December, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **56**, *3625—3631 (1983)* 3625

Circular Dichroism of Chromium(III) Complexes. IX. Circular Dichroism Spectra and Stereochemistry of Dinitritobis(diamine)chromium(III) Complexes

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

(Received May 28, 1983)

The circular dichroism (CD) spectra of optically active dinitritobis(diamine)chromium(III) complexes were measured in the visible and near-ultraviolet region, where the diamines used were ethylenediamine, trimethylenediamine, (*R*)-propylenediamine, (1*R*, 2*R*)-1,2-cyclohexanediamine, (2*R*, 4*R*)- and (2*R*, 4*S*)-2,4-pentanediamine. The stereochemistry and the conformational (rotational) isomerism of coordinated nitrito ligands were discussed on the basis of the solvent-dependent CD spectra in the near-ultraviolet region of an intraligand absorption band localized on nitrito ligands. It is proposed that the CD variation in the intraligand transition region among the complexes concerned is responsible for the chiral arrangement of nitrito ligands. Further, the conformation of trimethylenediamine chelate in the *trans*-dinitrito-(*R*)-propylenediamine complex is determined to take a chair form in comparison with the CD behavior of the corresponding (2*R*, 4*S*)-2,4-pentanediamine complex.

There have been few studies on stereochemistry of unidentate ligands in complexes. A new conformational or rotational isomerism of coordinated unidentate ligands has been first discovered for "brown" and "yellow" crystal forms of *mer*-$[Co(NO_2)_3(NH_3)(en)]$[1)] and established by X-ray structural analyses.[2)] Since these isomers show the identical physical properties in solution,[1)] it is difficult to recognize such a conformational isomerism in solution. It has been proposed that the solvent-dependent CD variation in the first ligand field band region of some dianionotetraamine Co^{III} complexes is responsible for optical activity due to rotational conformations of unidentate aniono ligands such as NO_2^- and N_3^-.[3)] However, CD spectra in the d-d band region are not appropriate for the investigation on stereochemistry of unidentate ligands in various circumstances brought about by different chelate rings, because they are susceptible to ring conformations and geometrical configurations of complexes. CD spectra associated with intraligand transitions of unidentate ligands will provide the stereochemical information about such unidentate ligands themselves. For instance, it has been found that for organic nitrites several well-defined vibronic CD peaks observed in the nitrite chromophore region (400—350 nm) are sensitive to the stereochemical environments around nitrites.[4)] In the corresponding region of oxygen-bonded nitritochromium(III) complexes, some inflections of the vibronic structure overlapping with a broad absorption band envelope due to the second d-d transition have been observed in dipolar aprotic solvents; they are ascribed to the intraligand $n\rightarrow\pi^*$ transition localized on the coordinated nitrito ligands.[5)] In addition to such spectral properties, taking into account the fact that nitrito Cr^{III} complexes are relatively stable and do not isomerize to N-bonded nitro complexes, the CD spectra in the intraligand transition region of these complexes may be useful for the stereochemical investigation of unidentate ligands. In a previous letter,[6)] the CD spectra in the intraligand band region of optically active *cis*- and *trans*-dinitritobis(diamine)-chromium(III) complexes have been explained in terms of the chiral arrangements of nitrito ligands. In this paper, the intraligand CD spectra of mononitrito and dinitrito chromium(III) complexes of various diamines are examined in order to assess the effect of the stereochemical environment around the coordinated diamine chelate rings on the rotational isomerism of coordinated nitrito ligands, where the diamines used are ethylenediamine(en), trimethylenediamine(tn), (*R*)-propylenediamine(*R*-pn), (1*R*, 2*R*)-1, 2-cyclohexanediamine(*R*,*R*-chxn), (2*R*,4*R*)- and (2*R*,4*S*)-2,4-pentanediamine(*R*,*R*-ptn and *R*,*S*-ptn).

Experimental

Preparation of Complexes. *1)* trans-$[Cr(ONO)_2(diamine)_2]ClO_4$: *trans*-Difluorobis(diamine) complexes were obtained as starting materials by the methods described elsewhere.[7—9)] These difluoro complexes were converted into *trans*-dibromobis(diamine)chromium(III) bromides by dissolving the difluoro complexes in 3.5 M (1 M=1 mol dm^{-3}) methanolic hydrogen bromide solutions.[8)] The nitrito complexes were obtained as anhydrous perchlorate salts by the reaction with lithium nitrite in weakly acidified solutions after aquating the corresponding dibromo complexes at about 60 °C for 5 min, and then by the addition of an excess amount of lithium perchlorate. The complexes were recrystallized from acetonitrile by the addition of ether.

2) trans-$[CrF(ONO)(R,R\text{-}chxn)_2]ClO_4\cdot 0.5LiClO_4$: This mono nitrito complex was prepared by a similar method to that for *trans*-$[CrF(ONO)(en)_2]ClO_4$.[10)]

3) $(+)^{\Delta\varepsilon}_{480}$-cis-$[Cr(ONO)_2(en)_2]ClO_4$ *and* $(+)^{\Delta\varepsilon}_{480}$-cis-$[Cr(ONO)_2(tn)_2]ClO_4\cdot 0.5LiClO_4$: As starting materials, the corresponding *cis*-dichloro complexes were prepared and resolved into the optical isomers according to the reported methods.[11—13)] The less soluble $(+)^{\Delta\varepsilon}_{520}$-optical isomers of these *cis*-dichlorobis(diamine)chromium(III) 3-bromo-*d*-camphor-8-sulfonate were aquated with an appropriate amount of silver nitrate in an ice-cold solution. After silver chloride was removed, the perchlorate salts of the corresponding dinitrito complexes were isolated by the successive addition of lithium nitrite and lithium perchlorate below 5 °C. Although the racemization of these optically active *cis*-bis(diamine) complexes should be taken into consideration, the CD intensity in the first band region is found to be comparable to that of other *cis*-$[CrX_2(en)_2]^+$ type complexes.[13)] Thus, it appears that the racemization of the dinitrito complexes is not significant during the preparation.

