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Metal Complexes Coordinating Pyridine Derivatives. III.[1] Stereoselective Formation of Chromium(III) Complexes of Chiral Quadridentate Ligands

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Dichloro mononuclear and di-μ-hydroxo dinuclear chromium(III) complexes were prepared with the following three ligands, (*S*)-*N*,*N'*-bis(2-pyridylmethyl)propylenediamine (abbrev. *S*-picpn), (*S*,*S*)-*N*,*N'*-bis(2-pyridylmethyl)-2,3-butanediamine (abbrev. *SS*-picbn), and (*S*,*S*)-*N*,*N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (abbrev. *SS*-picchxn). The *SS*-picbn and *SS*-picchxn ligands produce novel Λ(*SS*)-*cis*-α diastereomer of dichloro complex, in which the terminal chelate ring is formed by coordination of equatorially-oriented substituent on the secondary nitrogen atom. An explanation from the viewpoint of steric repulsion is given for the stereoselective formation of Λ(*SS*) diastereomers for the *cis*-α dichloro complexes of *SS*-picchxn and *SS*-picbn. A similar explanation is also given for stereoselective formation of a limited number of isomers of dinuclear μ-hydroxo complexes of *S*-picpn, *SS*-picbn, and *SS*-picchxn.

In a previous paper,[2] two diastereomers Δ(*S*) and Λ(*S*) were prepared for a *cis*-α-dichloro or dibromo chromium(III) complex of a quadridentate ligand (*S*)-*N*,*N'*-bis(2-pyridylmethyl)propylenediamine (abbrev. *S*-picpn). In the Δ(*S*)-*cis*-α diastereomer, the quadridentate ligand takes the most stable conformation, the aminomethylpyridine chelate ring being formed by coordination of an axially-oriented substituent on the secondary nitrogen atom. This fact was confirmed from the X-ray crystal structure analysis of Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]Cl.[3] On the other hand, the Λ(*S*)-*cis*-α diastereomer belongs to a rather rare type, in which the terminal chelate ring is formed by coordination of an equatorially-oriented substituent on the secondary nitrogen (Fig. 1). Another example of this type found in literature is a Δ-*cis*-α diastereomer of (oxalato or ethylenediamine) {(*R*,*R*)-*N*,*N'*-dimethyl-1,2-cyclohexanediamine(diacetato)}cobalt(III).[4]

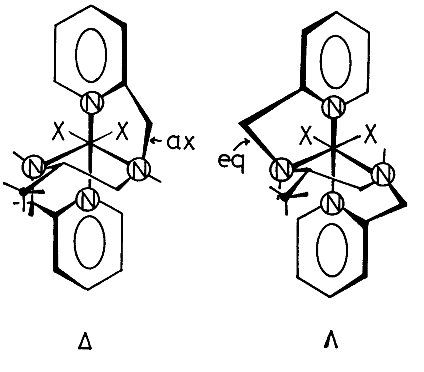

Fig. 1. Two *cis*-α diastereomers of [CrX_2(*S*-picpn)]$^+$, "ax" showing the axial orientation of the pyridylmethyl substituent on the secondary nitrogen atoms and "eq" the equatorial orientation.

In this paper, two kinds of chiral ligands, (*R*,*R*)-*N*,*N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (abbrev. *RR*-picchxn) and (*S*,*S*)-*N*,*N'*-bis(2-pyridylmethyl)-2,3-butanediamine (abbrev. *SS*-picbn), were used for preparation of dichloro and di-μ-hydroxo type chromium(III) complexes, turning our attention to the *cis*-α structure. For convenience, the explanation is made in Results and Discussion using *SS*-picchxn, actually *RR*-picchxn being used in Experimental.

