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Metal Complexes Coordinating Pyridine Derivatives. II.[1] Circular Dichroism and Magnetic Circular Dichroism Spectra of Chromium(III) Complexes in the Region of Pyridine Ring Absorption Band

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Dianionochromium(III) complexes coordinating (*S*)-*N*,*N′*-bis(2-pyridylmethyl)propylenediamine (abbrev. *S*-picpn) or (*S*)-1-(2-pyridyl)ethylamine (abbrev. *S*-pea) show CD spectra of a dispersion type in the region of pyridine ring absorption band. Utilizing the data of X-ray crystal structure analysis of *Δ*-*cis*-α-$[\mathrm{CrCl_2}(S\text{-picpn})]\mathrm{Cl}$, the difluoro complex shows the correct exciton CD sign pattern expected from a simple theory but the dichloro and dibromo complexes the inverse sign pattern. The latter fact is explained in terms of overlapping of the pyridine ring absorption band with the halogeno-to-chromium charge transfer band, referring to MCD spectra. The absorption and MCD bands appeared in the region 30—35×10³ cm⁻¹ for all the chromium(III) complexes are assigned to the spin-forbidden π→π* transition of the coordinated pyridine group.

When two or three ligands having a π electron system coordinate to take a chiral configuration around a metal ion, an exciton splitting of the CD (circular dichroism) band emerges in the region of the π→π* transition,[2–4] 1,10-phenanthroline, 2,2′-bipyridine, acetylacetonato,[5,6] and tropolonato[7] ligands being typical examples. Several reports are available also for the exciton CD splitting of pyridine ring absorption band, but the treatment remained so far quite unsatisfactory. Bosnich pointed out firstly the occurence of exciton coupling in *cis*-α-$[\mathrm{CoX_2}(S\text{-picpn})]^{n+}$ and *cis*-$[\mathrm{CrCl_2}(S\text{-picpn})]^{+}$ complexes[8] (*S*-picpn=(*S*)-*N*,*N′*-bis(2-pyridylmethyl))propylenediamine). Later Cragel and Brubaker discussed the case of the *cis*-β-cobalt(III) complexes,[9] but assigned incorrectly the *cis*-β structure for a violet $(+)^{\mathrm{CD}}_{600}$-*cis*-α-$[\mathrm{CoCl_2}(S\text{-picpn})]^{+}$.[1] On the other hand, it has been claimed by Branca *et al.* that no exciton interaction occurs between the two pyridine rings in *trans* positions for iron(III) complexes coordinating *N*,*N′*-bis(2-pyridylmethyl)ethylenediamine (abbrev. picen) because of far distance of the two pyridine rings.[10]

In the present paper, we deal with the exciton splitting of chromium(III) and cobalt(III) complexes of *S*-picpn, picen, pma (=2-pyridylmethylamine), and *S*-pea (=(*S*)-1-(2-pyridyl)ethylamine), referring to the MCD (magnetic circular dichroism) spectra. Moreover, the assignment of a weak absorption band which emerges in the region of 30—35×10³ cm⁻¹ for the complexes having the coordinated pyridine group, is attempted.

Experimental

Ligands. *2-Pyridylmethylamine (pma)*: This ligand was purchased from Aldrich Co.

*(*S*)-1-(2-Pyridyl)ethylamine (*S*-pea)*: The (*R*,*R*)-hydrogen tartrate diastereomer was prepared by the method in literature;[11] $[\alpha]_{589}$ +3.9° (c=1.00×10⁻² g cm⁻¹, water) (lit,[11] $[\alpha]_{589}$ +4.3°). To an aqueous solution of the diastereomer was added an equimolar amount of barium chloride. After filtering off the precipitated barium (*R*,*R*)-tartrate, an excess amount of potassium hydroxide was added to the filtrate. An oily product separated was extracted with ether. The ether solution was dried on anhydrous sodium sulfate and ether was evaporated off to obtain the free amine. The free amine was distilled at atmospheric pressure; bp 189 °C, $[\alpha]^{14}_{589}$ −27.7° (c=0.01 g cm⁻³, water).

(S)-N,N′-Bis(2-pyridylmethyl)propylenediamine (S-picpn) and N,N′-Bis(2-pyridylmethyl)ethylenediamine (picen): These were prepared from (*S*)-propylenediamine or ethylenediamine and 2-pyridinecarbaldehyde by the method of Goodwin and Lions.[12]

Cobalt(III) Complexes. *Λ*-$(-)_{589}$-$[\mathrm{CoCl_2(en)_2}]\mathrm{Cl\cdot H_2O}$: The racemic complex was resolved with ammonium $(+)_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromocamphor-9-sulfonate.[13]

trans(py)cis(H₂O)-$[\mathrm{Co(H_2O)_2(pma)_2}]\mathrm{HSO_4\cdot SO_4}$: The complex was prepared by the method of literature.[14]

cis-$[\mathrm{Co(H_2O)_2(en)_2}]\mathrm{Cl_3}$: This was prepared by the method of the literature.[15]

Δ-cis-α-$[\mathrm{CoCl_2}(S\text{-picpn})]\mathrm{Cl}$: The complex was prepared previously.[1]

Chromium(III) Complexes. Λ-$(-)_{589}$-$[\mathrm{CrCl_2(en)_2}]\mathrm{Cl\cdot H_2O}$: The racemic complex was prepared as reported by Pedersen[16] and resolved by the method of Selbin and Bailar[17] with ammonium $(+)_{589}$-(1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate.

cis-$[\mathrm{CrF_2(en)_2}]\mathrm{I}$: This was prepared by the method of literature.[18]

trans-$[\mathrm{CrF_2(py)_4}]\mathrm{Br}$: This complex was prepared by the method of literature.[19]

Δ-trans(py)cis(Cl)-$[\mathrm{CrCl_2(pma)_2}]\mathrm{ClO_4}$, trans(py)cis(F)-$[\mathrm{CrF_2(pma)_2}]\mathrm{Br}$, trans(py)cis(Cl)-$[\mathrm{CrCl_2(pma)_2}]\mathrm{Cl}$, trans(py)cis(H₂O)-$[\mathrm{Cr(H_2O)_2(pma)_2}](\mathrm{NO_3})_3$, cis-α-$[\mathrm{CrCl_2(picen)}]\mathrm{Cl}$, *and* cis-β-$[\mathrm{CrCl_2(picen)}]\mathrm{NO_3}$: These were prepared by the methods of Michelsen.[20]

fac-$[\mathrm{CrCl_3(py)_3}]$: This was prepared by the method in the literature.[21]

Λ-trans(py)cis(Cl)-$[\mathrm{CrCl_2}(S\text{-pea})_2]X$: The samples prepared by the following three methods showed the same CD spectra; that is, only one isomer was obtained.