Table 1. Analytical data of the complexes

Complex	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
trans-$[Cr(ONO)_2(R\text{-pn})_2]ClO_4$	18.18	18.40	5.24	5.15	21.54	21.45
trans-$[Cr(ONO)_2(R,R\text{-ptn})_2]ClO_4$	26.59	26.82	6.47	6.30	19.10	18.77
trans-$[Cr(ONO)_2(R,R\text{-chxn})_2]ClO_4$	30.05	30.55	6.09	5.98	17.80	17.81
trans-$[CrF(ONO)(R,R\text{-chxn})_2]ClO_4\cdot 0.5LiClO_4$	28.82	28.94	5.93	5.67		
trans-$[Cr(ONO)_2(en)(R\text{-pn})]ClO_4$	15.23	15.90	4.64	4.80	22.10	22.25
trans-$[Cr(ONO)_2(tn)(R\text{-pn})]ClO_4$	18.12	18.40	5.11	5.15	21.11	21.46
trans-$[Cr(ONO)_2(R\text{-pn})(R,R\text{-ptn})]ClO_4$	23.00	22.89	5.68	5.76	19.02	20.02
trans-$[Cr(ONO)_2(R\text{-pn})(S,S\text{-ptn})]ClO_4$	22.84	22.89	5.78	5.76	20.08	20.02
trans-$[Cr(ONO)_2(R\text{-pn})(R,S\text{-ptn})]ClO_4$	22.51	22.89	5.71	5.76	19.45	20.02
trans-$[Cr(ONO)_2(en)(R,R\text{-ptn})]ClO_4$	20.45	20.72	5.39	5.47	20.34	20.71
$(+)^{\Delta\varepsilon}_{480}$-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$	13.63	13.21	4.63	4.43	23.29	23.11
$(+)^{\Delta\varepsilon}_{480}$-*cis*-$[Cr(ONO)_2(tn)_2]ClO_4\cdot 0.5LiClO_4$	16.34	16.20	4.55	4.53	19.34	18.89

The elemental analyses of the complexes are presented in Table 1.

Measurements. Absorption and CD spectra were recorded with a Shimadzu UV-200S spectrophotometer and a JASCO MOE-1 spectropolarimeter, respectively. All the solvents used are of spectrograde. The concentrations of the complexes were 2×10^{-3} to 4×10^{-3} M. CD measurements in KBr disks were carried out by a similar procedure to that of Bosnich *et al.*[14]

Results and Discussion

Stereochemistry of Nitrito Ligands. The geometrical structures of the dinitritobis(diamine)chromium(III) complexes are assigned by comparing their visible and near-ultraviolet absorption spectra with those of the known *cis*- and *trans*-dinitritobis(ethylenediamine)chromium(III) complexes;[5] the geometrical structure is retained on the anation of the corresponding diaqua complexes with nitrite ions in acidic solutions. As shown in Fig. 1, the first d-d absorption bands of *cis*- and *trans*-isomers of the complexes differ from each other, while the isomers give a similar spectral behavior in the second

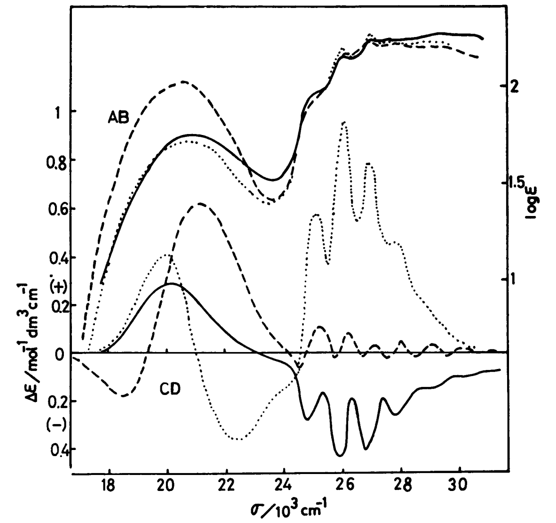

Fig. 1. Absorption (AB) and CD curves of $(+)^{\Delta\varepsilon}_{480}$-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$ (——), *trans*-$[Cr(ONO)_2(R\text{-pn})_2]ClO_4$ (------), and *trans*-$[Cr(ONO)_2(R,R\text{-ptn})_2]ClO_4$ (······) in DMF.

