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Circular Dichroism of Chromium(III) Complexes. VIII. Circular Dichroism Spectra of Mixed Diamine Complexes of *trans*-$[CrF_2(N)_4]^+$ Type

Sumio KAIZAKI

Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

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The ligand field absorption and circular dichroism (CD) spectra were examined not only for *trans*-difluoro bis(diamine)chromium(III) complexes with two identical chiral diamines but also for nine new mixed diamine complexes of the same type with different diamines, which were ethylenediamine, trimethylenediamine, (*R*)- and (*S*)-propylenediamine, (1*R*, 2*R*)-1,2-cyclohexanediamine, (2*R*, 4*R*)- and (2*R*, 4*S*)-2,4-pentanediamine. The additivity of the CD contributions from the individual chiral diamines were substantiated for most of these complexes. On this basis, the conformational and the vicinal CD contribution due to puckered diamine rings and asymmetric carbon atoms, respectively, were differentiated, and the CD origins of all the present complexes were discussed in connection with stereochemistry.

It has been considered that there are two stereochemical sources from which the circular dichroism (CD) of so-called praseo type complexes with chiral diamines arises: The conformational effect due to puckered chelate rings and the vicinal effect due to asymmetric atoms on ligands. Hawkins *et al.*[1] suggested that the CD spectra of *trans*-$[CoCl_2(diamine)_2]^+$ with (*R*)-propylenediamine (*R*-pn) and (1*R*,2*R*)-1,2-cyclohexanediamine (*R*,*R*-chxn) are contributed exclusively by the conformational effect rather than by the vicinal effect. This has been supported by the CD studies on Co^{III} complexes with analogous chiral diamines.[2,3] More explicit information about the CD origins of *trans*-$[MX_2(N)_4]$ type complexes will be afforded by the CD spectra of mixed diamine complexes of this type with different diamines; it may become feasible to test the additivity of the CD contributions from individual chiral diamines and moreover to differentiate between the conformational and the vicinal effect in this type of complexes. However, there has been no investigation on the CD spectra of mixed diamine complexes with *R*-pn, *R*,*R*-chxn, or (2*R*,4*R*)-2,4-pentanediamine (*R*,*R*-ptn), though a few CD studies in such a system have been reported on *trans*-$[CoCl_2(N)_4]^+$ containing *N*,*N*'-dimethylethylenediamine and the related diamines.[4,5] For this purpose, chromium(III) complexes are considered to be suitable, because a few mixed diamine chromium(III) complexes of the same type have already been prepared[6] and because the CD spectra in the first ligand field band region of Cr^{III} complexes behave similarly to those of Co^{III} complexes.

In this paper, the synthetic method for the known *trans*-difluoro mixed diamine chromium(III) complexes[6] is applied to the preparation for nine new Cr^{III} complexes with different diamines, which are pairs of *R*- and *S*-pn or ethylenediamine (en) with trimethylenediamine (tn), *R*,*R*-chxn, *R*,*R*-ptn, or (2*R*,4*S*)-2,4-pentanediamine (*R*,*S*-ptn). The ligand field absorption and CD spectra of these complexes are discussed in comparison with those of the same type complexes containing two identical chiral diamines. It is demonstrated that the CD contributions from the individual chiral diamines to the complexes are almost separable and additive except for such complexes as the bis(*R*-pn) and the bis(*R*,*R*-chxn) one, and that the conformational and the vicinal CD contributions from the chiral diamines are separated. The anomalous CD behavior of the bis(*R*-pn) and the bis(*R*,*R*-chxn) complexes is interpreted in terms of an additional chirality due to donor nitrogen atom distortions.

Experimental

Preparation of Ligands. The chiral diamines used were obtained by the methods described previously: *S*- and *R*-pn,[7] *R*,*R*-chxn,[8] *R*,*R*-ptn·2HCl,[2] and *R*,*S*-ptn·2HCl.[2]

Preparation of Complexes. *1)* trans-$[CrF_2(R\text{-}pn)_2]ClO_4$, trans-$[CrF_2(R,R\text{-}chxn)_2]Cl\cdot H_2O$, *and* trans-$[CrF_2(R,R\text{-}ptn)_2]ClO_4$: These complexes were prepared according to the literature methods for the *R*-pn, *R*,*R*-chxn complexes,[9] and *R*,*R*-ptn complex.[10] The *R*,*R*-chxn complex was originally isolated as the perchlorate salt and then converted to the chloride salt with an anion exchange resin of chloride form in a batchwise operation. Found: C, 38.71; H, 8.21%. Calcd for $[CrF_2(R,R\text{-chxn})_2]Cl\cdot H_2O$: C, 38.76; H, 8.13%.