Experimental

Ligands. *(S,S)-2,3-Butanediamine*: This was prepared and resolved by the method in the literature.[5] The absolute configuration is considered to be (*S*, *S*) from the literature.[6]

(R,R)-1,2-Cyclohexanediamine: This was resolved by the method in the literature.[7]

The quadridentate ligands *S*-picpn, *SS*-picbn, and *RR*-picchxn were prepared from (*S*)-propylenediamine, (*S*, *S*)-2,3-butanediamine, or (*R*,*R*)-1,2-cyclohexanediamine and 2-pyridinecarbaldehyde by the method of Goodwin and Lions.[8]

Mononuclear Complexes. *Preparation I*: Anhydrous chromium(III) chloride (1.0 g) was suspended in 0.1 cm^3 of dimethyl sulfoxide, the equimolar amount (1.79 g) of *SS*-picbn (1.8 g in the case of *RR*-picchxn) being added slowly with stirring. After thirty minutes, unreacted material was filtered off and the filtered solution was poured onto an SP-Sephadex C-25 column (ϕ30×700 mm) and the adsorbed band was eluted with 0.1 mol dm^{-3} NaCl aqueous solution. Three bands were eluted, a purple one (i), a red-violet one (ii), and a violet one (iii). The first band proved to contain only one diastereomer by examining circular dichroism (CD) spectra of the fractions of this band collected with a fraction collector. To the concentrated solution of the eluate was added sodium perchlorate and obtained precipitates were recrystallized from warm water. For the *SS*-picbn complex: Found; C, 38.24; H, 4.56; N, 10.97%. Calcd for [$CrCl_2$(*SS*-picbn)]$ClO_4\cdot0.5H_2O$ $=C_{16}H_{22}N_4O_4Cl_3Cr\cdot0.5H_2O$: C, 38.30; H, 4.62; N, 11.17%. For the *RR*-picchxn complex: Found; C, 41.24; H, 4.68; N, 10.68%. Calcd for [$CrCl_2$(*RR*-picchxn)]$ClO_4\cdot0.5H_2O=C_{18}H_{24}N_4O_4Cl_3Cr\cdot0.5H_2O$: C, 40.96; H, 4.77; H, 10.62%. The band (ii) contained two species but decomposed during the concentration procedure even below 25 °C. The band (iii) seemed to be a di-μ-hydroxo complex, but its yield was very low. In the same way the *S*-picpn dichloro complex has been prepared, both Δ and Λ diastereomers being isolated.[2]

Preparation II: Chromium shot (0.50 g) was crushed and dissolved in hydrochloric acid under nitrogen atmosphere. the blue solution was evaporated to dryness, to which was added 2.56 g of *SS*-picbn (2.86 g in the case of *RR*-picchxn) in 4 cm^3 of pyridine. While refluxing for ten minutes, a pyridine solution (10 cm^3) of iodine (2.44 g) was added. The deposited product was dissolved in water and passed through the Dowex 1-X8 column (Cl$^-$ form). After concentrating the eluate, 60% perchloric acid was added. The precipitate was recrystallized from hot water. Only one diastereomer was obtained, the CD spectrum being the same as the band

(i) in Preparation I. For the *SS*-picbn complex: Found; C, 38.65; H, 4.57; N, 11.24%. Calcd for [CrCl$_2$(*SS*-picbn)]ClO$_4$·0.5H$_2$O=C$_{16}$H$_{22}$N$_4$O$_4$Cl$_3$Cr·0.5H$_2$O: C, 38.30; H, 4.62; N, 11.17%. For the *RR*-picchxn complex: Found; C, 40.88; H, 4.72; N, 10.54%. Calcd for [CrCl$_2$(*RR*-picchxn)]ClO$_4$·0.5H$_2$O=C$_{18}$H$_{24}$N$_4$O$_4$Cl$_3$Cr·0.5H$_2$O: C, 40.96; H, 4.77; N, 10.62%. This method of preparation gave only the more stable diastereomer (*Δ*) in the case of the *S*-picpn ligand.[2]