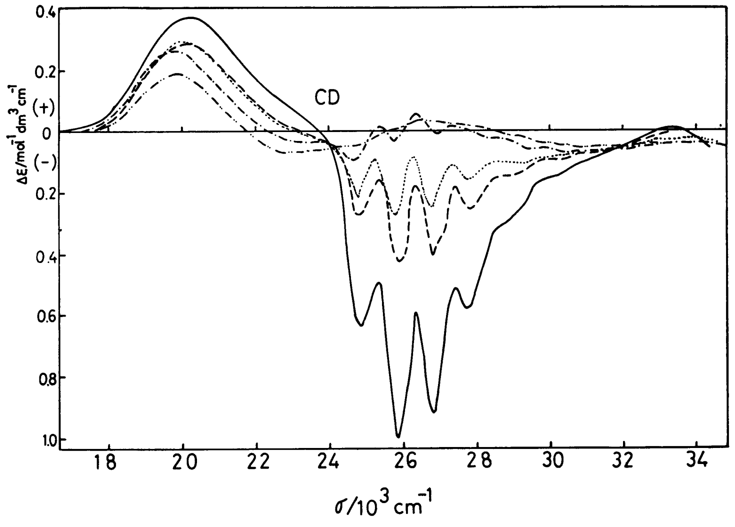

Fig. 2. CD curves of *trans*-$[Cr(ONO)_2(R\text{-pn})_2]ClO_4$.
Solvents: DMA (——); DMF (------); NMF (······); formamide (—·—); H_2O (—··—).

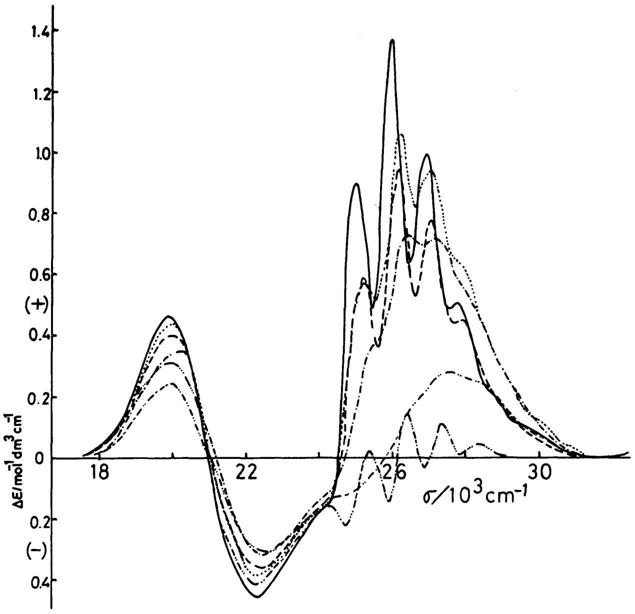

Fig. 3. CD curves of *trans*-$[Cr(ONO)_2(R,R\text{-ptn})_2]ClO_4$. Solvents: DMA (——); DMF (------); NMF (······); formamide (—·—); H_2O (—··—); acetonitrile (—···—).

d-d band region where the n→π* intraligand transition within nitrito ligands occurs. Some characteristic inflections on this absorption band are observed for *cis*- and *trans*-dinitritobis(diamine)chromium(III) complexes in aprotic solvents such as *N*,*N*-dimethylformamide (DMF).[5] On their CD spectra in the region from 24000 to 30000 cm^{-1}, more marked characteristics of the intraligand transition are recognized in aprotic solvents than those on the absorption spectra.[6] The CD spectra of the complexes in DMF give more remarkable and well resolved peaks, of which each position corresponds to that of the absorption spectra as seen in Fig. 1. The absorption maxima and CD extrema consist of the progression of about 1000 cm^{-1}, originating from 25000 cm^{-1}, due to the N–O stretching vibration as found in the vibronic structure of $NaNO_2$ crystals.[15] The intensity distribution of the CD spectra is found to be in line with that of alkyl nitrites.[4] Therefore, each vibronic CD component in this region is certainly associated with the intraligand n→π* transition of the coordinated nitrito ligands in the complexes. Figures 2—4 show the remarkable solvent-dependent variation of the CD spectra of some complexes. It is found that the intensity enhancement of the vibronic CD components is more pronounced than that of the CD in the first d-d band region. As shown in Figs. 2 and 3, a positive CD band in the second band region at about 27500 cm^{-1} for *trans*-dinitritobis(diamine) complexes in H_2O may correspond to the second ligand field ($^4T_{1g}$←$^4A_{2g}$) transition, because this lies at the expected position for the $^4E_g(D_{4h})$ component of the $^4T_{1g}$ parentage and in general *trans*-dihalogenobis(diamine)chromium(III) complexes with *R*-pn and *R*,*R*-ptn ligands give a positive CD component due to the second ^4E_g←$^4B_{1g}$ transition.[8] This suggests that the vibronic CD components of the *trans*-bis(*R*-pn) complex undergo sign inversions by changing the solvent from water to aprotic solvents in contrast with the CD behavior of the *trans*-bis(*R*,*R*-ptn) complex where no CD sign inversion occurs with solvent change. In addition to these CD behavior, the considerable CD intensity enhancement of *trans*-bis(diamine) complexes in aprotic solvents as shown in Figs. 2 and 3 will also support the exclusive contribution of optical activity associated with the intraligand transition within nitrito ligands to the vibronic CD components.