(a) Chromium shot (0.5 g, 10 mmol) was crushed and dissolved in 6 mol dm⁻³ hydrochloric acid (15 cm³) under a current of nitrogen. The blue solution was evaporated in a vacuum rotary evaporator and heated to dryness. To the residue was added *S*-pea (2.5 g, 20 mmol in 10 cm³ pyridine). The mixture was heated and then a solution of iodine (1.2 g, 4.7 mmol in 4 cm³ pyridine) was added. After refluxing for twenty minutes, the violet precipitate was filtered and washed with ethanol. The crude product was treated with silver chloride, the resulting iodide being filtered. The filtered solution was poured onto an SP-

Sephadex C-25 column ($\phi 35\times 400$ mm) and eluted with 0.1 mol dm^{-3} sodium chloride aqueous solution acidified with hydrochloric acid (0.12 mol dm^{-3}). Only one band was eluted and collected in several fractions. The former 90% parts of the fractions showed the same CD spectrum; they were combined and concentrated in a vacuum rotary evaporator. The deposited sodium chloride was removed from the concentrated solution, to which was added sodium iodide. The desired violet complex precipitated. Found: C, 31.53; H, 4.43; N, 10.33%. Calcd for $[CrCl_2(S\text{-pea})_2]I\cdot 2H_2O=C_{14}H_{20}N_4Cl_2CrI\cdot 2H_2O$: C, 31.72; H, 4.56; N, 10.57%.

(*b*) The preparation was performed as in (*a*) using hydrobromic acid instead of hydrochloric acid. The obtained complex was adsorbed on an SP-Sephadex C-25 column and eluted with 0.5 mol dm^{-3} sodium chloride aqueous solution. The only one band was eluted and collected in several fractions, all of which showed the same CD spectrum. The product was a dinuclear complex. Found: C, 28.62; H, 4.12; N, 9.55%. Calcd for $[\{Cr(OH)(S\text{-pea})_2\}_2]I_4\cdot 2.5H_2O=C_{28}H_{42}\ N_8O_2Cr_2I_4\cdot 2.5H_2O$: C, 28.52; H, 4.02; N. 9.50%. The dinuclear complex was dissolved in water and sodium perchlorate was added. The obtained perchlorate salt of dinuclear complex was dissolved in concd hydrochloric acid. After 10 d, several drops of 70% perchloric acid was added. After ten more days, violet crystals of the desired mononuclear complex appeared. Found: C, 33.64; H, 4.74; N, 11.11%. Calcd for $[CrCl_2(S\text{-pea})_2]ClO_4\cdot 2H_2O=C_{14}H_{20}N_4O_4Cl_3Cr\cdot 2H_2O$: C, 33.45; H, 4.81; N, 11.41%.

(*c*) Anhydrous chromium(III) chloride (3.9 g, 24.6 mmol) was suspended in dimethyl sulfoxide (12 cm^3). Six grams of *S*-pea (49.1 mmol) was added with stirring. After half an hour, ethanol (20 cm^3) was added to the reaction mixture, and the red-violet product was filtered. The product was extracted with an appropriate amount of hot water (70 °C). The extracted solution was poured onto an SP-Sephadex C-25 column ($\phi 40\times 400$ mm) and eluted with 0.1 mol dm^{-3} sodium chloride aqueous solution acidified with hydrochloric acid (0.12 mol dm^{-3}). Five bands, a violet one (i), a red-violet one (ii), blue violet one (iii), and two violet ones (iv) and (v), were eluted in this order. Eluate (i) was condensed to a small volume in a vacuum rotary evaporator; violet crystals began to appear and whole was left in a refrigerator overnight. Violet crystals were filtered and washed with ethanol–water (1:1), ethanol and ether. Found: C, 37.75; H, 5.42; N, 12.51%. Calcd for $[CrCl_2(S\text{-pea})_2]Cl\cdot 2.5H_2O=C_{14}H_{20}N_4Cl_3Cr\cdot 2.5H_2O$: C, 37.56; H, 5.63; N, 12.51%. From eluates (ii), (iii), (iv), and (v), no pure crystals were obtained.

Λ-trans*(py)*cis*(F)*-$[CrF_2(S\text{-}pea)_2]Br$: To a solution of $[CrF_2(py)_4]Br$ (0.50 g) in 2-methoxyethanol was added *S*-pea (0.25 g) and the mixture was refluxed for twenty minutes, A saturated ethanol solution of LiBr was added to it and the precipitates obtained were recrystallized twice from water by adding a saturated ethanol solution of LiBr. Found: C, 30.37; H, 4.56; N, 10.09%. Calcd for $[CrF_2(S\text{-pea})_2]Br\cdot 2.5H_2O\cdot LiBr=C_{14}H_{20}N_4BrCrF_2\cdot 2.5H_2O\cdot LiBr$: C, 31.05; H, 4.56; N, 10.34%. The complex was dissolved in concd HCl and saturated with HCl gas. After three days, the solution was concentrated and the precipitate was recrystallized from water. Found: C, 34.95; H, 5.02; N, 11.70%. Calcd for $[CrCl_2(S\text{-pea})_2]Br\cdot 2H_2O=C_{14}H_{20}N_4BrCl_2Cr\cdot 2H_2O$: C, 34.80; H, 5.01; N, 11.60%. The CD spectrum of this dichloro complex was the same as that of $[CrCl_2(S\text{-pea})_2]X$ prepared in the above section.

Δ-cis-α-*[CrCl$_2$(*S-*picpn)]Cl*, Λ-cis-α-*[CrCl$_2$(*S-*picpn)]Cl*, Δ-cis-α-*[CrBr$_2$(*S-*picpn)]I*, Λ-cis-α-*[CrBr$_2$(*S-*picpn)]Br*, *and* Λ-cis-α-*[CrF$_2$(*S-*picpn)]Br*: The preparations of these complexes was described in a previous paper.[1]

cis-α-*[CrF$_2$(picen)]Br*: To a solution of $[CrF_2(py)_4]Br$ in 2-methoxyethanol was added the stoichiometric amount of picen and the mixture was refluxed for thirty minutes. After cooling, a saturated ethanol solution of LiBr was added. The obtained precipitates were recrystallized from water. The product was eluted with 0.1 mol dm^{-3} NaCl aqueous solution on an SP-Sephadex C-25 column, only one band being observed. Found: C, 34.06; H, 4.85; N, 11.88%. Calcd for $[CrF_2(picen)]Br\cdot 2.5H_2O\cdot 0.3LiBr=C_{14}H_{18}N_4BrCrF_2\cdot 2.5H_2O\cdot 0.3LiBr$: C, 34.58; H, 4.77; N, 11.52%. The complex was dissolved in concd HCl and saturated with HCl gas below −13 °C. The solution was left for three days and then concentrated with a rotary evaporator. The precipitated product was recrystallized from water and dried in a vacuum desiccator over CaCl$_2$. Found: C, 41.12; H, 4.43; N, 13.76%. Calcd for $[CrCl_2(picen)]Cl\cdot 0.5H_2O=C_{14}H_{18}N_4Cl_3Cr\cdot 0.5H_2O$: C, 41.05; H, 4.68; N, 13.68%. The absorption spectrum of this dichloro complex was the same as that of *cis*-α-$[CrCl_2(picen)]Cl$. Thus, the structure of the difluoro picen complex is determined to be *cis*-α.