2) trans-$[CrF_2(en)(R\text{-}pn)]Br\cdot H_2O$, trans-$[CrF_2(tn)(R\text{-}pn)]Br\cdot 1.5H_2O$, trans-$[CrF_2(R\text{-}pn)(R,R\text{-}chxn)]Br$, *and* trans-$[CrF_2(S\text{-}pn)(R,R\text{-}chxn)]Br\cdot 0.5H_2O$: The preparation of these mixed diamine complexes were carried out by the method of Vaughn and Marziwski[6] except that the chiral diamines (*R*-, *S*-pn, and *R*,*R*-chxn) were used instead of the racemic ones. Although they obtained only one isomer (*cis* one) for $[CrF_2(pn)(dach)]Br\cdot H_2O$ where pn and dach stand for *rac*-pn and *rac*-chxn, respectively, another isomer (*trans* one) of the corresponding complexes with the chiral diamines could be isolated after the reaction at about 50 °C. Found: C, 18.20; H, 6.16; N, 17.57%. Calcd for $[CrF_2(en)(R\text{-pn})]Br\cdot H_2O$: C, 18.64; H, 6.26; N, 17.39%. Found: C, 20.88; H, 6.65; N, 16.28%. Calcd for $[CrF_2(tn)(R\text{-pn})]Br\cdot 1.5H_2O$: C, 20.89; H, 6.72; N, 16.23%. Found: C, 31.18; H, 6.81%. Calcd for $[CrF_2(R\text{-pn})(R,R\text{-chxn})]Br$: C, 30.18; H, 6.75%. Found: C, 28.63; H, 6.69%. Calcd for $[CrF_2(S\text{-pn})(R,R\text{-chxn})]Br\cdot 0.5H_2O$: C, 29.44; H, 6.86%.

3) trans-$[CrF_2(en)(R,R\text{-}chxn)]Br\cdot 2H_2O$: This was prepared with use of *trans*(F)-$[CrF_2(H_2O)_2(en)]Br$[11] by a similar method to that for *trans*-$[CrF_2(R\text{-pn})(R,R\text{-chxn})]Br$. Found: C, 24.71; H, 6.60; N, 14.55%. Calcd for $[CrF_2(en)(R,R\text{-chxn})]Br\cdot 2H_2O$: C, 25.27; H, 6.89; N, 14.74%.

4) trans-$[CrF_2(en)(R,R\text{-}ptn)]Br\cdot H_2O$, trans-$[CrF_2(R\text{-}pn)(R,R\text{-}ptn)]Br\cdot H_2O$, trans-$[CrF_2(S\text{-}pn)(R,R\text{-}ptn)]Br\cdot 1.5H_2O$, *and* trans-$[CrF_2(R\text{-}pn)(R,S\text{-}ptn)]Br\cdot H_2O$: Pure sodium (0.3 g) was dissolved in 8 cm^3 of absolute ethanol. To this solution was added 1.1 g of *R*,*R*-ptn·2HCl or *R*,*S*-ptn·2HCl by portions; then white powder of sodium chloride was precipitated during vigorous stirring. After it was removed by