It is noted that the signs of the intraligand CD spectra for the *trans*-bis(*R*-pn) and -bis(*R*,*R*-ptn) complexes are opposite to each other though the diamines have the same absolute configuration, and also that the CD behavior of the $(+)^{\Delta\varepsilon}_{480}$-*cis*-bis(en) complex differs from that of the $(+)^{\Delta\varepsilon}_{480}$-*cis*-bis(tn) complex as well as that of the *trans*-bis(diamine) complexes as seen in Figs. 2—5. Such differences in intraligand CD among these complexes may be attributed to the different stereochemical environment experienced by nitrito ligands in the complexes. There are two possible coordination modes of unidentate nitrito ligands with respect to the rotation about the (O)N–O(Cr) bond. As revealed in $[Cr(ONO)(NH_3)_5](ClO_4)_2$ and other nitrito metal complexes by X-ray structural analyses,[16,17] a nitrito ligand in a

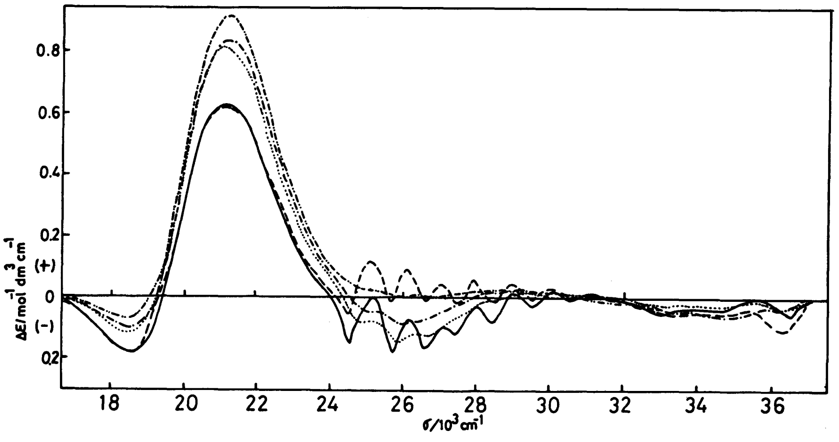

Fig. 4. CD curves of $(+)^{\Delta\varepsilon}_{480}$-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$. Solvents: DMA (——); DMF (------); NMF (······); formamide (—·—); H_2O (—··—).

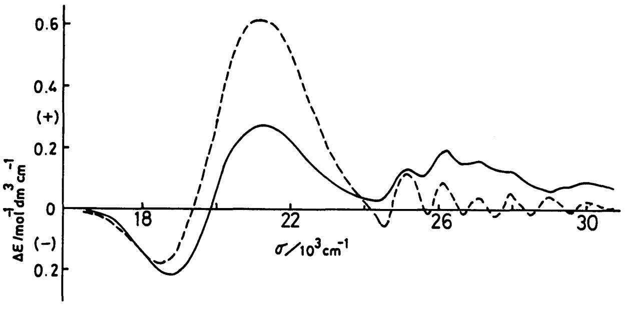

Fig. 5. CD curves of $(+)^{\Delta\varepsilon}_{480}$-*cis*-[Cr(ONO)$_2(tn)_2$]ClO$_4$ (——) and $(+)^{\Delta\varepsilon}_{480}$-*cis*-[Cr(ONO)$_2(en)_2$]ClO$_4$ (------) in DMF.

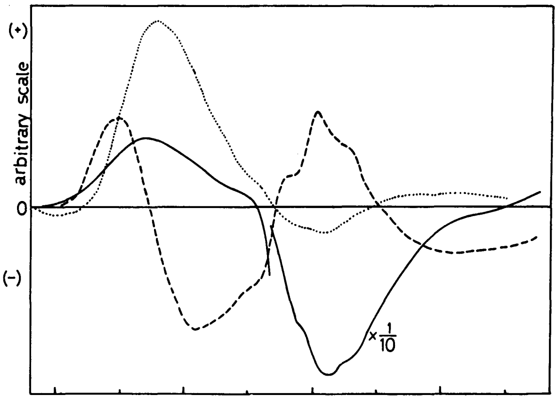

Fig. 6. CD curves of *trans*-[Cr(ONO)$_2$(*R*-pn)$_2$]ClO$_4$ (——), *trans*-[Cr(ONO)$_2$(*R*,*R*-ptn)$_2$]ClO$_4$ (------), and $(+)^{\Delta\varepsilon}_{480}$-*cis*-[Cr(ONO)$_2(en)_2$]ClO$_4$ (······) in a KBr disk.

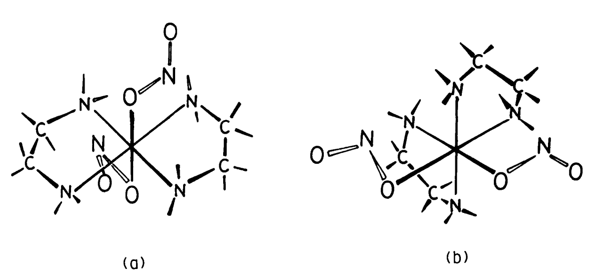

Fig. 7. Proposed configurations due to rotamer conformations of two nitrito ligands in (a) *trans*-[Cr(ONO)$_2$(*R*-pn)$_2$]ClO$_4$ and (b) $(+)^{\Delta\varepsilon}_{480}$-*cis*-[Cr(ONO)$_2(en)_2$]ClO$_4$ with a $\Lambda(\delta\delta)lel_2$ configuration. The methyl group of *R*-pn and all protons are omitted for clarity.