Di-μ-hydroxo Dinuclear Complexes. Chromium(III) bromide hexahydrate (2.0 g) was dissolved in 2-methoxyethanol (15 cm^3). After adding zinc powder, *S*-picpn (1.28 g) was added with stirring. After ten minutes, the zinc powder and violet precipitate were filtered off, and the filtrate was poured onto an SP-Sephadex C-25 column ($\phi 30\times700$ mm). Eluting with 0.5 mol dm^{-3} NaCl aqueous solution, three bands were obtained, a brown one (i), and two violet ones (ii) and (iii). Pure crystalline product was obtained by concentrating the eluate (ii) and adding an aqueous solution of sodium perchlorate. For the *S*-picpn complex: Found; C, 32.44; H, 4.24; N, 9.95%. Calcd for [{Cr(OH)(*S*-picpn)}$_2$](ClO$_4$)$_4$·3.5H$_2$O=C$_{30}$H$_{42}$N$_8$O$_{18}$Cl$_4$Cr$_2$·3.5H$_2$O: C, 32.42; H, 4.44; N, 10.08%. For the *SS*-picbn complex: Found; C, 33.32; H, 4.52; N, 9.59%. Calcd for [{Cr(OH)(*SS*-picbn)}$_2$] (ClO$_4$)$_4$·3H$_2$O=C$_{32}$H$_{46}$N$_8$O$_{18}$Cl$_4$Cr$_2$·3H$_2$O; C, 33.99; H, 4.64; N, 9.91%. For the *RR*-picchxn complex: Found; C, 35.92; H, 4.83; N, 9.24%. Calcd for [{Cr(OH)(*RR*-picchxn)}$_2$](ClO$_4$)$_4$·4H$_2$O=C$_{36}$H$_{50}$N$_8$O$_{18}$Cl$_4$Cr$_2$·4H$_2$O: C, 36.01; H, 4.87; N, 9.33%. The eluate (i) seemed to be a mononuclear species. From (iii) pure crystals could not be obtained in spite of repeated crystallizations. This may be a polynuclear complex.

The dinuclear complex [{Cr(OH)(*RR*-picchxn)}$_2$](ClO$_4$)$_4$ was dissolved in concd hydrochloric acid. After 6 d, 30% perchloric acid was added to it and the obtained perchlorate salt was recrystallized from water. Found: C, 40.41; H, 4.68; N, 10.40%. Calcd for [CrCl$_2$(*RR*-picchxn)]ClO$_4$·H$_2$O=C$_{18}$H$_{24}$N$_4$O$_4$Cl$_3$Cr·H$_2$O: C, 40.28; H, 4.88; N, 10.44%. The CD spectrum of this mononuclear complex was the same as those of the samples prepared in Preparations I and II.

Other Complexes. The dinuclear complexes [{Cr(OH)(picen)}$_2$](ClO$_4$)$_4$, [{Cr(OH)(pma)$_2$}$_2$](ClO$_4$)$_4$ (pma=2-pyridylmethylamine), and *meso*-[{Cr(OH)(en)$_2$}$_2$]Cl$_4$ were prepared by the methods in the literatures.[9–12]

ΛΛ-trans(py)*trans*(py)-[{Cr(OH)(*S*-pea)$_2$}$_2$]I$_4$ (*S*-pea=(*S*)-1-(2-pyridyl)ethylamine) was prepared in a previous paper.[1]

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu UV-200 and a Hitachi 330 spectrophotometer. The CD spectra were measured on a JASCO MOE-1 spectropolarimeter. The dichloro complexes were measured in 0.1 mol dm^{-3} HCl and the dinuclear ones in water.

Results and Discussion

Structure Assignments. The absorption and CD spectra of the mononuclear dichloro complexes of *SS*-picbn and *SS*-picchxn are shown in Fig. 2. The geometries and absolute configurations were determined from the CD spectra in the first d-d absorption band region. As stated in a previous paper,[2] the CD of *Δ*-*cis*-α complex of chromium(III) or cobalt(III) coordinated with pcen derivative shows a typical (+, −) dispersion pattern from the lower energy side and that of *Λ*-*cis*-α (−, +), the |Δε| value at the each extremum being larger than 1.0. From this criterion, the present complexes of *SS*-picbn and *SS*-picchxn are assigned *Λ*-*cis*-α form. The absorption and CD spectra of di-μ-hydroxo dinuclear complexes of *S*-picpn, *SS*-picbn, and *SS*-picchxn are shown in Figs. 3 and 4 together with those of *ΔΔ*-*trans*(py)*trans*(py)-[{Cr(OH)(picen)}$_2$](ClO$_4$)$_4$ (picen=*N,N'*-bis(2-pyridylmethyl)ethylenediamine)(each parts linked by two hydroxyl groups take *trans*(py)*trans*(py) structure(cis-α structure)), which takes the *trans*(py)*trans*(py) structure stereoselectively because of the steric hindrance between pyridine rings.[10] The CD curve of *S*-picpn complex is nearly a mirror image to that of the picen complex of *ΔΔ* configuration. Thus the configuration of the *S*-picpn complex is assigned