filtration and washed with a small amount of ethanol, *trans*(F)-[$CrBrF_2(H_2O)$(*R*-pn)] (or *trans*(F)-[$CrBrF_2(H_2O)$(*S*-pn)]) (1.7 g) or *trans*(F)-[$CrF_2(H_2O)_2$(en)]Br (1.7 g) was added to the filtrate and washings. The mixture was warmed on a water bath at about 50 °C for several hours. Then pink orange precipitate was obtained. After cooling in an ice bath, it was filtered off and recrystallized from methanol by the addition of ether. Found: C, 23.29; H, 6.81; N, 15.96%. Calcd for [CrF_2(en)(*R*,*R*-ptn)]Br·H_2O: C, 24.00; H, 6.91; N, 16.00%. Found: C, 25.88; H, 7.11; N, 15.23%. Calcd for [CrF_2(*R*-pn)(*R*,*R*-ptn)]Br·H_2O: C, 26.38; H, 7.20; N, 15.38%. Found: C, 25.72; H, 7.40; N, 15.20%. Calcd for [CrF_2(*S*-pn)(*R*,*R*-ptn)]Br·1.5H_2O: C, 25.74; H, 7.29; N, 15.01%. Found: C, 25.97; H, 7.35; N, 15.30%. Calcd for [CrF_2(*R*-pn)(*R*,*S*-ptn)]Br·H_2O: C, 26.38; H, 7.20; N, 15.38%.

Measurements. The electronic absorption spectra were measured by a Shimadzu UV-200S spectrophotometer. The CD spectra were recorded with a JASCO MOE-1 spectropolarimeter. These measurements were made on aqueous solutions ranging in concentration from 4×10^{-3} to 6×10^{-3} mol dm^{-3} at room temperature.

Results and Discussion

1) Absorption Spectra. The absorption spectral data of the present complexes are given in Table 1. Their positions and intensities are similar to those of *trans*-[$CrF_2(en)_2$]$^+$. Thus, it is apparent that these complexes have a *trans* geometrical structure.

The first ($^4T_{2g}\leftarrow{}^4A_{2g}$) and the second ($^4T_{1g}\leftarrow{}^4A_{2g}$) ligand field transition split into two components respectively; they have been assigned to the $^4E(^4T_{2g})$, $^4B_2(^4T_{2g})$, $^4E(^4T_{1g})$, and $^4A_2(^4T_{1g})$ states in D_4 symmetry from the longer wavelength side.[12] The absorption band intensities for *trans*-difluoro complexes with two identical diamines are found to be similar to one another, whereas those with different diamines give larger molar absorptivities than the former group of the complexes (Table 1). Such an intensity difference between the former and the latter group of the complexes is observed more clearly and more reliably for the $^4B_2$ and $^4A_2$ nondegenerate components than for the two ^4E components, because these nondegenerate components always exhibit prominent band peaks but not shoulders nor plateaus. On the theoretical basis, it has been pointed out that the absorption band intensities of the $^4B_2$ and $^4A_2$ components depend on the ligands on the xy plane; *i.e.*, the $(N)_4$ ligands in *trans*-[$CrF_2(N)_4$]$^+$ type complexes.[13] As seen through the absorption band intensities of the complexes with two identical diamines, the hyperchromic properties of the five- and six-membered diamines seem to be similar to one another. Therefore, the increase in intensity for the mixed diamine complexes is not caused by the hyperchromic properties of the diamines, but this may be responsible for the descent from D_2 to C_2 symmetry of the $(N)_4$ plane in these complexes.