complex prefers the trans form to the cis one, minimizing the steric interaction with the amine ligands. With this coordination mode, the rotation of nitrito ligands about the Cr–O(NO) bond seems to have immediate influence on optical activity of the intraligand transition localized on nitrito ligands. Restricted rotation can form rotamers of different conformations at equilibrium and can produce new chirality with respect to the whole molecule, while complete free rotation can contribute little to optical activity. In the latter case, the intraligand transition acquires the rotational strength only through so-called "vicinal effect" which originates from the chiral diamine chelates. It is probable that the equilibrium of such rotamers depends on a given stereochemical circumstance around nitrito ligands. The interaction between the nitrito ligands and the diamine chelate rings in dinitritobis(diamine) complexes may play an important role in the formation of the predominant rotamer conformations for nitrito ligands. It has been found in *trans*-[Ni(ONO)$_2$(Me$_2$NC$_2$H$_4$NH$_2$)$_2$] and -[Zn(ONO)$_2$(Me$_2$NC$_2$H$_4$NH$_2$)$_2$] by X-ray analyses[18,19] that the nitrito nitrogen atoms are located around the amine nitrogen atoms in which the nearest protons are equatorial. This suggests that the congestion brought about by the diamine chelate rings around the nitrito ligands is released in the neighbourhood of the amino equatorial NH protons where the predominant rotamers can settle beacause the equatorial protons are more distant from the nitrito nitrogen atoms than the axial protons; thus the steric interaction between them decreases. In view of the fact that the intraligand CD spectrum in a KBr disk of *trans*-[Cr(ONO)$_2$(*R*-pn)$_2$]ClO$_4$ is about ten times as intense as the CD in the first d-d band region as shown in Fig. 6, the nitrito ligands are expected to take a chiral configuration. It is supposed that in the solid state of this complex two nitrito ligands are arranged in such a way that their nitrogen atoms are located near the NH equatorial protons of (*R*)-propylenediamines with the λ ring conformation as shown in Fig. 7. Since such an arrangement results in configurational chirality with respect to the intraligand transition of nitrito ligands, the CD intensity in this region is expected to be enhanced. On the other hand, according to the empirical method based on the CD in the first d-d band region,[13a] $(+)^{\Delta\varepsilon}_{480}$-*cis*-[Cr(ONO)$_2(en)_2$]ClO$_4$ is assumed to take a Λ absolute configuration, presumably with a stable $\delta\delta(lel_2)$ conformation of the ethylenediamine rings. Then, the location of the nitrito nitrogen atoms in the vicinity of the NH equatorial protons for the ethylenediamine chelates gives rise to the achiral configuration in which two nitrito ligands lie in the same plane as the CrN$_2$O$_2$ one as depicted in Fig. 7. The proposed rotamer configuration is deduced from the fact that the intraligand CD of $(+)^{\Delta\varepsilon}_{480}$-*cis*-bis(en) complex perchlorate in a KBr disk is much weaker than the CD in the first d-d band region as shown in Fig. 6.

In solution, the solvent effect on the distribution of the rotamer conformations must be taken into account, since the intraligand CD spectra of the present complexes vary remarkably with solvent as compared with the CD in the first d-d band region. As shown in Figs 2—4, the fine structures of the CD spectra in the corresponding region become more resolved, sharper, and more amplified with solvent in the order, formamide$<$ *N*-methylforamide(NMF)$<$DMF$<$*N*,*N*-dimethylacetamide (DMA). This order for the CD variation is in accordance with the increasing order of the donor number of solvents,[20] and is similar to the order derived from the solvent-dependent CD and NMR study of cobalt(III) complexes by Hawkins *et al.*[21] They postulated the stereoselective solvation to the amino NH equatorial protons in the complexes. As shown in Figs. 2 and 3, more marked CD enhancement is observed in DMA than in DMF, though the donor number of