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu UV-200 and a Hitachi 330 spectrophotometers. The CD and MCD spectra were measured on a JASCO MOE-1 spectropolarimeter. The specific rotation was measured with a JASCO DIP-4 polarimeter. All the measurements were performed at room temperature.

Results and Discussion

Structural Assignments of the Complexes. The structures of *S*-picpn complexes were assigned previously.[1] Only one isomer was prepared for the dinuclear *S*-pea complex, $[\{Cr(OH)(S\text{-pea})_2\}_2]^{4+}$, the structure of which has been determined as Δ-*trans*(py)*trans*(py),[22] the most probable one from the viewpoint of avoiding the steric hindrance between four pyridine rings. The $[CrCl_2(S\text{-pea})_2]^+$ complex derived from the dinuclear complex is assigned to the *trans*(py)*cis*(Cl) structure. The absolute configuration of this *S*-pea complex is assigned to Δ from the comparison of CD spectrum in the d-d transition region with that of Δ-$[CrCl_2(en)_2]^+$. No other isomer was obtained for the dichloro complex in any of the three different preparations. The stereospecificity may exist in the formation of $[CrCl_2(S\text{-pea})_2]^+$ complex to produce only the Δ-*trans*(py) isomer. The structures of $[CrF_2(S\text{-pea})_2]^+$ and $[CrF_2(picen)]^+$ are Δ-*trans*(py)*cis*(F), and *cis*-α, respectively (see Experimental).

Exciton Interaction between Pyridine Rings. When two identical chromophores (π system) exist in a chiral molecule, they couple to produce an exciton splitting in absorption and related CD bands, the splitting interval being expressed by exciton interaction energy $2V_{12}$ (Fig. 1).[23] The following explanation is restricted to the coupled chromophore having C_2 symmetry, being harmonized with all the present complexes, which have at least one C_2 or pseudo C_2 axis. In Fig. 1 is shown the exciton splitting for positive V_{12}; the splitting component due to the transition moment pair A symmetry is higher in energy than that of B. The rotatory strength R of A and B com-

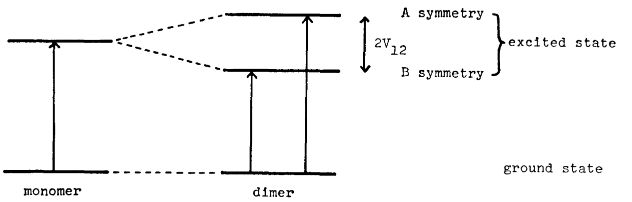

Fig. 1. The exciton splitting with positive V_{12}.

ponents are given by $(\pi\bar{\nu}/2)R'$ and $-(\pi\bar{\nu}/2)R'$, respectively, $\bar{\nu}$ being the wave number of the transition. The rotatory element, R', is written as follows:

$$\vec{R}' = \vec{\mu}_1 \times \vec{R}_{12} \times \vec{\mu}_2 \quad (1)$$

$$= \mu^2\, d\sin\alpha\ \sin\beta\ \sin\theta, \quad (1)'$$

$$(0<\alpha<180^\circ,\ 0<\beta<180^\circ)$$

where $\vec{\mu}_k$ (k=1 or 2) are transition moments, $\vec{R}_{12}$ is vector from the center of gravity of $\vec{\mu}_2$ to that of $\vec{\mu}_1$, and μ is the magnitude of transition moment. The definition of parameters, d, α, β, and θ are shown in Fig. 2, where d is the distance between the two transition moments AB (chromophore 1) and A′B′ (chromophore 2), and θ the dihedral angle between the two planes BCC′ and B′C′C, its displayed orientation being taken as positive. Thus, R′ is positive at $0<\theta<180^\circ$; and negative at $0>\theta>-180^\circ$.

The absorption spectrum of pma is shown in Fig. 3. In this study the lower energy band, ^1L_b, of pyridine ring at about 39800 cm^{-1} is treated. The transition moment direction of this absorption band is depicted with an arrow in Fig. 3, and supposed to be independent of the alkyl substitution (R) at 2 position of pyridine ring.

In Fig. 4 is shown the transition moments in the case of Δ-*cis*-α-[CrCl$_2$(picen)]$^+$. The exciton interaction energy, V_{12}, is generally written,[23b)]

$$V_{12} = \frac{1}{d^3}\{(\vec{\mu}_1\cdot\vec{\mu}_2)-3(\vec{\mu}_1\cdot\vec{R}_{12})(\vec{\mu}_2\cdot\vec{R}_{12})/d^2\}. \quad (2)$$

The centers of gravity of transition moments being set on the x axis and the exciton interaction energy being approximated as coulomb interaction energy between point dipoles, V_{12} can be written as follows,[23b)]

$$V_{12} = \frac{\mu^2}{d^3}(m_1m_2+n_1n_2-2l_1l_2),$$

where l_k, m_k, and n_k (k=1 or 2) are the direction cosines for the transition moment k against the coordination axes x, y, and z, respectively (x, y, and z are taken as shown in Fig. 4).

It has been reported for Δ-*fac*-[Co(S-pea)$_3$]$^{3+}$ [24)] that the angles <NCrN$_{py}$ (N$_{py}$ stands for pyridine nitrogen) in the chelate rings are not exactly 90°. Thus the angles ω_{x1} and ω_{x2}, which are the angles between the transition moments and the +x axis, are introduced as shown in Fig. 5, where $\omega_{x1}+\omega_{x2}=180^\circ$. Consequently, the interaction energy V_{12} is approximately expressed as follows:

$$V_{12} = \frac{\mu^2}{d^3}(\cos\theta+2\cos^2\omega_{x1}). \quad (2)'$$

The rotatory element R' and the exciton interaction energy V_{12} can be calculated approximately from the relative orientation of the transition moments on the two pyridine rings by Eqs. 1 and 2 (or Eqs. 1′ and

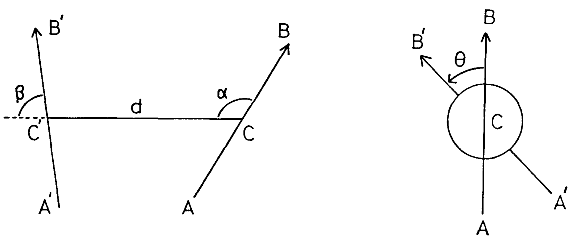

Fig. 2. The parameters, d, α, β, and θ defining the rotatory element R'.

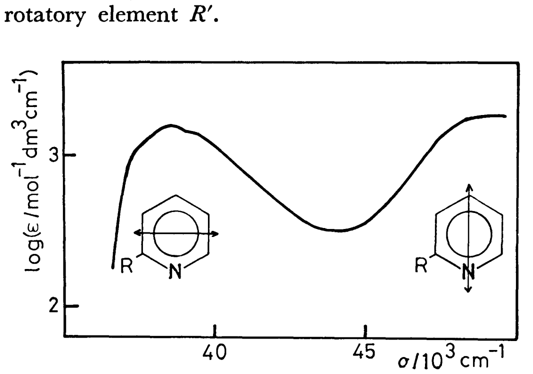

Fig. 3. Absorption Spectrum of pma (R=CH$_2$NH$_2$) in water, and the directions of transition moments for ^1L_b (lower energy) and ^1L_a (higher energy) bands.

