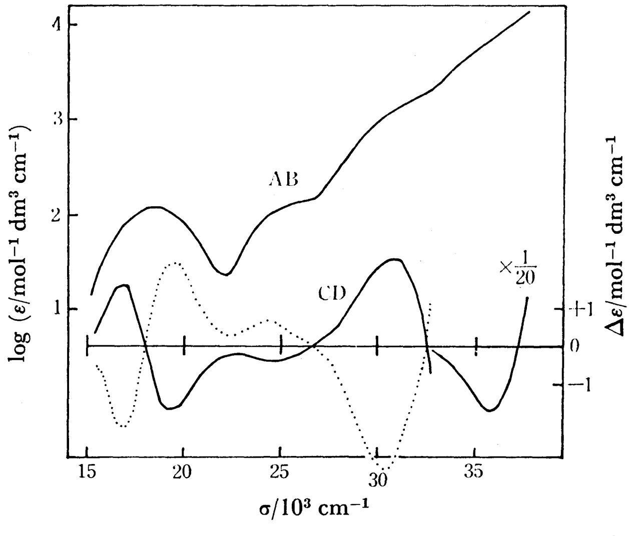

Fig. 3. The absorption (AB) and CD spectra of $(+)^{\mathrm{CD}}_{600}$-[$CoCl_2$(*S*-picpn)]Cl (——), and the qualitative CD spectrum of former fraction of [$CoCl_2$(picen)]$^+$ eluted with sodium antimony(III) $(+)_{589}$-tartrate (···).

TABLE 1. ABSORPTION AND CD DATA OF *cis*-α- AND *cis*-β-$[\mathrm{CoCl_2(tetradentate)}]^+$ COMPLEXES[a)]

Ligand	Configuration	Absorption		CD		Ref.
		$\sigma_{\mathrm{max}}/\mathrm{cm}^{-1}$	$\log\varepsilon$[d)]	$\sigma_{\mathrm{ext}}/\mathrm{cm}^{-1}$	$\Delta\varepsilon$[d)]	
(*S*)-picpn	*Δ-cis-α*	18520	2.10	16670	+1.67	b)
				19230	−1.65	
		26040 sh	2.13	24510	−0.41	
				30490	+2.34	
(3*S*,8*S*)-dimetrien	*Λ-cis-α*	18450	2.09	16340	−1.49	13)
				18940	+2.78	
		26040	2.02	24270	+0.59	
				27100	−0.57	
(2*S*,9*S*)-dimetrien	*Λ-cis-α*	18350	2.09	16290	−1.71	13)
				18690	+2.19	
		25970	2.04	24100	+0.35	
				26810	−0.89	
(3*S*,8*S*)-dimetrien	*Δ-cis-β*	18420	2.11	18690	−1.18	13)
		25190	2.10	24330	−0.60	
(2*S*,9*S*)-dimetrien	*Δ-cis-β*	18800	2.21	19050	−1.55	13)
		25320	2.18	24630	−0.40	
bnpic	*Δ-cis-β*	19000		17000	−0.31	15)[c)]
				20000	−0.80	

a) Abbreviations of ligands: (3*S*,8*S*)-dimetrien= (2*S*,7*S*)-2,7-dimethyl-3,6-diazaoctane-1,8-diamine; (2*S*,9*S*)-dimetrien= (1*S*,8*S*)-1,8-dimethyl-3,6-diazaoctane-1,8-diamine; bnpic= (2*S*,3*S*)-*N*,*N*′-bis(2-pyridylmethyl)-2,3-butanebiamine. b) This work; sh=shoulder. c) Values taken from the figure in the paper. d) Given in $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ unit.