DMA (27.8) is not much different from that of DMF (26.6). This implies that the bulkiness as well as the donor number of the solvents is responsible for the optical activity associated with the intraligand transition in nitrito ligands, solvation in DMA being more stereoselective. As proposed for the solvent-dependent CD spectra of cobalt(III) complexes,[3] such stereoselective solvation in the present complexes will form more chirally defined second coordination spheres and will assist more restricted rotation of nitrito ligands in making their predominant rotamer conformations in the increasing order of the bulkiness as well as the donor number of the solvents, enhancing optical activity in the intraligand transition region. In acetonitrile, the intraligand CD spectrum of the *trans*-bis(*R*-pn) complex is similar to that in DMF, whereas the *trans*-bis(*R*,*R*-ptn) complex gives a quite different CD pattern in this solvent from that in DMF as shown in Fig. 3. In the last case, the CD diminishes considerably, but still exhibits the prominent vibronic structure. This fact together with the sign inversion of the intraligand CD behavior for the *trans*-bis(*R*-pn) and the *trans*-bis(*R*,*R*-ptn) complex reflects a subtle difference in the stereochemical circumstance containing the first solvation sphere around nitrito ligands between these complexes. The different disposition of the amino NH equatorial protons in the complexes may impose the different orientation of higher order on the solvent molecules or may cause the formation of different chirally defined second coordination spheres. Judging from the fact that the intraligand CD intensity of the *trans*-bis(diamine) complexes in aprotic solvents is much stronger than that in water and that of the optically active *cis*-bis(diamine) complexes in aprotic solvents, chiral configurations caused by restricted rotation of two nitrito ligands in the *trans*-bis(diamine) complexes as in the case of the solid state may be retained to some extent even in solutions. This postulate is confirmed by comparing the CD intensity of *trans*-$[\mathrm{CrF(ONO)}(R,R\text{-chxn})_2]^+$ with that of *trans*-dinitritobis(*R*,*R*-chxn) complex in DMF. The CD spectrum of the mononitrito complex is found to be much weaker by about one sixth than that of the dinitrito complex as shown in Fig. 8. A comparison of the CD for *trans*-$[\mathrm{Cr(ONO)_2(en)}(R\text{-pn})]^+$ and -$[\mathrm{Cr(ONO)_2(en)}(R,R\text{-ptn})]^+$ with that for *trans*-$[\mathrm{Cr(ONO)_2}(R\text{-pn})_2]^+$ and -$[\mathrm{Cr(ONO)_2}(R,R\text{-ptn})_2]^+$, respectively, also ensures the chiral arrangement of two nitrito ligands in the complexes; *i.e.*, the intraligand CD intensities of the mono(*R*-pn) and mono (*R*,*R*-ptn) complexes are not half but about one fourth as weak as those of the corresponding *trans*-bis(*R*-pn) and -bis(*R*,*R*-ptn) complexes as seen in Figs. 2, 3, 9, 10. These findings are contrary to the anticipation that the vicinal CD contribution from the chirality in diamine ligands (configurations of asymmetric carbons and conformations of chelate rings) is proportional to the number of chiral ligands and/or nitrito chromophores in the absence of the chirality due to the rotational arrangements of two nitrito ligands.

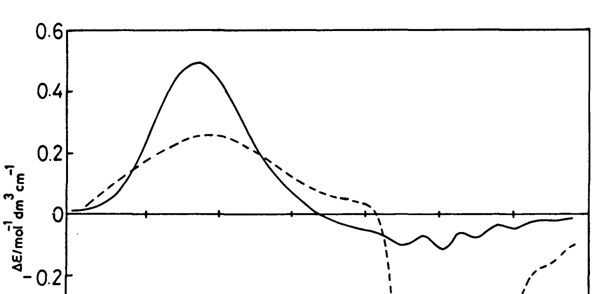

Fig. 8. CD curves of *trans*-$[\mathrm{CrF(ONO)}(R,R\text{-chxn})_2]\mathrm{ClO_4}$ (——) and *trans*-$[\mathrm{Cr(ONO)_2}(R,R\text{-chxn})_2]\mathrm{ClO_4}$ (------) in DMA.

Even though the rotamer conformations of the nitrito ligands in the complexes in solutions are much less rigid and much more flexible than in the solid state, it might be expected that due to the intra- and intermolecular interactions of nitrito ligands with diamine chelates and/or the solvation molecules the most probable location of nitrito ligands at equilibrium is in the neighbourhood of amino nitrogen atoms along the line connecting between equivalent symmetry-related (by a C_2 axis) NH equatorial protons where nitrito ligands would

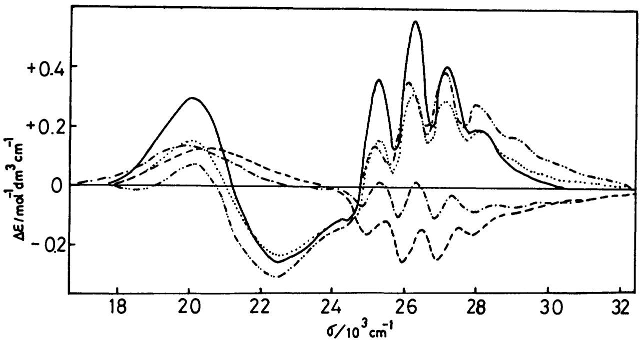

Fig. 9. CD curves of *trans*-dinitrito mixed diamine Cr(III) complexes in DMA.
(*R*-pn·*R*,*R*-ptn) (——); (en·*R*-pn) (------); (en·*R*,*R*-ptn) (······); (tn·*R*-pn) (—·—); (*S*-pn·*R*,*R*-ptn) (—··—).

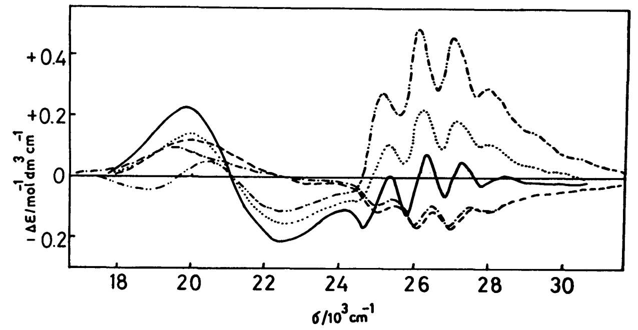

Fig. 10. CD curves of *trans*-dinitrito mixed diamine Cr(III) complexes in acetonitrile.
(*R*-pn·*R*,*R*-ptn) (——); (*R*-pn·en) (------); (en·*R*,*R*-ptn) (······); (tn·*R*-pn) (—·—); (*S*-pn·*R*,*R*-ptn) (—··—).