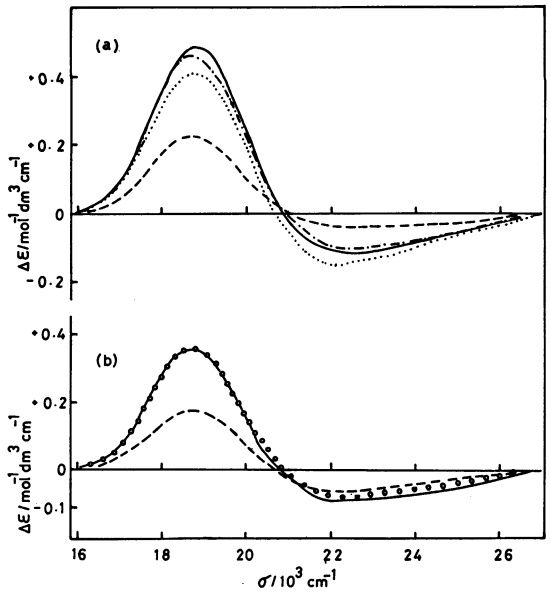

Fig. 1. a) CD curves of *trans*-[CrF_2(*R*-pn)(*R*,*R*-chxn)]$^+$ (——), *trans*-[CrF_2(*S*-pn)(*R*,*R*-chxn)]$^+$ (------), *trans*-[CrF_2(*R*-pn)$_2$]$^+$ (·····), and *trans*-[CrF_2(*R*,*R*-chxn)$_2$]$^+$ —·—); b) CD curves of *trans*-[CrF_2(en)(*R*-pn)]$^+$ (–––), *trans*-[CrF_2(en)(*R*,*R*-chxn)]$^+$ (——), and *trans*-[CrF_2-(*rac*-pn)(*R*,*R*-chxn)]$^+$ ($1/2\{\Delta\varepsilon$(*R*-pn·*R*,*R*-chxn)$+\Delta\varepsilon$(*S*-pn·*R*,*R*-chxn)$\}$) (ooooo).

Table 1. Absorption data of *trans*-[CrF_2(diamine)$_2$]$^+$ complexes

Diamine	$\sigma/10^3$ cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})			
	$^4E(^4T_{2g})$	$^4B_2(^4T_{2g})$	$^4E(^4T_{1g})$	$^4A_2(^4T_{1g})$
(*R*-pn)$_2$	19.3 (17.4)[b]	21.5 (22.9)	25.0 (14.5)	28.5 (15.1)
(*R*,*R*-chxn)$_2$	18.9 (17.2)[b]	21.6 (24.1)	25.3 (15.2)	28.3 (16.2)
(*R*,*R*-ptn)$_2$	18.5 (19.1)[b]	21.3 (22.9)	25.0 (18.2)	27.8 (18.2)
(en)$_2$[a]	18.9 (16.5)[b]	21.5 (21.0)	25.2 (13.9)	28.5 (14.4)
(tn)$_2$[a]	18.6 (16.8)[b]	21.4 (20.7)	25.1 (16.5)	27.8 (16.3)
(en)(*R*-pn)	19.1 (19.8)[b]	21.3 (21.9)	25.1 (15.5)	28.4 (16.3)
(tn)(*R*-pn)	18.9 (19.6)[b]	21.4 (27.4)	25.2 (19.4)	28.2 (24.8)
(en)(*R*,*R*-chxn)	19.1 (22.8)[b]	21.6 (29.5)	25.6 (22.5)	28.4 (24.9)
(en)(*R*,*R*-ptn)	18.9 (20.2)[b]	21.4 (27.5)	25.3 (18.6)	28.3 (25.4)
(*R*-pn)(*R*,*R*-chxn)	18.9 (27.3)[b]	21.7 (37.0)	25.7 (32.7)	28.6 (36.2)
(*S*-pn)(*R*,*R*-chxn)	18.9 (25.3)[b]	21.5 (32.7)	25.3 (25.5)	28.4 (28.0)
(*R*-pn)(*R*,*R*-ptn)	18.9 (21.9)[b]	21.3 (28.8)	25.3 (19.7)	28.2 (26.3)
(*S*-pn)(*R*,*R*-ptn)	19.0 (21.2)[b]	21.4 (28.4)	25.1 (20.0)	28.2 (24.7)
(*R*-pn)(*R*,*S*-ptn)	19.0 (21.6)[b]	21.4 (30.5)	25.2 (22.0)	28.2 (28.4)

a) J. Glerup, J. Josephsen, K. Michesen, E. Pedersen, and C. E. Schäffer, *Acta Chem. Scand.*, **24**, 247 (1970). b) Shoulder.