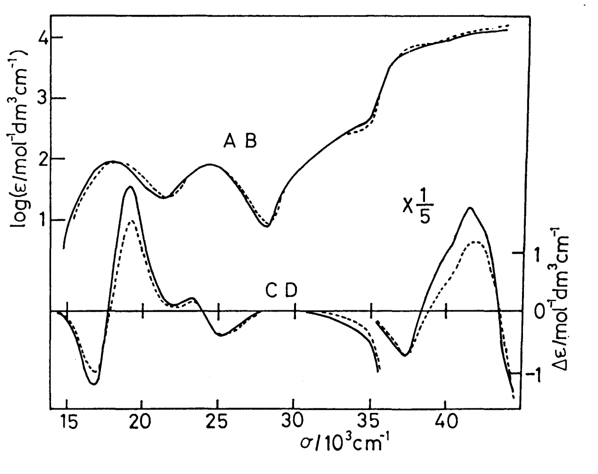

Fig. 2. The absorption (AB) and CD spectra of *Λ*-*cis*-α-[CrCl$_2$(*SS*-picchxn)]ClO$_4$ (——) and *Λ*-*cis*-α-[CrCl$_2$(*SS*-picbn)]ClO$_4$ (------).

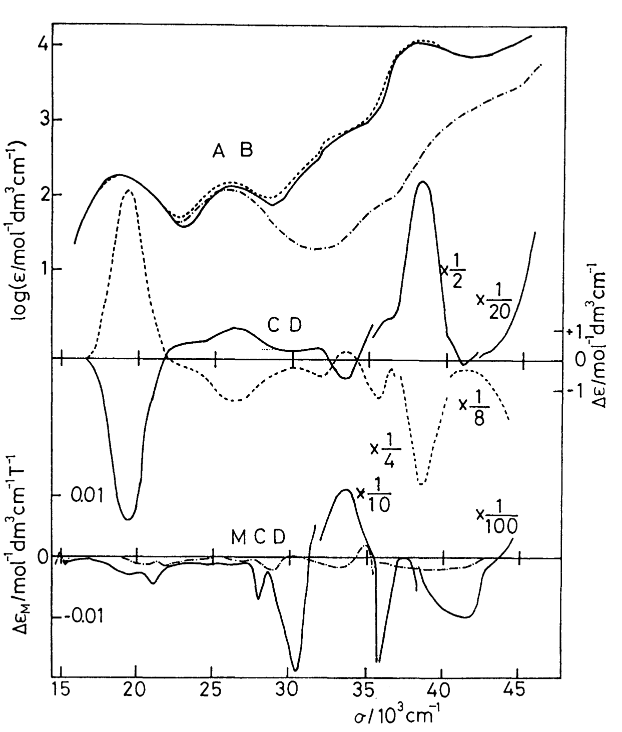

Fig. 3. The absorption (AB) and CD spectra of *ΔΔ*-*trans*(py)*trans*(py)[{Cr(OH)(picen)}$_2$](ClO$_4$)$_4$ (——) and *ΛΛ*-*trans*(py)*trans*(py)[{Cr(OH)(*S*-picpn)}$_2$](ClO$_4$)$_4$ (------). The AB and MCD spectra of *meso*-[{Cr(OH)(en)$_2$}$_2$]Cl$_4$ (-·-·-·) and MCD of *trans*(py)*trans*(py)[{Cr(OH)(picen)}$_2$](ClO$_4$)$_4$ (——) are also presented.