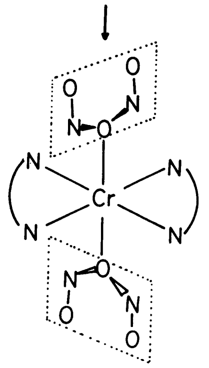

Fig. 11. The most probable paired locations of nitrito ligands at two equivalent symmetry-related sites near equatorial NH protons of diamines; the disorder over the pairs results in forming the planes.

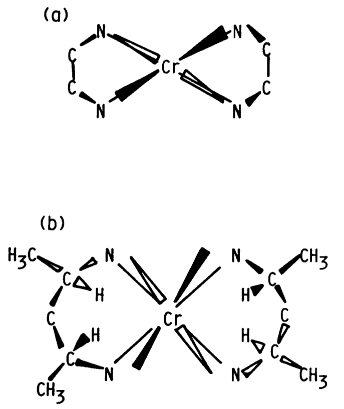

Fig. 12. View along the (ON)O–Cr–O(NO) bond axis from the arrow of Fig. 11 for *trans*-bis(*R*-pn) complex (a) and *trans*-bis(*R*,*R*-ptn) complex (b); the shaded and open elongated triangles indicate the upper and lower nitrito ligands, respectively.

rotate more sluggishly and reside for a longer time than anywhere else. In other words, it seems that the time-averaged orientation of two nitrito ligands results in the formation of two planes as shown in Fig. 11. Non-orthogonality and non-coplanarity of the two planes are expected to induce a new chirality. Construction of molecular models shows that the dihedral angles between the planes are sensitive to the N–Cr–N chelate angles of diamines and/or the crowding brought about by the chelate ring backbone. For the *trans*-bis(*R*-pn) complex, the dihedral angles may be smaller than 90°, because the chelate N–Cr–N angles of five-membered diamine rings are usually about 85°. On the other hand, the *trans*-dinitritobis(*R*,*R*-ptn) complex may give the angle of larger than 90°, due mainly to the steric interaction between the nitrito nitrogen atoms and the axially oriented protons on 2- and 4-carbons of the skew boat *R*,*R*-ptn chelate ring by which the nitrogen atoms might be pushed away from over the chelate plane as shown in Fig. 12. Then such chiral arrangements composed of the nitrito ligand planes in the *R*-pn and *R*,*R*-ptn complexes have the enantiomeric relation to each other in an approximate manner as depicted in Fig. 12. Thus, it is plausible that this enantiomeric pair causes the sign inversion of the intraligand CD components between the *R*-pn and *R*,*R*-ptn complexes.

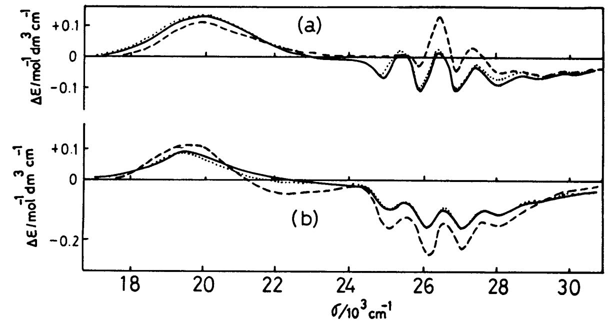

Fig. 13. CD curves of *trans*-[Cr(ONO)$_2$(tn)(*R*-pn)]ClO$_4$ (——) and *trans*-[Cr(ONO)$_2$(*R*-pn)(*R*,*S*-ptn)]ClO$_4$ (⋯⋯), and the CD curves calculated by Eq. 1 for *trans*-[Cr(ONO)$_2$(*R*-pn)(*rac*-ptn)]$^+$ (------) in DMA (a) and in acetonitrile (b).

Conformation of Diamine Chelates. In order to examine the additivity of the CD contributions from the different chiral diamines in a complex and to reveal ethylenediamine and trimethylenediamine chelate ring conformations in the mixed diamine complexes in aprotic solvents, the CD curves of *trans*-[Cr(ONO)$_2$(*R*-pn)(*rac*-ptn)]$^+$ and -[Cr(ONO)$_2$(*rac*-pn)(*R*,*R*-ptn)]$^+$ are calculated by using the following equations:

$$\Delta\varepsilon(R\text{-pn}\cdot rac\text{-ptn}) = 1/2\{\Delta\varepsilon(R\text{-pn}\cdot R,R\text{-ptn}) - \Delta\varepsilon(S\text{-pn}\cdot R,R\text{-ptn})\}, \quad (1)$$

$$\Delta\varepsilon(rac\text{-pn}\cdot R,R\text{-ptn}) = 1/2\{\Delta\varepsilon(R\text{-pn}\cdot R,R\text{-ptn}) + \Delta\varepsilon(S\text{-pn}\cdot R,R\text{-ptn})\}. \quad (2)$$