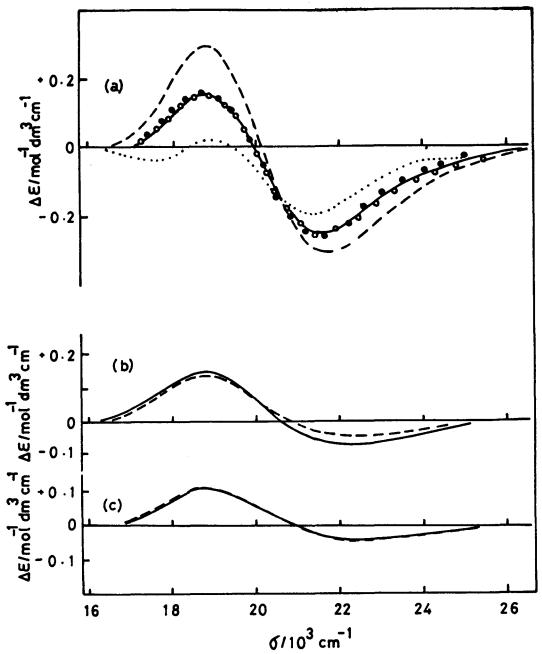

Fig. 2. a) CD curves of *trans*-$[CrF_2(R\text{-pn})(R,R\text{-ptn})]^+$ (------), *trans*-$[CrF_2(S\text{-pn})(R,R\text{-ptn})]^+$ (·····), *trans*-$[CrF_2(en)(R,R\text{-ptn})]^+$ (——), *trans*-$[CrF_2(R,R\text{-ptn})_2]^+$ (1/2 $\Delta\varepsilon$) (••••), and *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-ptn})]^+$ (1/2{$\Delta\varepsilon$(*R*-pn·*R*,*R*-ptn)+$\Delta\varepsilon$(*S*-pn·*R*,*R*-ptn)}) (○○○○○○); b) CD curves of *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$ (1/2{$\Delta\varepsilon$(*R*-pn·*R*,*R*-ptn)−$\Delta\varepsilon$(*S*-pn·*R*,*R*-ptn)}) (——) and *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$ (1/2{$\Delta\varepsilon$(*R*-pn·*R*,*R*-chxn) −$\Delta\varepsilon$(*S*-pn·*R*,*R*-chxn)}) (------); c) CD curves of *trans*-$[CrF_2(tn)(R\text{-pn})]^+$ (——) and *trans*-$[CrF_2(R\text{-pn})(R,S\text{-ptn})]^+$ (-----).

TABLE 2. CD DATA OF *trans*-$[CrF_2(DIAMINE)_2]^+$ COMPLEXES

$(diamine)_2$	$\sigma_{ext}/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})	
$(R\text{-pn})_2$	18.8 (+0.41)	22.0 (−0.15)
$(R,R\text{-chxn})_2$	18.7 (+0.46)	22.0 (−0.11)
(en)(*R*-pn)	18.9 (+0.17)	22.3 (−0.06)
(tn)(*R*-pn)	18.8 (+0.11)	22.3 (−0.04)
(*R*-pn)(*R*,*S*-ptn)	18.8 (+0.11)	22.7 (−0.04)
(en)(*R*,*R*-chxn)	18.8 (+0.33)	22.6 (−0.09)
(*R*-pn)(*R*,*R*-chxn)	18.8 (+0.48)	22.3 (−0.12)
(*S*-pn)(*R*,*R*-chxn)	18.7 (+0.22)	22.3 (−0.04)
$(R,R\text{-ptn})_2$	18.7 (+0.31)	21.7 (−0.53)
(en)(*R*,*R*-ptn)	18.9 (+0.15)	21.7 (−0.26)
(*R*-pn)(*R*,*R*-ptn)	18.8 (+0.29)	21.2 (−0.31)
(*S*-pn)(*R*,*R*-ptn)	17.4 (−0.05) 18.9 (+0.01)	21.5 (−0.21)