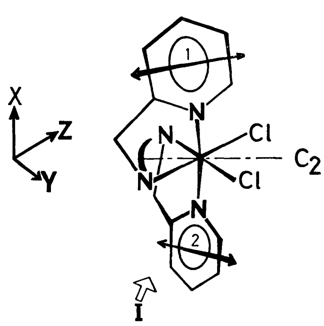

Fig. 4. The structure of Δ-*cis*-α-[CrCl$_2$(picen)]$^+$ and the directions of the transition moments for the ^1L_b band. The C$_2$ axis coincides with the bisector between y and z axis.

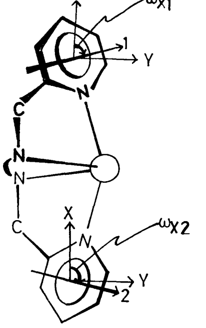

Fig. 5. The transition moment pair of A symmetry viewed from −z direction (from the arrow I in Fig. 4).

2′) respectively. The expected CD patterns are given in Table 1 for the four combinations of R' and V_{12}; for example, when R' and V_{12} are positive, a negative and then a positive component from the lower energy side, (−,+), are expected.

CD and MCD Spectra of the Pyridine Ring Absorption Band (^1L_b Transition). The absorption and CD data of *cis*-α-[CrX_2(*S*-picpn)]$^+$ (X=F, Cl, and Br) are exhibited in Table 2 (the band assignments are shown in the Table) and Figs. 6, 7, and 9. All the *S*-picpn complexes show (+,−) or (−,+) dispersion type CD pattern in the pyridine ring absorption band region (^1L_b transition). For the Λ difluoro complex, a typical (+,−) pattern is observed clearly (Fig. 6). The CD sign pattern is (−,+) from the lower energy side for the Λ complexes except for the difluoro complex, and that of the Δ complexes is (+,−) for the dichloro and the dibromo complexes (Table 2).

By using the atomic positions (Table 3) of pyridine ring carbon atoms determined in the X-ray structure analysis of Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]Cl,[25] the exciton CD pattern is estimated from Eqs. 1′ and 2. The numbering scheme of the carbon atoms is shown in Fig. 8. In the explanation of the component A symmetry, the directions of transition moments are taken from the midpoint of C(4) and C(5) to that of C(1) and C(2), and from the midpoint of C(10) and C(11) to that of C(13) and C(14). The evaluated values of R' and V_{12} from Eqs. 1′ and 2 are both negative. Thus the expected CD pattern is (−,+) from the lower energy side (Table 1), which is inverse to those observed for the dichloro and dibromo Δ complexes.

Table 1. Expected CD pattern in the exciton region

R'	V_{12}	CD sign pattern from the lower energy side
+	+	(−, +)
+	−	(+, −)
−	+	(+, −)
−	−	(−, +)

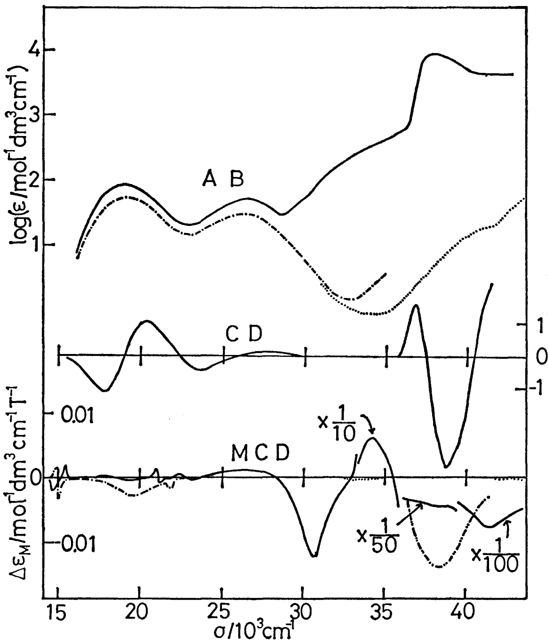

Fig. 6. Absorption (AB) and CD spectra of Λ-*cis*-α-[CrF_2(*S*-picpn)]Br in water (——). Absorption spectrum of *cis*-[$CrF_2(en)_2$]I (-·-·-) and an eluted solution passed through Dowex 1-x8 (Cl^- form) (···). MCD spectra of *cis*-α-[CrF_2(picen)]Br (——), *cis*-[$CrF_2(en)_2$]I (-·-·-), the eluted solution (······), and pma (-·····-) in water.

For the Λ complex, the expected exciton CD pattern is (+,−), since it is probable that the relative orientation of the two pyridine rings in the Λ complex is not so much different from the mirror image of that in the Δ complex. Only the difluoro Λ complex matches this calculated CD pattern.

The absorption and CD spectra of *cis*-[$CrX_2(en)_2$]$^+$ (X=F or Cl) are shown in Figs. 6 and 7. The ligand-to-metal charge-transfer (CT) band of the dichloro complex is located near the pyridine ^1L_b band, but

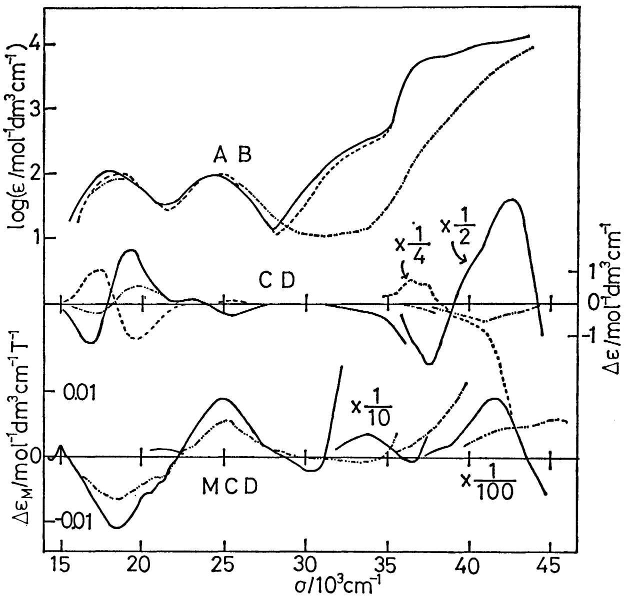

Fig. 7. Absorption (AB) and CD spectra of Λ-*cis*-α-[$CrCl_2$(*S*-picpn)]Cl, (——), Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]Cl (- - -), and Λ-*cis*-[$CrCl_2(en)_2$]Cl (-······-) in 0.1 mol dm^{-3} HCl. MCD spectra of *cis*-α-[$CrCl_2$(picen)]Cl in 0.1 mol dm^{-3} HCl (——) and *cis*-[$CrCl_2(en)_2$]Cl (-······-) in methanol.

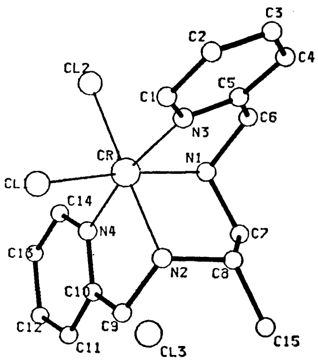

Fig. 8. The structure of Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]Cl and the numbering scheme of the atoms.