of this complex, the CD spectrum was compared with those of the *cis*-α-$[\mathrm{CoCl_2(dimetrien)}]^+$ (dimetrien= dimethyl derivative of triethylenetetramine) complexes (Table 1). The *Λ-cis*-α-$[\mathrm{CoCl_2(dimetrien)}]^+$ complexes show a negative and then a positive CD extremum from the lower energy side in the first absorption band region, while the corresponding *cis*-β complex show no such dispersion type pattern.[13,14] Thus, it is confirmed that the $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CoCl_2}(S\text{-picpn})]^+$ complex has *Δ-cis-α* configuration. Bosnich and Kneen prepared the *Δ-cis-β*-$[\mathrm{CoCl_2(bnpic)}]\mathrm{Cl}$ complex,[15] which shows no dispersion type CD pattern (bnpic=(2*S*,3*S*)-*N*,*N*′-bis(2-pyridylmethyl)-2,3-butanediamine). Gibson and McKenzie,[4a] and Michelsen[5] prepared the *cis*-β dichloro complex with the picen ligand, but the *cis*-β complex of the *S*-picpn ligand was not formed by our methods. The reason why the *cis*-β complex could not be prepared for this ligand is unknown.

$(+)^{\mathrm{CD}}_{600}$- and $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$: The CD spectrum of $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$ shown in Fig. 4 (broken line) is quite enantiomeric to the qualitative CD spectrum (dotted line) of *cis*-α-$[\mathrm{CrCl_2(picen)}]$,[5] which was resolved by a chromatographic method. Thus, the $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$ complex is assigned to the *cis*-α configuration. The IR spectra of the two complexes, $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CoCl_2}(S\text{-picpn})]\mathrm{Cl}$ and $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$, were measured, and the wave numbers of the absorption bands corresponding to the $\mathrm{CH_2}$-rocking and -twisting are given in Table 2. The peak positions of the two complexes almost agree. The IR data of another complex, $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$, also given in Table 2, differ from those of the former two

TABLE 2. INFRARED ABSORPTION OF $[\mathrm{MCl_2}(S\text{-picpn})]$ Cl COMPLEXES (M=Co and Cr)

	$(+)^{\mathrm{CD}}_{600}$-Co	$(+)^{\mathrm{CD}}_{600}$-Cr	$(-)^{\mathrm{CD}}_{600}$-Cr
$\mathrm{CH_2}$-rocking	868	868	885
(860—940 $\mathrm{cm^{-1}}$)	932	932	901
$\mathrm{CH_2}$-twisting	1005	1008	
(980—1100 $\mathrm{cm^{-1}}$)	1035	1033	1028
	1060	1057	1040
	1072	1070	1057
	1098	1095	

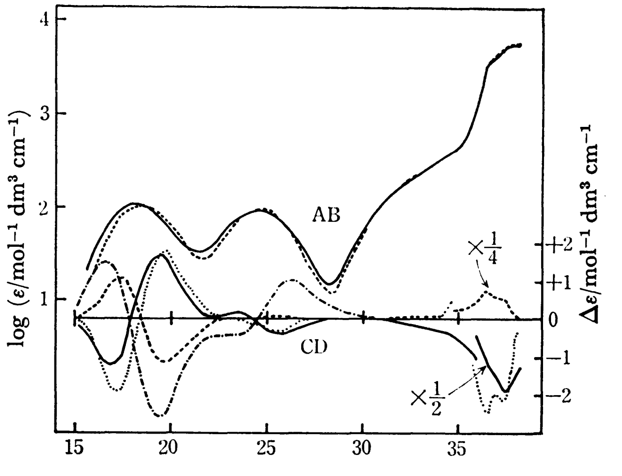

Fig. 4. The absorption (AB) and CD spectra of $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$ (-----), and $(-)^{\mathrm{CD}}_{600}$-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$ (——); and the qualitative CD spectra of *cis*-α-$[\mathrm{CrCl_2(picen)}]^+$ (····) and *cis*-α-$[\mathrm{CrCl_2(trien)}]^+$ (latter fraction) (-·-·-).