As shown in Fig. 13, the CD curves of *trans*-[Cr(ONO)$_2$(tn)(*R*-pn)]$^+$ in acetonitrile and DMA are almost identical with those of *trans*-[Cr(ONO)$_2$(*R*-pn)(*R*,*S*-ptn)]$^+$ in those solvents, respectively, but not with those of *trans*-[Cr(ONO)$_2$(*R*-pn)(*rac*-ptn)]$^+$. This means that the ring conformation of the coordinated trimethylenediamine in the dinitrito complex takes the same chair form as that in the *R*,*S*-ptn complex as has been revealed from the CD study of *trans*-difluorobis(diamine) complexes.[7] It appears that the CD difference in the intraligand band region between the *rac*-ptn and *R*,*S*-ptn (or tn) dinitrito complexes reflects the subtle difference in the first and/or the second coordination sphere arising from the skew boat and chair conformations of the six-membered chelate rings. The CD curve calculated by Eq. 2 in acetonitrile is similar to the CD curve of *trans*-[Cr(ONO)$_2$(en)(*R*,*R*-ptn)]$^+$, but the CD of this ethylenediamine complex in DMA differs from the calculated one of the *rac*-pn complex with *R*,*R*-ptn in DMA as shown in Fig. 14. In view of this fact, the ethylenediamine chelate ring in the *trans*-dinitrito complex in acetonitrile may have the same conformation as the *rac*-propylenediamine in *trans*-[Cr(ONO)$_2$(*rac*-pn)(*R*,*R*-ptn)]$^+$; free puckering of the ethylenediamine may occur in acetonitrile as found for the CD spectrum of *trans*-[CrF$_2$(en)(*R*,*R*-ptn)]$^+$ in water.[7] In DMA, it is likely that the stereoselective solvation of bulky DMA with the amine NH protons gives rise to the displacement of the conformational equilibrium of the ethyeledi-

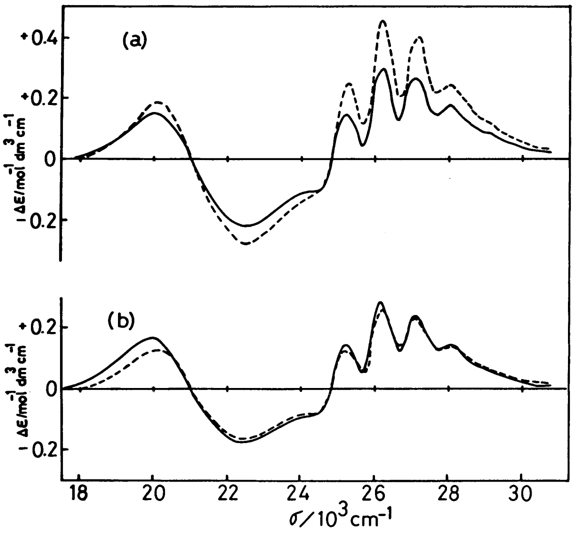

Fig. 14. CD curves of *trans*-[Cr(ONO)$_2$(en)(*R*,*R*-ptn)]ClO$_4$ (——) and the CD curves calculated by Eq. 2 for *trans*-[Cr(ONO)$_2$(*rac*-pn)(*R*,*R*-ptn)]$^+$ (------) in DMA (a) and in acetonitrile (b).

amine ring puckering in *trans*-[Cr(ONO)$_2$(en)(*R*,*R*-ptn)]$^+$. In other words, the CD contribution from different diamines to *trans*-dinitrito mixed diamine complexes with nonidentical diamines are separable and additive in acetonitrile but not in DMA.

The author wishes to express his thanks to Prof. Yoichi Shimura of Osaka University for the guidance of this study and for making the CD spectra available for the present work. This study was supported by a Grant-in-Aid for Scientific Research No. 354223 from the Ministry of Education, Science and Culture.

References

1) K. G. Jensen, Hans Soling, and N. Thorap, *Acta Chem. Scand.*, **24**, 908 (1970).

2) T. E. MacDermott and Sven Barfold, *Acta Chem. Scand.*, **24**, 924 (1970).

3) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 828 (1975).

4) a) C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Am. Chem. Soc.*, **57**, 2835 (1963); b) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, New York (1965), p. 149.

5) W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, **6**, 87 (1967).

6) S. Kaizaki and Y. Shimura, *Chem. Lett.*, **1979**, 1.

7) S. Kaizaki, Bull. Chem. Soc. Jpn., **56**, 3620 (1983).

8) S. Kaizaki and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 3611 (1975).

9) J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen, and C. E. Schäffer, *Acta Chem. Scand.*, **24**, 247 (1970).

10) J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnusson, *Inorg. Chem.*, **7**, 736 (1968); J. W. Vaughn and J. Marzowski, *ibid.*, **12**, 2346 (1973).

11) E. Pedersen, *Acta Chem. Scand.*, **24**, 3362 (1970).

12) J. Selbin and J. C. Bailer, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

13) a) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094; b) I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem.*, **37**, 1359 (1975).

14) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972).

15) J. W. Sidman, *J. Am. Chem. Soc.*, **76**, 2669 (1957).

16) E. Norden, *Acta Crystallogr., Sect. B*, **34**, 2285 (1978).

17) M. A. Hitchman and G. Rowbottom, *Coord. Chem. Rev.*, **42**, 55 (1982).

18) M. G. B. Drew, D. M. L. Goodman, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, **1964**, 363; A. J. Finny, M. A. Hitchman, C. L. Raston, G. L. Rowbottom, and A. H. White, *Aust. J. Chem.*, **34**, 2047 (1981).

19) A. J. Finny, M. A. Hitchman, C. L. Raston, G. L. Rowbottom, and A. H. White, *Aust. J. Chem.*, **34**, 2061 (1981).

20) V. Gutman, *Struc. Bonding*, **12**, 113 (1972).

21) C. J. Hawkins, G. A. Lawrence, and R. M. Peachey, *Aust. J. Chem.*, **30**, 2115 (1970).