TABLE 2. ABSORPTION AND CD DATA OF Cr(III) AND Co(III) COMPLEXES MEASURED IN 0.1 mol dm^{-3} HCl AND IN METHANOL (sh=shoulder)

Complex	Absorption		CD		Absorption		CD		Assignment
	σ_{max}/cm^{-1}	log $\varepsilon^{a)}$	σ_{ext}/cm^{-1}	$\Delta\varepsilon^{a)}$	σ_{max}/cm^{-1}	log $\varepsilon^{a)}$	σ_{ext}/cm^{-1}	$\Delta\varepsilon^{a)}$	
	(in HCl)				(in methanol)				
Λ-*cis*-α-[CrF$_2$(*S*-picpn)]Br$^{b,c)}$					18690	1.88	17180	−0.98	d-d
							19720	+0.79	
							23040	−0.69	
					26460	1.68	26740	+0.25	
	34000(sh)	2.4	29850	+0.06	33000(sh)	2.4	35000(sh)	+0.35	py(triplet)
			30960	+0.04					
			31750	+0.03					
	38020	3.89	36740	+1.69	37880	3.83	36630	+1.43	py(^{1}L$_b$)
			38760	−3.37					
			43670	+5.35			39060	−2.70	
Λ-*trans*(py)*cis*(F)-[CrF$_2$(*S*-pea)$_2$]Br$^{b)}$	19270	2.03	18350	−0.73	19010	1.88	18280	−0.60	d-d
			20580	+0.87			20450	+0.40	
	26810	1.77	25910	−0.28	27170	1.65	23810	−0.22	
							27550	−0.14	
	31000(sh)	2.2	28900	−0.07			33670	+0.15	py(triplet)
	34000(sh)	2.6	34250	+0.24					
	37740	3.90	37040	+6.79	38020	3.88	37040	+5.36	py(^{1}L$_b$)
			39840	−0.64			38760	−0.86	
			46080	+5.12			42370	+4.04	
cis-[CrF$_2$(en)$_2$]I$^{b)}$	19160	1.74							d-d
	26250	1.48							
cis-[CrF$_2$(en)$_2$]Cl$^{b)}$	40000(sh)	1.12							d-d
trans-[CrF$_2$(py)$_4$]Br$^{b)}$	19080	1.44			18760	1.42			d-d
	24450	1.04			24210	0.91			
	29410(sh)	1.49			29590(sh)	1.61			py(triplet)
	30300(sh)	1.74			30490(sh)	1.81			
	31750(sh)	2.11			31750(sh)	2.04			
	32790(sh)	2.33							
	37170(sh)	2.82			38460	3.99			py(^{1}L$_b$)
	38170	3.97							
	38610(sh)	3.95							
	45050	3.99			42190	4.01			
Δ-*cis*-α-[CrCl$_2$(*S*-picpn)]Cl$^{c)}$					18050	2.00	16860	+1.00	d-d
							19340	−1.03	
					24270	2.02	22730	+0.23	
			30300	+0.02	34000(sh)	2.6	34000(sh)	−0.27	py(triplet)
			31250	+0.05					
	34000(sh)	2.5	32260	+0.09					
	36500(sh)	3.6	36230	+3.13					py(^{1}L$_b$)
	37390	3.77	37040	+2.40	37000	3.8	36230	+1.59	
			39200(sh)	−1.7					
	48540	4.40	43860	−18.1			43290	−15.9	
Λ-*cis*-α-[CrCl$_2$(*S*-picpn)]Cl$^{c,e)}$					17700	2.03	16390	−1.09	d-d
							18800	+1.41	
					24100	2.10	21790	−0.24	
							23420	+0.07	
							25320	−0.27	
	34000(sh)	2.6	33500(sh)	−0.3	34000(sh)	2.6	34000(sh)	−0.25	py(triplet)
	36500	3.58	36360(sh)	−4.9	37000	3.8	37040	−5.08	py(^{1}L$_b$)
	37390	3.77	37310	−7.96			38760	+2.53	
			38170(sh)	−4.6					
			39600(sh)	+3.0					
			42370	+13.1			42020	+9.07	
			46950	−41.8					
Δ-*trans*(py)*cis*(Cl)-[CrCl$_2$(pma)$_2$]ClO$_4$	18520	1.97	17420	+0.63	18020	1.97	17180	+0.60	d-d
			19570	−0.85			19420	−0.58	

TABLE 2. (Continued)

Complex	Absorption		CD		Absorption		CD		Assignment
	σ_{max}/cm^{-1}	log ε[a]	σ_{ext}/cm^{-1}	$\Delta\varepsilon$[a]	σ_{max}/cm^{-1}	log ε[a]	σ_{ext}/cm^{-1}	$\Delta\varepsilon$[a]	
	(in HCl)				(in methanol)				
	24880	1.94	24570	+0.15	24630	1.97	23640	+0.17	
	34000(sh)	2.5	30670	−0.01	34000(sh)	2.5	29590	+0.02	py(triplet)
			31650	−0.02			30400	+0.02	
			33300	+0.15					
	37810	3.78	36830	−1.23	37000(sh)	3.7	35340	+0.34	py(^{1}L$_b$)
			38020	−1.14			37740	−3.31	
			38850	−1.10			39840	+0.84	
			44250	−14.6			43100	−9.94	
Λ-*trans*(py)*cis*(Cl)-[CrCl$_2$(*S*-pea)$_2$]Cl	18600	2.02	17480	−0.57	18180	2.02	17390	−0.48	d-d
			19570	+1.03			19490	+0.74	
	24060	1.99	24630	−0.21	24880	2.01	24000	−0.22	
	34000(sh)	2.4	28820	+0.02	33000(sh)	2.4	29070	+0.02	py(triplet)
			29940	+0.03			29760	+0.02	
			30770(sh)	+0.05					
			31550(sh)	+0.08					
	37000(sh)	3.7	36580	+3.85			35100	−0.25	py(^{1}L$_b$),CT
	37590	3.81	37790	(−)[d]			38760	+5.91	
			39900(sh)	+4.22					
			43980	+15.78			43500	+10.7	
Λ-*cis*-[CrCl$_2$(en)$_2$]Cl	19010	1.87	17240	−0.29					d-d
	19800		19800	+0.59					
	24810	1.83	24040	+0.23					
			40820	−1.70					CT
	47390	4.11	46080	+1.70					
Δ-*cis*-α-[CoCl$_2$(*S*-picpn)]Cl[c]	30000(sh)	3.1	30490	+2.34					CT
	34500(sh)	3.7	35590	−18.45					
	39530	4.30	39220	+36.60					py(^{1}L$_b$),CT
			43000(sh)	+16					
			46510	−21					
Λ-*cis*-[CoCl$_2$(en)$_2$]Cl	18690	1.98	16390	−0.55					d-d
			18870	−0.72					
	25640	1.95	24510	+0.22					
	32000(sh)	2.9	33670	−1.23					
	38500(sh)	4.1	37590	+7.97					CT
	42920	4.28	42370	−14.65					
Δ-*cis*-α-[CrBr$_2$(*S*-picpn)]I[e]					17180	2.07	16530	+0.78	d-d
							18940	−0.82	
					23420	2.18	24510	+0.07	
	33000	3.15	33000	+0.95	34000(sh)	3.5	31550	+0.81	CT
	37500(sh)	4.0	36560	−2.88			34960	−1.84	
			36830	(+)[d]	37600(sh)	4.0	36500	−1.23	py(^{1}L$_b$),CT
			39920	−9.60			39680	−8.61	
	44400	4.48	44250	+23.06					
Λ-*cis*-α-[CrBr$_2$(*S*-picpn)]Br[e]					17120	2.02	16130	−1.17	d-d
							18420	+1.53	
					23420	2.03	22320	+0.29	
							24390	−0.48	
	33000	3.3	32470	−1.68	34000(sh)	3.4	31250	−1.74	CT
			35090	+1.58			35090	+2.94	
			36300(sh)	+0.97					
	37500(sh)	4.0	37370	−2.59	37600(sh)	4.0	37170	−1.79	py(^{1}L$_b$),CT
			39630	+5.83			38910	+2.20	
			43860	−29.03			42640	−21.0	
2-Pyridylmethylamine	37500(sh)	3.04							py(^{1}L$_b$)
	38460	3.20							
	39500(sh)	3.13							