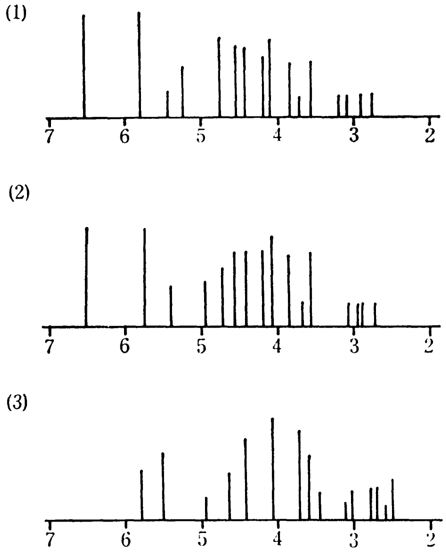

Fig. 5. The X-ray powder patterns: The *d*-spacings (in Å) of the complexes, $(+)^{\rm CD}_{600}$-[$CoCl_2$(*S*-picpn)]ClO_4 (1), $(+)^{\rm CD}_{600}$-[$CrCl_2$(*S*-picpn)]ClO_4 (2), and $(-)^{\rm CD}_{600}$-[$CrCl_2$(*S*-picpn)]ClO_4 (3).

$(+)^{\rm CD}_{600}$ complexes. Results of measurement of X-ray powder patterns of the three complexes (perchlorate salts) are shown in Fig. 5. The patterns of the cobalt(III) and the $(+)^{\rm CD}_{600}$ chromium(III) complexes are very similar but that of the $(-)^{\rm CD}_{600}$ chromium(III) complex is different. The CD spectra of the *Δ-cis-α*-$(+)^{\rm CD}_{600}$-[$CoCl_2$(*S*-picpn)]Cl, $(+)^{\rm CD}_{600}$-[$CrCl_2$(*S*-picpn)]Cl, and *cis*-*α*-[$CrCl_2$(trien)]$^+$ (latter fractions) complexes show a similar pattern (a positive and then a negative sign from the lower energy side) in the first absorption band region but that of the $(-)^{\rm CD}_{600}$-[$CrCl_2$(*S*-picpn)]Cl complex shows the opposite dispersion type pattern (Fig. 4). It can be concluded that the former three complexes have the same *Δ-cis-α* configuration and the latter one *Λ-cis-α*. The latter *Λ-cis-α* configuration has been expected to be more unstable than the *Δ-cis-α* configuration from a strain energy minimization calculation.[3] This trend is reflected on the observed positions of the first absorption bands, *viz*., the first absorption band (18180 cm^{-1}) of the *Λ* complex is in the slightly lower energy side than that (18520 cm^{-1}) of the *Δ* complex.

The Other Complexes: Absorption and CD spectra are shown on Figs. 6 and 7; the data are given in Table 3. Since the fluoro, chloro, bromo, and isothiocyanato ligands lie in the same (weaker) side on the spectrochemical series as compared with organic amine ligands,[16] the CD patterns of the fluoro, bromo, and isothiocyanato complexes are expected to resemble those of the corresponding chloro complexes in the first absorption band region, as seen in Table 3. All the complexes are assigned to the *cis-α* configuration, and the complexes which show a positive and then a negative CD extremum from the lower energy side in the first absorption band region to the *Δ-cis-α* configuration. The complexes with the inverse sign can be assigned to the *Λ-cis-α* configuration.

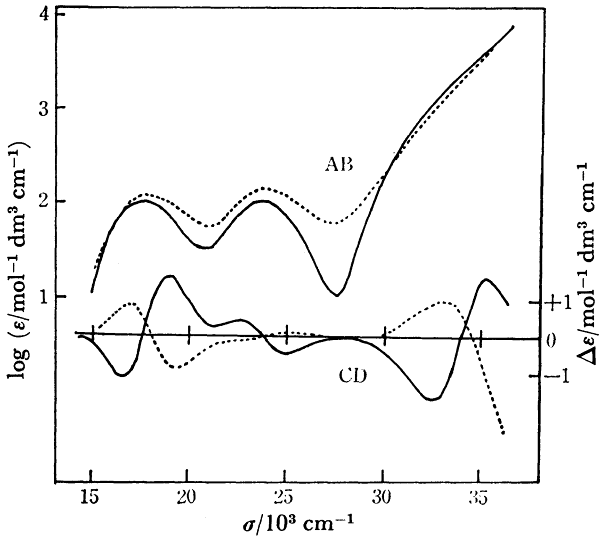

Fig. 6. The absorption (AB) and CD spectra of $(+)^{\rm CD}_{600}$-[$CrBr_2$(*S*-picpn)]I (-----) and $(-)^{\rm CD}_{600}$-[$CrBr_2$(*S*-picpn)]Br (——).