2) CD Spectra. The CD spectra of the present complexes are given in Figs. 1 and 2, and their data are summarized in Table 2. Since the CD spectrum of *trans*-$[CrF_2(R,R\text{-chxn})_2]^+$ resembles that of *trans*-$[CrF_2(R\text{-pn})_2]^+$ (Fig. 1 and Table 2), it appears that the overall CD of these complexes arise mainly from the conformational effect due to the λ ring conformation[10] rather than from the vicinal effect as found for the CD spectra of Co^{III} complexes.[1-3] From this result, it might be predicted that the CD spectrum of *trans*-$[CrF_2(en)(R\text{-pn})]^+$ should be similar to that of *trans*-$[CrF_2(en)(R,R\text{-chxn})]^+$, and that *trans*-$[CrF_2(S\text{-pn})(R,R\text{-chxn})]^+$ should give negligibly weak CD. These are not observed for the present complexes. That is, the CD intensity of *trans*-$[CrF_2(en)(R,R\text{-chxn})]^+$ is twice as strong as that of *trans*-$[CrF_2(en)(R\text{-pn})]^+$, and *trans*-$[CrF_2(S\text{-pn})(R,R\text{-chxn})]^+$ gives appreciable CD intensity (Fig. 1 and Table 2). These facts indicate that each contribution of the *R*-pn and *R*,*R*-chxn ligands to optical activity of the mixed diamine complexes differs significantly from that of the bis(*R*-pn) and the bis(*R*,*R*-chxn)-complex. In order to examine the difference in CD behavior between the complexes with identical diamines and those with different diamines in more detail, the separation of each CD contribution from the *R*-pn and the *R*,*R*-chxn ligand to the mixed diamine complexes is attempted by the addition and the substraction of the CD curves of *trans*-$[CrF_2(R\text{-pn})(R,R\text{-chxn})]^+$ and *trans*-$[CrF_2(S\text{-pn})(R,R\text{-chxn})]^+$. The same treatment is carried out for *trans*-$[CrF_2(R\text{-pn})(R,R\text{-ptn})]^+$ and *trans*-$[CrF_2(S\text{-pn})(R,R\text{-ptn})]^+$. The CD contributions of the chiral diamines thus obtained correspond to the CD curves of *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-chxn})]^+$ and *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$ for the former case, and to those of *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-ptn})]^+$ and *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$ for the latter case. They are compared with each other in Figs. 1 and 2. The CD contribution from the *R*,*R*-chxn to *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-chxn})]^+$ and that from the *R*,*R*-ptn to *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-ptn})]^+$ are identical with the overall CD curve of *trans*-$[CrF_2(en)(R,R\text{-chxn})]^+$ and that of *trans*-$[CrF_2(en)(R,R\text{-ptn})]^+$ (and also one half that of *trans*-$[CrF_2(R,R\text{-ptn})_2]^+$), respectively. For *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$, the CD contribution from the *R*-pn is similar to that from the *R*-pn to *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$, especially in the region of the longer wavelength CD component, but does not agree appreciably with the CD curve of *trans*-$[CrF_2(en)(R\text{-pn})]^+$, *trans*-$[CrF_2(tn)(R\text{-pn})]^+$, and one half that of *trans*-$[CrF_2(R\text{-pn})_2]^+$. Accordingly, it can be seen that the CD contributions of the chiral diamines to the present complexes are separable and additive except for the cases of the bis(*R*-pn), bis(*R*,*R*-chxn), and the mono(*R*-pn) complexes with ethylenediamine and trimethylenediamine. In view of such additivity of the CD for the complexes, there may be no significant interaction between two different diamines in the complexes; free puckering of the ethylenediamine ring occurs for *trans*-$[CrF_2(en)(R,R\text{-chxn})]^+$ and *trans*-$[CrF_2(en)(R,R\text{-ptn})]^+$ in solution. As to *trans*-$[CrF_2(tn)(R\text{-pn})]^+$, the CD spectrum is quite identical with the CD of *trans*-$[CrF_2(R\text{-pn})(R,S\text{-ptn})]^+$, but differs from that of *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$ (Fig. 2). This fact suggests that the coordinated trimethylenediamine takes the same conformation as the *R*,*S*-ptn ligand, which has been determined to have a chair form by the X-ray structural analysis of $(+)_{560}$-$[Co(ox)(R,S\text{-ptn})_2]ClO_4\cdot H_2O$.[14] This will be substantiated more evidently by the CD study on *trans*-$[Cr(ONO)_2(R\text{-pn})(R,S\text{-ptn})]^+$ and *trans*-$[Cr(ONO)_2(tn)(R\text{-pn})]^+$ as discussed in a subsequent paper.[15] The CD behavior of *trans*-$[CrF_2(en)(R\text{-pn})]^+$ may be interpreted as follows. From a similarity in absorption