TABLE 1. THE ABSORPTION AND CD DATA (sh=shoulder)

Complex	Absorption		CD		
	σ_{max}/cm^{-1}	log ε_{max} a)	σ_{ext}/cm^{-1}	$\Delta\varepsilon$ a)	Assignment
Λ-cis-α-[CrCl$_2$(*SS*-picbn)]ClO$_4$ (Fig. 2)	18280	1.96	16980	−1.01	d-d
			19230	+1.49	
	24570	1.92	23310	+0.15	
			25450	−0.44	
			30030	−0.01	py(triplet)
			30490	−0.01	
	34000(sh)	2.45	31060	+0.03	
	36360(sh)	3.85	37370	−7.50	py(^{1}L$_b$), CT
			39220(sh)	+1.75	
			42190	+11.2	
			46730	−35.5	
Λ-cis-α-[CrCl$_2$(*SS*-picchxn)]ClO$_4$ (Fig. 2)	18080	1.97	16860	−1.21	d-d
			19080	+2.06	
	24390	1.94	23260	+0.22	
			25320	−0.43	
			30770	+0.33	py(triplet)
	34000(sh)	2.5	32150	+0.06	
	36360(sh)	3.63	37310	−7.29	py(^{1}L$_b$), CT
			39220(sh)	+5.70	
			41490	−17.0	
			46950	+39.9	
ΛΛ-[{Cr(OH)(*SS*-picbn)}$_2$](ClO$_4$)$_4$ (Fig. 4)	18760	2.27	19270	+6.59	d-d
	25910	2.17	26040	−1.54	
			31550	−0.46	py(triplet), *μ*-OH
	32790(sh)	2.86	33110	+0.64	
			35090	−1.06	
			36100	+2.08	py(^{1}L$_b$)
	38020	4.14	38170	−15.0	
ΛΛ-[{Cr(OH)(*SS*-picchxn)}$_2$](ClO$_4$)$_4$ (Fig. 4)	18980	2.24	19120	+6.59	d-d
	25910	2.17	26040	−1.36	
			31550	−0.50	py(triplet), *μ*-OH
	32790(sh)	2.82	33060	+0.50	
			35090	−1.22	
			36230	+1.75	py(^{1}L$_b$)
	38170	4.33	38460	−15.0	
ΛΛ-[{Cr(OH)(*S*-picpn)}$_2$](ClO$_4$)$_4$ (Fig. 3)	18870	2.24	19230	+5.61	d-d
	26040	2.21	26600	−1.58	
			31750	−0.61	py(triplet), *μ*-OH
	32790(sh)	2.83	33330	+0.36	
			35590	−1.34	
	38460	4.12	38310	−16.8	py(^{1}L$_b$)
ΔΔ-[{Cr(OH)(picen)}$_2$](ClO$_4$)$_4$ (Fig. 3)	18800	2.29	19160	−5.39	d-d
	26040	2.16	25910	+1.06	
			31750	+0.39	py(triplet), *μ*-OH
	32790(sh)	2.80	33330	−0.74	
			36230	+3.03	
	38020	4.10	38310	+11.9	py(^{1}L$_b$)
			40980	−0.19	
ΔΔ-[{Cr(OH)(pma)$_2$}$_2$](ClO$_4$)$_4$	18400	2.29	17090	+0.34	d-d
			19720	−5.38	
	26050	2.06	26600	+1.53	
	32790(sh)	2.76	32260	+0.08	py(triplet), *μ*-OH
			33840	−1.16	
	38000	4.12	36870	−9.02	py(^{1}L$_b$)
			39000	+6.3	
ΛΛ-[{Cr(OH)(*S*-pea)$_2$}$_2$]I$_4$ (Fig. 6)	18500	2.32	17000	−0.27	d-d
			19800	+5.29	
	26450	2.12	26620	−1.75	
	32790(sh)	2.82	32270	−0.25	py(triplet), *μ*-OH
			33950	+1.23	
			35400	−0.40	
	38300	4.21	37330	+16.8	py(^{1}L$_b$)
			39100	−1.20	
			41350	+3.50	
	44600	4.73			

a) ε is given in mol^{-1} dm^3 cm^{-1}.