a) ε is defined in mol^{-1} dm^3 cm^{-1} unit. b) Measured in water. c) The data in the d-d transition region are reported in the previous paper.[1] d) The negative (positive) peak is in the positive (negative) area in fact because of the overlapping of intense positive (negative) band in close proximity. e) The perchlorate salt was measured in methanol.

TABLE 3. THE POSITIONS OF PYRIDINE RING CARBON ATOMS

	x	y	z
C (1)	2.25	2.56	3.86
C (2)	2.88	3.28	4.86
C (3)	3.02	2.78	6.13
C (4)	2.52	1.54	6.43
C (5)	1.96	0.78	5.41
C (10)	−1.38	−1.13	1.56
C (11)	−2.22	−1.98	0.83
C (12)	−1.72	−3.16	0.28
C (13)	−0.35	−3.45	0.48
C (14)	0.42	−2.59	1.26

that of the difluoro complex is far from the pyridine ^1L_b band (the absorption band at ca. 40000 cm^{-1} in *cis*-$[CrF_2(en)_2]^+$ is the third spin-allowed d-d transition band). Also in Figs. 6 and 7 are shown the MCD spectra of *cis*-α-$[CrX_2(picen)]^+$, *cis*-$[CrX_2(en)_2]^+$ (X=F or Cl), and pma. No MCD band was observed for the *cis*-$[CrF_2(en)_2]^+$ complex in the 35000—40000 cm^{-1} region, but a very strong tail of higher energy MCD band for the dichloro complex, *cis*-$[CrCl_2(en)_2]^+$, in that region. In *cis*-α-$[CrF_2(picen)]^+$ complex a broad MCD band of pyridine rings is observed, while in the *cis*-α-$[CrCl_2(picen)]^+$ complex, the rather complicated MCD spectra indicate an overlap of the bands due to pyridine ring and CT transitions.

It has been established that exciton coupling is not observed in MCD spectra of tris(phenanthroline) metal complexes.[26] Likewise, the present complexes having two pyridine rings show no exciton coupling in the MCD spectra. The exciton coupling CD pattern in the dichloro complexes is considered to suffer from the overlap of CT bands. The CD spectrum of the difluoro complex shows the unperturbed pattern and correct signs in this region. In the dibromo complexes, it is clear that the bromo-to-chromium CT bands overlap with the pyridine ring absorption band. The exciton treatment can not be made in the case of overlapping of charge transfer band to the pyridine ring absorption band and the overlapping of CT band can be distinguished more clearly by using MCD spectrum.

The absorption and CD spectra of *trans*(py)*cis*(F)-$[CrF_2(S\text{-pea})_2]^+$ are shown in Fig. 9 with the MCD spectrum of *trans*(py)*cis*(F)-$[CrF_2(pma)_2]^+$. The MCD spectra in the pyridine ring absorption band region shows a similarity to that of pma; that is, only the B term of pyridine ring is observed.[27] The exciton CD spectra of the difluoro complexes are expected to show the CD pattern estimated by the simple theory. Though the observed CD spectrum is somewhat shifted to the positive area, the CD pattern is (+,−) from the lower energy side. This case is explained by using the Eqs. 1′ and 2′ and Fig. 5. An X-ray analysis of Λ-*fac*-$[Co(S\text{-pea})_3](ClO_4)_3\cdot 2H_2O$ showed that the pyridine ring of each *S*-pea ligand is tilted against the plane determined by cobalt and two nitrogen atoms of the ligand.[24] The tilt angle is 13—17°. Since the central chelate ring in Fig. 5 is absent, the angle $|\theta|$ becomes larger than 90°, being estimated to be *ca.* 120°. From Eqs. 1′ and 2′ (ω_{x1}=*ca.* 84° was estimated from the X-ray analysis of Δ-*cis*-α-$[CrCl_2(S\text{-picpn})]Cl$[25]) the value of V_{12} becomes negative and R' is positive. Thus, a (+,−)CD pattern is expected from Table 1, which coincides with the observed pattern. It is established that the exciton CD between the two pyridine rings depends on the chelate ring conformations containing the pyridine rings.

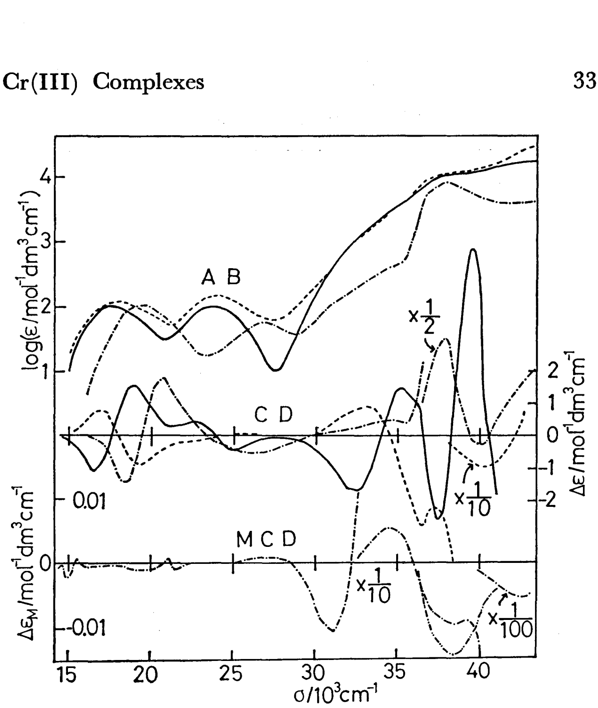

Fig. 9. Absorption (AB) and CD spectra of Δ-*cis*-α-$[CrBr_2(S\text{-picpn})]Br$ (- - -), Λ-*cis*-α-$[CrBr_2(S\text{-picpn})]I$ (——) in 0.1 mol dm^{-3} HCl, and Λ-*trans*(py)*cis*(F)-$[CrF_2(S\text{-pea})_2]Br$ in water (-·-·-). MCD spectra of *trans*(py)*cis*(F)-$[CrF_2(pma)_2]Br$ in water (-·-·-) and pma in water (-·····-).