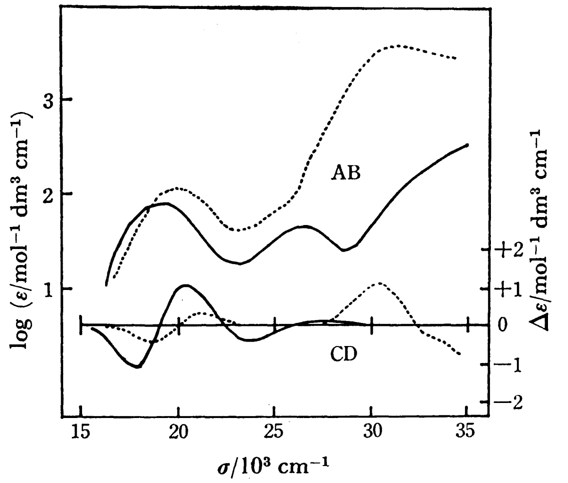

Fig. 7. The absorption (AB) and CD spectra of $(-)^{\rm CD}_{600}$-[CrF_2(*S*-picpn)]Br (——) and $(-)^{\rm CD}_{600}$-[$Cr(NCS)_2$(*S*-picpn)]SCN (-----).

Spectral Properties: The wave number of the first absorption band maximum of the *Λ-cis-α*-[$CrBr_2$(*S*-picpn)]$^+$ complex is slightly smaller than that of the *Δ-cis-α*-[$CrBr_2$(*S*-picpn)]$^+$ complex (Table 3). The same trend was observed between the corresponding dichloro complexes, suggesting that the *S*-picpn ligand is strained to a greater extent in the *Λ-cis-α* configuration than in the *Δ-cis-α* one. The CD strength in the first absorption band region increases in the order $NCS < F < Br < Cl$.

The complexes [$CrCl_2$(*S*-picpn)]$^+$ and [CrF_2(*S*-picpn)]$^+$ show a broad absorption band of low intensity (log $\varepsilon = 1.2$—2.6) in the region 30000—35000 cm^{-1}, where weak CD bands are observed. The low intensity absorption band might correspond to the third d-d band due to two electron excitation. An alternative explanation is to assign it to a $d \rightarrow \pi^*$ transition.[17] A similar band was observed in the [$Ni(phen)_3$]$^{2+}$ and [$Ni(bpy)_3$]$^{2+}$ complexes[18] in the region 22200—28600 cm^{-1} (phen=1,10-phenanthroline and bpy=2,2′-bi-

TABLE 3. ABSORPTION AND CD DATA OF CHROMIUM(III) COMPLEXES OF *cis*-α CONFIGURATION

Complex	Absorption		CD	
	σ_{max}/cm^{-1}	$\log \varepsilon^{a)}$	σ_{ext}/cm^{-1}	$\Delta\varepsilon^{a)}$
Δ-[$CrCl_2$(*S*-picpn)]Cl	18520	2.01	17240	+1.13
			19610	−1.21
	24630	2.01	25250	+0.08
			36230	+3.13
			37040	+2.44
Δ-[$CrBr_2$(*S*-picpn)]I	17910	2.07	16950	+0.82
			19270	−0.87
	23920	2.16	25060	+0.08
			33000	+0.95
Δ-[$CrCl_2$(picen)]ClO_4	18350	2.02	17240	+1.15
			19610	−1.16
	24510	2.01	25510	+0.12
			36320	+2.79
			36900	+2.28
			37230	+2.57
Λ-[CrF_2(*S*-picpn)]Br	19120	1.91	17450	−1.13
			22620	+1.08
	26460	1.69	23580	−0.43
			27550	+0.08
Λ-[$CrCl_2$(*S*-picpn)]Cl	18180	2.00	16890	−1.29
			19230	+1.70
	24510	1.97	23420	+0.19
			25450	−0.42
			37310	−7.96
Λ-[$CrBr_2$(*S*-picpn)]Br	17700	2.02	16530	−1.12
			18870	+1.60
	23810	2.03	22680	+0.43
			24840	−0.50
Λ-[$Cr(NCS)_2$(*S*-picpn)]-SCN	19960	2.07	18690	−0.42
			21190	+0.34
			30300	+1.11
	31350	3.59		

a) Given in $mol^{-1}\ dm^3\ cm^{-1}$ unit.