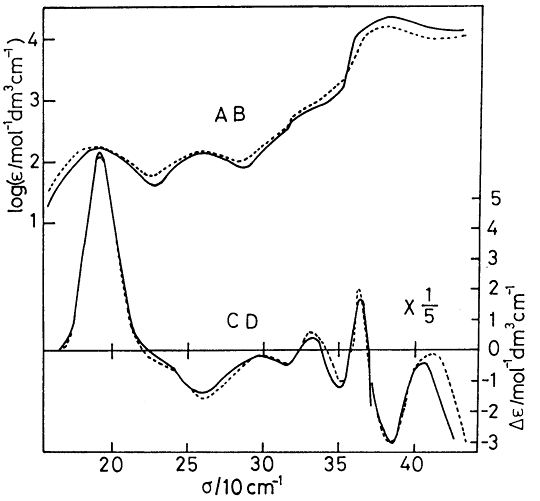

Fig. 4. The absorption (AB) and CD spectra of *ΛΛ*-*trans*-(py)*trans*(py)-$[\{Cr(OH)(SS\text{-picchxn})\}_2](ClO_4)_4$ (——) and *ΛΛ*-*trans*(py)*trans*(py)-$[\{Cr(OH)(SS\text{-picbn})\}_2](ClO_4)_4$ (------).

ΛΛ-*trans*(py)*trans*(py). From the CD spectra in Fig. 4, the *SS*-picbn and *SS*-picchxn complexes are assigned *ΛΛ*-*trans*(py)*trans*(py). These assignments are supported by the decomposition experiment of the dinuclear complex into the mononuclear complex. The numerical data for the absorption and CD spectra are collected in Table 1.

Stereoselective Formation of Diastereomers. The *Λ* and *ΛΛ* diastereomers of the mononuclear and dinuclear complexes were prepared, respectively, for the ligands, *S*-picpn, *SS*-picbn, and *SS*-picchxn, in this study. They belong to the type in which the terminal chelate ring are formed by coordination of the equatorially-oriented substituents on the secondary nitrogen atoms (Fig. 1). Both *Δ* and *Λ* diastereomers of *S*-picpn dichloro mononuclear complex were obtained by the method of Preparation I, but only the more stable *Δ* one in Preparation II. On the other hand, only one isomer was obtained in the case of *SS*-picchxn and *SS*-picbn in either method of preparation. In Fig. 5 the two diastereomers, *Δ*-*cis*-α and *Λ*-*cis*-α of mononuclear *SS*-picchxn complex are shown. The central chelate ring takes the most stable δ conformation for the *SS*-picchxn ligand. In the *Δ* form, there is a steric repulsion between one of the methylene proton (1 in Fig. 5) of the terminal chelate ring and the proton (2 in Fig. 5) attached to the cyclohexane carbon atom adjacent to the asymmetric one. In this form the terminal chelate ring is less strained than that of the *Λ* form. On the other hand, in the *Λ* form there is no such steric repulsion as in the *Δ* form, though the terminal chelate ring in the *Λ* form is more strained than that in *Δ* form. If the steric hindrance predominates, only the *Λ* form will be formed. A preliminary X-ray crystal structure analysis revealed that the *Λ*-*cis*-α-$[CrCl_2(SS\text{-picchxn})]ClO_4$ has in fact the terminal chelate rings of equatorially-oriented pyridylmethyl groups on the secondary nitrogen atoms.[13] In the case of *SS*-picbn ligands, the steric repulsion between the methylene proton and the methyl group on the central chelate ring is considered to be similar to the case of *SS*-picchxn ligand. Thus the *Λ* form was actually isolated.

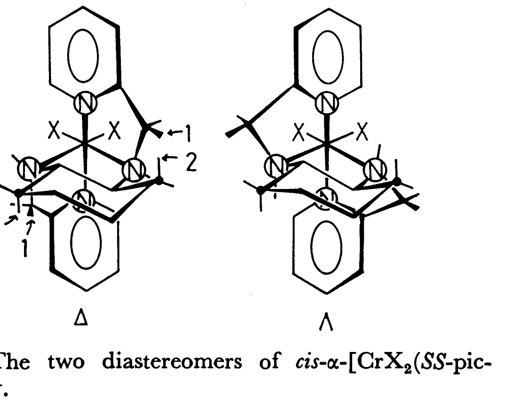

Fig. 5. The two diastereomers of *cis*-α-$[CrX_2(SS\text{-picchxn})]^+$.