In the case of Λ-*trans*(py)*cis*(Cl)-$[CrCl_2(S\text{-pea})_2]^+$ complex, (Fig. 10), the observed (+,−,+) CD pattern does not coincides with the expected exciton pattern. For the complex Δ-*trans*(py)*cis*(Cl)-$[CrCl_2(pma)_2]^+$, a vibrational pattern is observed in the CD spectrum. Moreover, the *S*-pea and pma complexes change the CD spectra by solvent change.

The observed CD pattern in the pyridine ring absorption band of Δ-*cis*-α-$[CoCl_2(S\text{-picpn})]^+$ (Fig. 10) coincides with the expected pattern. In the cobalt(III) complex, the chloro-to-cobalt CT band overlaps with the pyridine ring absorption band. Thus the coincidence between the observed and expected patterns might be accidental.

Solvent Effect. The absorption and CD spectra of all the chromium(III) complexes treated here were also measured in methanol and the spectral data are shown in Table 2. The absorption spectra in methanol are generally shifted to the lower energy side as compared with those measured in hydrochloric acid or water in the d-d transition region. But they show rather small change in the pyridine ring absorption band region. A solvent effect studies have been reported previously for the typical cobalt(III) and chromium(III) complexes,[28] which showed red shift by the solvent change from water to alcohols,

TABLE 4. MCD SPECTRAL DATA, MEASURED IN WATER OR 0.1 mol dm^{-3} HCl AND IN METHANOL (sh=shoulder)

Complex	σ_{ext}/cm^{-1} (in water or HCl)	$10^2\,\Delta\varepsilon_M$[a)] (in water or HCl)	σ_{ext}/cm^{-1} (in methanol)	$10^2\,\Delta\varepsilon_M$[a)] (in methanol)	Assignment
cis-α-[CrF_2(picen)]Br	14810	−0.39	14810	−0.21	d-d (doublet)
	15460	+0.21	15410	+0.17	
	17390	+0.05	20880	+0.15	d-d (quartet)
	20000	−0.10			
	20960	+0.31	21070	−0.21	d-d (doublet)
	21140	−0.31			
	21830	−0.05			
	22470	+0.09			
	23150	−0.07			d-d (quartet)
	26670	+0.17	26320	+0.4	
	30770	−2.1	30960	−1.6	py (triplet)
	34250	+9.9	34480	+11	
	36360	−34			py (^1L_b)
	37590	−33			
	41490	−132	41490	−82	
			46510	−100	
trans(py)*cis*(F)-[$CrF_2(pma)_2$]Br	14930	−0.24	14840	−0.18	d-d (doublet)
	16390	−0.07	15420	+0.08	
	19610	−0.11	20900	+0.07	d-d (quartet)
	21050	+0.04	21280	−0.09	d-d (doublet)
	21510	−0.11			
	23150	−0.04			d-d (quartet)
	27030	+0.09	27030	+0.09	
	31060	−0.04	30960	−1.3	py (triplet)
	34480	+0.09	34480	+6.5	
	38460	−1.0	36360	−17	py (^1L_b)
	42550	−53	41670	−70	
cis-[$CrF_2(en)_2$]I	14880	+0.15			d-d (doublet)
	15060	−0.36			
	19610	−0.31			d-d (quartet)
	21880	−0.19			d-d (doublet)
	23040	−0.06			d-d (quartet)
	26320	+0.13			
trans-[$CrF_2(py)_4$]Br	14480	+0.03	14410	+0.01	d-d (doublet)
	14660	−0.04	14560	−0.01	
	14930	−0.03	14710	−0.01	
	15060	−0.03	14840	+0.04	
	15150	+0.01	15040	+0.06	
	15290	−0.05	15200	−0.02	
	15580	−0.01	15460	−0.08	
			15720	−0.07	
	23150	−0.03	18870	+0.02	d-d (quartet)
			22080	+0.02	
	29850	−0.08	30770	−0.51	py (triplet)
	34480	+3.92	34970	+6.42	
	39220	+52	39220	+63	py (^1L_b)
	41320	−18			
cis-α-[$CrCl_2$(picen)]Cl	14390	−0.11	14600	−0.12	d-d (doublet)
	14970	+0.16	14810	+0.06	
	18520	−1.1	17860	−0.97	d-d (quartet)
	20620	−0.56	20000	−0.42	d-d (doublet)
	21280(sh)	−0.39	20200	−0.46	
			20830	−0.27	
			21050(sh)	−0.23	
	25000	+0.89	25000	+0.87	d-d (quartet)
	30770	−0.22	30770	−0.73	py (triplet)

Table 4. (Continued)

Complex	σ_{ext}/cm^{-1}	$10^2\,\Delta\varepsilon_M$[a]	σ_{ext}/cm^{-1}	$10^2\,\Delta\varepsilon_M$[a]	Assignment
	(in water or HCl)		(in methanol)		
	33900	+3.5	33670	+5.3	
	36360	−10	35590	−0.60	py (^{1}L$_b$), CT
	41490	+94	40490	+68	
cis-*β*-[$CrCl_2$(picen)]NO_3	14900	+0.21			d-d (doublet)
	18180	−0.81	c)		d-d (quartet)
	19880	−0.51			d-d (doublet)
	20660	−0.50			
	24690	+0.73			d-d (quartet)
	30030	−0.54	29850	−1.1	py (triplet)
	33900	+4.2			
	39220	+62	37740	+39	py (^{1}L$_b$), CT
	42550	+44	42190	+57	
trans(py)*cis*(Cl)-[$CrCl_2$(pma)$_2$]Cl	14390	−0.36	14290	−0.19	d-d (doublet)
	15150	+0.13	15040	+0.34	
	18520	−0.85	17860	−1.4	d-d (quartet)
	20830	−0.430	20200	−0.52	d-d (doublet)
	21550(sh)	−0.33	20620	−0.67	
			21050	−0.45	
			21280(sh)	−0.46	
	25000	+0.76	25000	+1.4	d-d (quartet)
	303000	−0.26	30770	−1.3	py (triplet)
	33900	+3.0	33900	+7.5	
	37040	−4.0	35840	−2.8	py (^{1}L$_b$), CT
	41840	+75	39680	−120	
cis-[$CrCl_2$(en)$_2$]Cl[b]			14490	−0.25	d-d (doublet)
			15150	+0.06	
			18520	−0.06	d-d (quartet)
			21510	−0.33	d-d (doublet)
			25000	+0.57	d-d (quartet)
			33330	−0.09	
			42000(sh)	+46	CT
			45450	+61	
2-Pyridylmethylamine	38460	−14			py (^{1}L$_b$)

a) $\Delta\varepsilon_M$ is given in mol^{-1} dm^3 cm^{-1} T^{-1}. b) Measured in methanol, because of decomposition in water or in 0.1 mol dm^{-3} HCl. c) Data were not obtained because of low solubility. CT: Charge transfer band.