pyridine). The bands in the present chromium(III) complexes seem to correspond to the "Ir(III)–pyridine band."[17] No such band is observed in the [$CrBr_2$(*S*-picpn)]$^+$ and [$CoCl_2$(*S*-picpn)]$^+$ complexes, in which the band is covered by charge transfer bands due to the bromo or chloro ligands.[19]

In the [CrX_2(*S*-picpn)]$^+$ complex, three kinds of chiralities should be considered: configurational (Δ and Λ), asymmetric carbon atoms (*S*), and conformational of the central chelate ring (δ and λ). Since the chiralities of the secondary amine nitrogen atoms in the *cis*-α complex depend on configurational chirality, the contributions of these two chiral nitrogen atoms are combined with that of the chirality Δ or Λ.

By applying the additivity rule,[20] CD contributions for the three complexes, Λ-*cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ (1), Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ (2), and Λ-*cis*-α-[$CrCl_2$(picen)]$^+$ (3), are written as follows.

$$\Delta\varepsilon(1) = \Lambda + \delta + S \qquad \text{(i)}$$

$$\Delta\varepsilon(2) = \Delta + \delta + S \qquad \text{(ii)}$$

$$\Delta\varepsilon(3) = \Lambda + \lambda \qquad \text{(iii)}$$

The vicinal contribution (δ+*S*) of the ligand *S*-picpn is calculated by 1/2{(1)+(2)}:

$$\frac{1}{2}\{\Delta\varepsilon(1)+\Delta\varepsilon(2)\} = \delta + S$$

The configurational contribution (Λ) is calculated by 1/2{(1)−(2)}:

$$\frac{1}{2}\{\Delta\varepsilon(1)-\Delta\varepsilon(2)\} = \Lambda \qquad \text{(iv)}$$

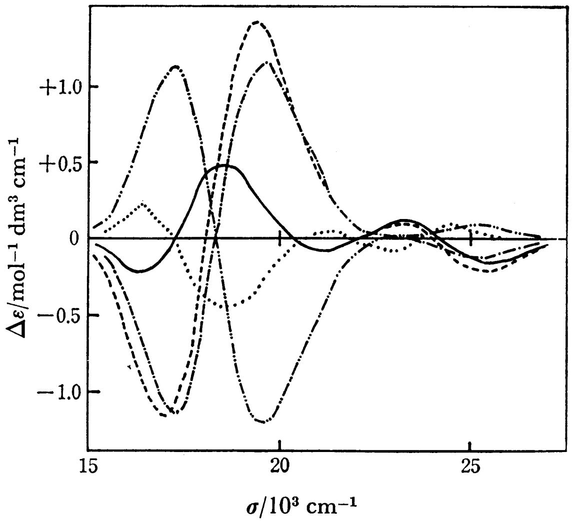

Fig. 8. Configurational and vicinal CD curves: configurational Λ (----), vicinal δ+*S* (——), and conformational λ (····). The observed CD curves of Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ (-·····-) and Λ-*cis*-α-[$CrCl_2$(picen)]$^+$ (-····-) are also shown for comparison.

The calculated curves are shown in Fig. 8. We then obtain from (iii) and (iv) the conformational contribution (λ) (dotted line) of the central chelate ring,

$$\Delta\varepsilon(3) - \frac{1}{2}\{\Delta\varepsilon(1)-\Delta\varepsilon(2)\} = \lambda$$

This is nearly enantiomeric to the δ+*S* vicinal curve, indicating that the contribution of asymmetric atoms (*S*) is negligibly small. This is also substantiated by the fact that the observed CD curve of the Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ is almost identical to that of the Δ-*cis*-α-[$CrCl_2$(picen)]$^+$ (Table 3). Similar CD curves for the vicinal and the configurational contributions can be calculated for the dibromo complexes.

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