For the dinuclear complexes of *SS*-picchxn and *SS*-picbn, the stereoselective formation of diastereomers can be explained by the same way as in the mononuclear ones. For the *S*-picpn ligand, only the *ΛΛ* form was formed. One more factor must be taken into account. From the X-ray structure analyses of *meso*-$[\{Cr(OH)(en)_2\}_2](S_2O_6)_2$[14] and racemic $[\{Cr(OH)(phen)_2\}_2]I_4$–$4H_2O$[15] (phen=1,10-phenanthroline), the in-plane <NCrN angle of di-μ-hydroxo dinuclear complexes is larger than 90° ("in-plane" means that the N atoms are in the plane defined by two chromium and two hydroxo-oxygen atoms). On the other hand, the

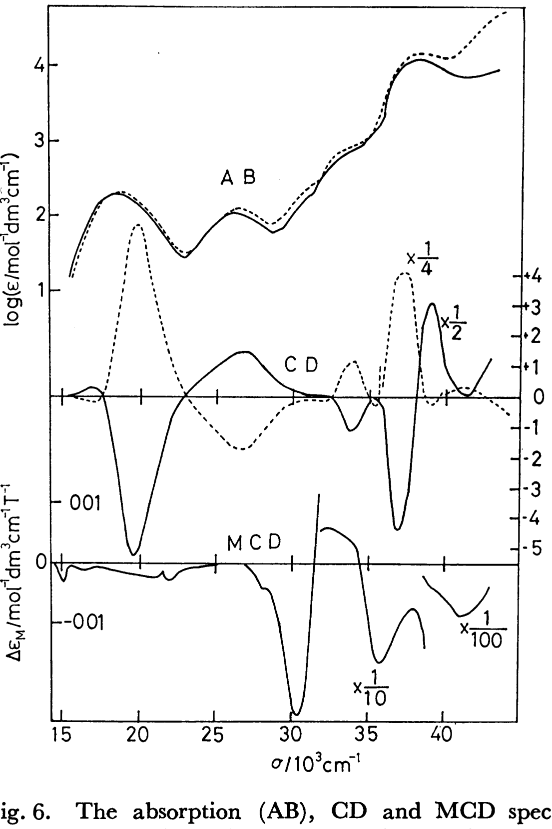

Fig. 6. The absorption (AB), CD and MCD spectra of *ΔΔ*-*trans*(py)*trans*(py)-$[\{Cr(OH)(pma)_2\}_2](ClO_4)_4$ (——), and AB and CD spectra of *ΛΛ*-*trans*(py)*trans*-(py)-$[\{Cr(OH)(S\text{-pea})_2\}_2]I_4$ (------).

TABLE 2. MCD SPECTRAL DATA (sh=shoulder)

Complex	σ_{ext}/cm^{-1}	$10^2\ \Delta\varepsilon_M$[a]	Assignment
$[\{Cr(OH)(en)_2\}_2]Cl_4$ (Fig. 3)	14390	−0.38	d-d(doublet)
	14860	+0.08	
	15380	−0.11	
	20830	−0.14	d-d(quartet)
	21880	−0.16	d-d(doublet)
	27030	−0.06	d-d(doublet)
	28900	−0.23	d-d(doublet)?
	29850	+0.04	
	33440	−0.15	
	34840	+0.25	
	38460	−1.67	
$[\{Cr(OH)(pma)_2\}_2](ClO_4)_4$ (Fig. 6)	15040	−0.35	d-d(doublet)
	16390	−0.13	d-d(quartet)
	20410	−0.24	
	21880	−0.32	d-d(doublet)
	28010	−0.42	d-d(doublet)?
	30490	−2.51	py(triplet), μ-OH
	32260	+5.82	
	33330(sh)	+4.91	
	35710	−17	py(^1L_b)
	40820	−88	
$[\{Cr(OH)(picen)\}_2](ClO_4)_4$ (Fig. 3)	14490	−0.14	d-d(doublet)
	14930	−0.14	
	15380	−0.10	
	16390	−0.07	d-d(quartet)
	19230	−0.29	
	21010	−0.46	d-d(doublet)
	24390	−0.14	d-d(quartet)
	26320	−0.13	
	27930	−0.68	d-d(doublet)?
	30300	−1.91	py(triplet), μ-OH
	33670	+12	
	35710	−18	py(^1L_b)
	41670	−100	

a) $\Delta\varepsilon_M$ is given in mol^{-1} dm^3 cm^{-1} T^{-1}.