The same trend is observed in this study. The CD spectra of all the complexes show the red shift in the d-d transition region and large shift or change in the pyridine ring absorption band region. Especially, the dichloro complexes show remarkable changes in this region; that is, the (+,−) or (−,+) dispersion type CD pattern can more clearly be observed in methanol solution than in hydrochloric acid solution, large shift to the lower energy side being also observed.

The spectral change in the dibromo complexes is also distinctive in the pyridine ring absorption band region. The red shift in 30—35×10^3 cm^{-1} region is larger than that in the other regions.

Spin-forbidden Transition of the Coordinated Pyridine Groups. The MCD spectral data are shown in Table 4. In the pyridine ring absorption band region, the MCD change by the solvent change show a similar tendency to that observed in the CD spectra.

Some peculiar MCD spectra are observed in 30—35×10^3 cm^{-1} region. Only weak CD spectra are observed in this region for the difluoro and dichloro complexes, but a (−,+) MCD pattern from the lower energy side is observed in all the complexes with coordinated pyridine groups. In methanol solution the strength of the band is strengthened for all the complexes including *cis*-*β*-[$CrCl_2$(picen)]$^+$ (Fig. 11) and *trans*-[$CrF_2(py)_4$]$^+$ (Fig. 11). There are three possibilities for the assignment of this band.

(1) CT transition from pyridine to chromium ($\pi\rightarrow$ d),

(2) CT transition from chromium to pyridine (d$\rightarrow\pi^*$),

(3) spin-forbidden transition of pyridine.

If it is the CT band (1), the position will change by changing the central metal, because the energy of the CT band is inversely proportional to the optical electronegativity of the metal (1.9 and 2.3 for Cr(III) and Co(III), respectively).[29] The absorption spectra of *cis*(H_2O)*trans*(py)-[Cr(H_2O)$_2$(pma)$_2$]$^{3+}$ and the cobalt(III) analog are shown in Fig. 11. The band for the chromium complex locates at lower energy than that for the cobalt complex. Moreover, from

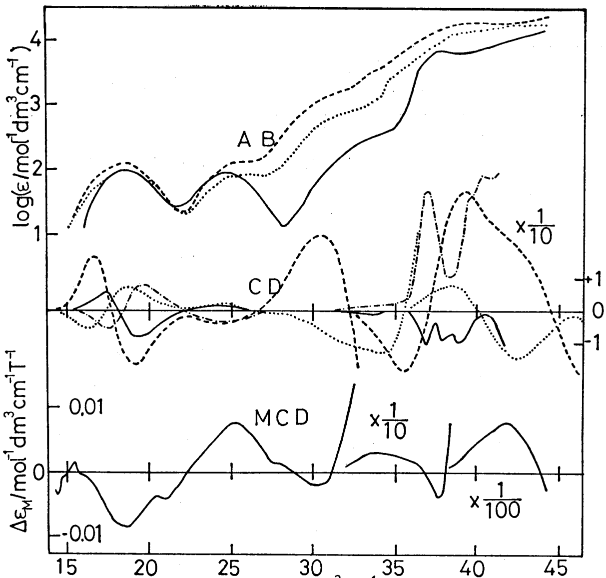

Fig. 10. Absorption (AB) and CD and MCD spectra of Δ- or *racemic-trans*(py)*cis*(Cl)-[CrCl$_2$(pma)$_2$]Cl in 0.1 mol dm^{-3} HCl (——). CD spectrum of Δ-*trans*-(py)*cis*(Cl)-[CrCl$_2$(*S*-pea)$_2$]Cl in 0.1 mol dm^{-3} HCl (-·-·-). Absorption (AB) and CD spectra of Δ-*cis*-α-[CoCl$_2$(*S*-picpn)]Cl (- - -), and Δ-*cis*-[CoCl$_2$(en)$_2$]Cl (···) in 0.1 mol dm^{-3} HCl.

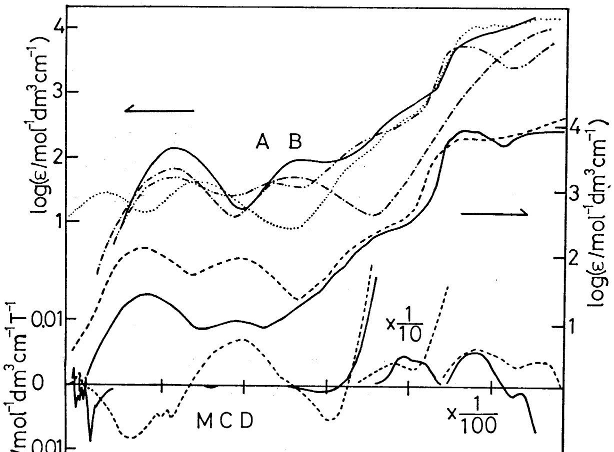

Fig. 11. Absorption (AB) (lower curves) and MCD spectra of *cis*-β-[CrCl$_2$(picen)]NO$_3$ in 0.1 mol dm^{-3} HCl (- - -) and *trans*-[CrF$_2$(py)$_4$]Br in water (——). Absorption (AB) (upper curves) spectra of *trans*(py)-*cis*(H$_2$O)-[Co(H$_2$O)$_2$(pma)$_2$]HSO$_4$·SO$_4$ (——), *cis*-[Co(H$_2$O)$_2$(en)$_2$]Cl$_3$ (-·-·-), *trans*(py)*cis*(H$_2$O)-[Cr(H$_2$O)$_2$(pma)$_2$](NO$_3$)$_3$ (-··-··-) in 0.1 mol dm^{-3} HCl, and [CrCl$_3$(py)$_3$] in methanol (···).

the data of [CrCl$_3$(py)$_3$] and [MoCl$_3$(py)$_3$][30] this kind of bands are observed in almost the same position (the optical electronegativity value of Mo(III) is 1.7[29]). Accordingly, the possibility of (1) is diminished. Jørgensen observed such band for several iridium(III) complexes coordinating pyridine and named it "Ir(III)-pyridine band,"[31] which changes the position by changing the number of the coordinated pyridine ligands or their relative positions in coordination octahedron. In our complexes treated here, the position does not change by the number of the coordinated pyridine groups. Furthermore, *cis*-α- and *cis*-β-[CrCl$_2$(picen)]$^+$ complexes, which has *trans*(py) and *cis*(py) structure, respectively, show the MCD bands of the transition at about the same position (Table 4). Thus the assignment (2) is ruled out. The third assignment is most plausible because the position of this band in absorption or MCD spectra is not so much deviated from complex to complex. Evans found a fine structure of the spin-forbidden band of pyridine in this region under a high pressure of oxygen and assigned it $\pi\rightarrow\pi^*$ singlet-triplet transition.[32] A similar vibrational structure is observed for the *trans*-[CrF$_2$(py)$_4$]$^+$ complex in the absorption band (Fig. 11 and Table 2), and for some present complexes in the CD band (Table 2).

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