band intensity between *trans*-$[CrF_2(en)(R\text{-pn})]^+$ and *trans*-$[CrF_2(R\text{-pn})_2]^+$ (Table 2) and from good coincidences in shape and size between the *R*-pn and ethylenediamine rings in complexes as revealed by X-ray structural analyses,[16,17] it is supposed that the effective symmetry of the $(N)_4$ plane in the former mono(*R*-pn) complex is similar to the D_2 symmetry of the rectangular $(N)_4$ plane in the latter bis(*R*-pn) complex as seen through the Section *1)*. In this case, the steric interaction between the *R*-pn and ethylenediamine ligands may occur owing to the proximity between the amine protons of the ethylenediamine and the adjacent ones of the *R*-pn. Meanwhile, there may be no significant interaction in the lower C_2 symmetry complexes with nonidentical diamines having the different N–Cr–N angles as noted above, probably because the deformation of the $(N)_4$ planes from the rectangle to the trapezoid may decrease the crowding between the two diamine moieties. This interaction appears to cause restricted puckering of the ethylenediamine ring, resulting in some CD contribution from the ethylenediamine ligand to this mixed diamine complex. This seems to be the reason why the CD spectrum of *trans*-$[CrF_2(en)(R\text{-pn})]^+$ differs from one half of the CD of the bis(*R*-pn) complex and from the CD contribution of the *R*-pn to *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$ and *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$.

The longer wavelength CD component of *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-chxn})]^+$ is more than twice as intense as that of *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$ and *trans*-$[CrF_2(R\text{-pn})(rac\text{-ptn})]^+$ (Figs. 1 and 2). Such a difference in CD contribution between the *R*-pn and the *R,R*-chxn ligand may be understood by the differentiation between the conformational and the vicinal effect. For this purpose, it is assumed that the CD contributions of the chiral diamines consist of the conformational effect ($\Delta\varepsilon(\lambda)$ for the *R*-pn and the *R,R*-chxn ligand; $\Delta\varepsilon(\lambda')$ for the *R,R*-ptn ligand) and the vicinal effect ($\Delta\varepsilon(R)$ for all these three diamines) as expressed in the following equations,

$$\Delta\varepsilon(R\text{-pn}\cdot R,R\text{-chxn}) = 3\Delta\varepsilon(R) + 2\Delta\varepsilon(\lambda),$$

$$\Delta\varepsilon(S\text{-pn}\cdot R,R\text{-chxn}) = \Delta\varepsilon(R),$$

$$\Delta\varepsilon(R\text{-pn}\cdot R,R\text{-ptn}) = 3\Delta\varepsilon(R) + \Delta\varepsilon(\lambda) + \Delta\varepsilon(\lambda'),$$

$$\Delta\varepsilon(S\text{-pn}\cdot R,R\text{-ptn}) = \Delta\varepsilon(R) - \Delta\varepsilon(\lambda) + \Delta\varepsilon(\lambda'),$$