∠NCrN angle of the mononuclear complexes is less than 90°. For example, that of Δ-*cis*-α-$[CrCl_2(S\text{-picpn})]^+$ is 83.9°.[3] Accordingly, the central chelate ring of the present dinuclear complexes approaches near planar, and the strain energy becomes not so different between the $\Delta\Delta$ and the $\Lambda\Delta$ forms, so the strain of the terminal chelate ring has a less important contribution. ("strain" means the deviation from the picen (=*N,N′*-bis(2-pyridylmethyl)ethylenediamine) chelate rings of the complex $[\{Cr(OH)(picen)\}_2]^{4+}$.) The steric repulsion between the methyl group and the terminal chelate ring is the main factor of the stereoselective formation of diastereomers. Thus only the $\Lambda\Delta$ form which has no such steric repulsion is considered to be isolated.

Spectral Properties. A shoulder is observed in the region of 33000—34000 cm^{-1} for the dinuclear complexes, overlapping to the spin-forbidden band[1] or pyridine ring band (Figs. 3 and 4). The CD pattern in this region is identical for all the dinuclear complexes treated here, three (+, −, +) or (−, +, −) bands are observed in 32500—37000 cm^{-1}. The absorption and CD spectra of di-μ-hydroxo dinuclear complexes of bidentate ligands are shown in Fig. 6 in which the same shoulder and CD pattern are also observed for $[\{Cr(OH)(pma)_2\}_2]^{4+}$ and $[\{Cr(OH)(S\text{-pea})_2\}_2]^{4+}$. The MCD spectra in this region are shown for $[\{Cr(OH)(picen)\}_2]^{4+}$ and $[\{Cr(OH)(pma)_2\}_2]^{4+}$ (Figs. 3 and 6). The two complexes show only a large positive MCD band in this region. The mononuclear complexes also display a large positive MCD band in this region.[1] The weak absorption band observed in this region for the di-μ-hydroxo en complex has been assigned tentatively to the weak exchange interaction between the two chromium(III) ions.[16] The MCD spectrum (Fig. 3) shows a small (−, +) dispersion in this region, which is a clear indication of existence of a band. The MCD spectral data are shown in Table 2 for $[\{Cr(OH)(en)_2\}_2]^{4+}$, $[\{Cr(OH)(pma)_2\}_2]^{4+}$, and $[\{Cr(OH)(picen)\}_2]^{4+}$. For the di-μ-hydroxo cobalt(III) complex, a strong band has been observed in the same region and assigned to be a hydroxo-to-cobalt charge transfer band, characteristic of this type complexes.[16] In view of the optical electronegativities of chromium(III) and cobalt(III), 1.9 and 2.3, respectively,[17] the shoulders found for the di-μ-hydroxo chromium(III) complexes seem to be due to some another origin than that for the cobalt(III) complexes.

References

1) Part II of this series: Y. Yamamoto and Y. Shimura, *Bull. Chem. Soc. Jpn.*, in press.

2) Y. Yamamoto and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **53**, 395 (1980).

3) Y. Hata, Y. Yamamoto, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 1255 (1981).

4) S. Yoshikawa, M. Asami, M. Inoue, and S. Yano, presented at the 29th Symposium on the Coordination Chemistry, Hamamatsu, 1979, Abstract, No. 1B09.

5) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

6) B. Bosnich and I. M. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972).

7) R. G. Asperger and C. F. Liu., *Inorg. Chem.*, **4**, 1492 (1965).

8) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5021 (1960).

9) K. Michelsen, *Acta Chem. Scand.*, *A*,**30**, 521 (1976).

10) K. Michelsen, *Acta Chem. Scand.*, *A*,**31**, 429 (1977).

11) K. Michelsen, *Acta Chem. Scand.*, *A*,**32**, 847 (1978).

12) J. B. Dubsky, *J. Prakt. Chem.*, **90**, 61 (1914).

13) Y. Yamamoto, Y. Hata, and Y. Shimura, *Chem. Lett.*, in contribution

14) S. J. Cline, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *J. Chem. Soc.*, *Dalton Trans.*, **1977**, 1662.

15) R. P. Scaringe, P. Singh, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 1127 (1975).

16) J. Springborg and C. E. Schäffer, *Inorg. Synth.*, **18**, 75 (1978).

17) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press (1962), p. 95.