where the *R* configuration of asymmetric carbons requires the λ conformation due to the equatorial preference of alkyl-substituents on ligands, and $\Delta\varepsilon(R) = -\Delta\varepsilon(S)$ and $\Delta\varepsilon(\lambda) = -\Delta\varepsilon(\delta)$. From the above equations, the conformational and the vicinal CD contribution are obtained as shown in Fig. 3. The considerable CD contribution from the vicinal effect due to the *R* configuration for the *R*-pn and the *R,R*-chxn ligand leads to the difference in CD contribution between the *R*-pn and the *R,R*-chxn ligand. It is noted that the net CD signs in the first ligand field $^4T_{2g} \leftarrow {}^4A_{2g}$ transition for the conformational contributions of both the *R*-pn(*R,R*-chxn) and the *R,R*-ptn ligand are the same as each other and are opposite to those for the vicinal contributions as seen in Fig. 3. The net CD signs for the λ conformation and the *R* configuration of asymmetric carbons, negative and positive, respectively, are consistent with the predicted ones in terms of the regional (hexadecadal) rule.[18] It is considered unlikely that the conformational and the vicinal CD contribution in the mixed diamine complexes with different diamines are much different from those in the bis(*R*-pn) and the bis(*R,R*-chxn) complexes. Thus, the inconsistency in CD behavior between the mixed diamine complexes and the bis(*R*-pn), bis(*R,R*-chxn) complexes may be explained on the assumption of an additional chirality probably due to donor nitrogen atom distortions in the latter complexes. As shown in Figs. 1 and 2, the CD spectrum of *trans*-$[CrF_2(R\text{-pn})_2]^+$ is more intense than twice the CD contribution of the *R*-pn to *trans*-$[CrF_2(R\text{-pn})(rac\text{-chxn})]^+$ or the calculated CD curve contributed solely from the conformational and the vicinal effects (*i.e.*, $2\Delta\varepsilon(R)+2\Delta\varepsilon(\lambda)$), whereas the CD spectrum of *trans*-$[CrF_2(R,R\text{-chxn})_2]^+$ is less intense than twice the CD contribution of the *R,R*-chxn to *trans*-$[CrF_2(rac\text{-pn})(R,R\text{-chxn})]^+$ or the calculated CD curve (*i.e.*, $4\Delta\varepsilon(R)+2\Delta\varepsilon(\lambda)$). This observation suggests that the CD contributions from an additional chirality to the bis(*R*-pn) and the bis(*R,R*-chxn) complex are not equivalent and opposite in sign to each other; positive and negative CD being contributed to the bis(*R*-pn) and the bis(*R,R*-chxn) complexes, respectively. The regional rule predicts that such an additional CD contribution is induced by donor nitrogen atoms which are skewed away from ideal octahedral edges in such a way that they lie in the same sector as the ring alkyl group ($-CH_2CH-$) for the bis(*R*-pn) complex and as the *C*-alkyl substituents for the bis(*R,R*-chxn) complex as depicted in Fig. 4. Similar displacement of the donor nitrogen atoms in the *R*-pn complex has been found by the X-ray structural crystallography of *trans*-$[CoCl_2(R\text{-pn})_2]Cl\cdot HCl\cdot H_2O$[14] as pointed out previously.[2,19] It is likely that such a distortion arises from the steric interaction between the identical diamines in the bis(*R*-pn) and the bis(*R,R*-chxn) complex. For *trans*-$[CrF_2(en)(R\text{-pn})]^+$, which encounters a similar situation to the bis(*R*-pn) complex as noted above, the crowding between the diamine moieties may be released by shifting the conformational equilibrium of the ethylenediamine ring puckering and/or by distorting the donor nitrogen atoms. For other mixed diamine complexes with

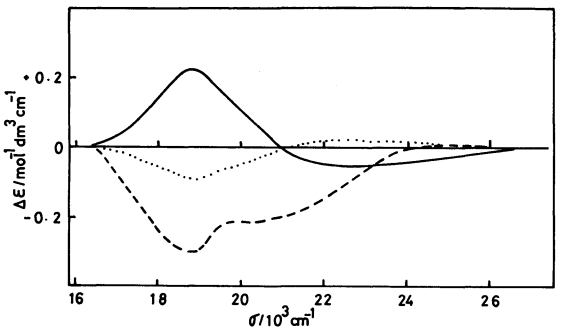

Fig. 3. The CD contribution from the vicinal effect due to the configuration of asymmetric carbons ($\Delta\varepsilon(R)$) (——); the CD contribution from the conformational effect due to five-membered chelate rings (*R*-pn and *R,R*-chxn) ($\Delta\varepsilon(\lambda)$) (·····) and of a six-membered one (*R,R*-ptn) ($\Delta\varepsilon(\lambda')$) (------).

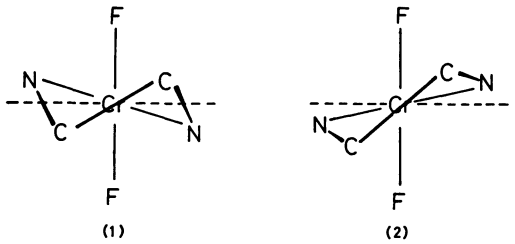

Fig. 4. Proposed donor nitrogen atom displacements from ideal octahedral edges for *R*-pn(1) and *R,R*-chxn (2) rings.

nonidentical diamines, it is plausible that there seems to be no observable CD contribution from the donor nitrogen atom distortions, because of no appreciable steric interaction between the different diamines in these complexes as mentioned above.

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