CHEMISTRY LETTERS, pp. 1-4, 1979. Published by the Chemical Society of Japan

CIRCULAR DICHROISM AND STEREOCHEMISTRY OF OPTICALLY ACTIVE BIS(DIAMINE)DINITRITOCHROMIUM(III) COMPLEXES

Sumio KAIZAKI and Yoichi SHIMURA*
Department of Chemistry, Faculty of Science, Nara Women's University
Nara 630
*Department of Chemistry, Faculty of Science, Osaka University
Toyonaka 560

From the CD spectra in the region of an intraligand absorption band localized on nitrito ligands of Λ-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$, *trans*-$[Cr(ONO)_2(R\text{-pn})_2]ClO_4$, and *trans*-$[Cr(ONO)_2(R,R\text{-ptn})_2]ClO_4$, where *R*-pn and *R,R*-ptn are (*R*)-propylenediamine and (*R,R*)-2,4-pentanediamine, respectively, the chirality due to the rotational isomerism of the unidentate nitrito ligands has been substantiated and its stereochemical implications have been discussed.

There has been no real evidence for the contribution of stereochemistry of unidentate ligands to optical activity of the metal complex, although it has been suggested that stereochemistry of unidentate ligands such as NO_2^-, N_3^-, SCN^-, and NO_3^- has some influence on CD spectra in the first d-d absorption band of cobalt(III) complexes.$^{1)}$ Since the CD spectra in the d-d band region have been much affected not only by the configurations and/or conformations of chelate rings but also by the geometrical structures of the complexes, they are not suitable for the stereochemical investigation of coordinated unidentate ligands. But the CD spectra associated with the intraligand transition of unidentate ligands may provide stereochemical informations about such ligands, because it has been found that for organic nitrous esters or nitrites several prominent peaks of the vibronic structure in the region of nitrite chromophore (400-350nm) are quite sensitive to stereochemical environment around the nitrite.$^{2)}$ In the corresponding region of the absorption spectra of nitritochromium(III) complexes in dipolar aprotic solvents, a band has been observed with some inflections of the vibronic structure, which have been assigned to the intraligand $n - \pi^*$ transition localized on the coordinated nitrito ligands.$^{3)}$ In addition, these nitritochromium(III) complexes are relatively stable and does not isomerize to N-bonded nitro complexes. Thus, the CD spectra in the intraligand transition of these complexes seem to be most advantageous for the stereochemical investigation of unidentate ligands. In the present letter, the stereochemistry of nitrito ligands in Λ-*cis*-$[Cr(ONO)_2(en)_2]^+$ and *trans*-$[Cr(ONO)_2(\text{diamine})_2]^+$ with (*R*)-propylenediamine(*R*-pn) and (*R,R*)-2,4-pentanediamine(*R,R*-ptn) are considered on the basis of their CD spectra in various kinds of solvents.

The nitrito complexes were derived from the corresponding dichloro or dibromo complexes *via* diaqua complexes by the same method as that for bis(ethylenediamine)dinitrito complexes,$^{3)}$ and obtained as anhydrous perchlorates. CD spectra were recorded with a Jasco MOE-1 spectropolarimeter. The solvents used were all spectrograde.

As shown in Fig. 1, some inflections characteristic of the intraligand n - π^* transition within nitrito ligands are observed on the absorption spectra, but the more marked characteristics of this transition are recognized on their CD spectra in the region from 24000 cm^{-1} to 30000 cm^{-1}. The CD spectra of the present complexes in dimethylformamide(DMF) give more marked and well resolved fine peaks, of which each component corresponds to that of the absorption spectra. Thus, each CD component of the vibronic structure in this region is certainly ascribed to the intraligand n - π^* transition of the coordinated nitrito ligands in the complexes. The vibronic CD behaviours depend not only upon the geometrical structure but also upon the coordinated chiral diamines. The *trans* *R*-pn and *R,R*-ptn complexes give four well resolved vibronic CD peaks with relatively strong intensities and same sign. It is noted that the CD signs of these two complexes in the intraligand transition region are opposite each other, although the diamine chelate rings of these *trans* complexes take the same λ conformation.[4)] The CD behaviour of Λ-*cis*-$[Cr(ONO)_2(en)_2]^+$ is quite different from that of *trans* complexes, showing weak intensities and mixed signs as in Fig. 1. The difference in the CD intensities of the *cis* and *trans* complexes may be attributed to the difference in the stereochemical environment around nitrito ligands in the complexes. Two coordination modes of unidentate nitrito ligands with respect to the rotation about the (O)N-O(Cr) bond are possible as in Fig. 2, and a nitrito ligand in a complex will prefer the trans rotational isomeric form to the cis one owing to the steric interaction with the diamine chelate rings.[3)] With this coordination mode, the rotation of nitrito ligands about the Cr-O(NO) bond seems to have much immediate influence on optical activity of the intraligand transition of nitrito ligands. Completely free rotation can contribute little to optical activity, while restricted rotation can form rotamers of different conformations at equilibrium and results in chirality with respect to the whole molecule. It is probable that the equilibrium of such rotamers is shifted by a given stereochemical circumstance or a congestion brought about by a given conformation of the diamine chelate rings. It may be the interaction between the nitrito nitrogen atom and the NH_2 protons of the diamine chelate rings that plays an important role in the steric requirement for the predominance of a rotamer of nitrito ligands as is found for *trans*-$[Ni(ONO)_2(Me_2NC_2H_4NH_2)_2]$ by the X-ray structural analysis.[5)]

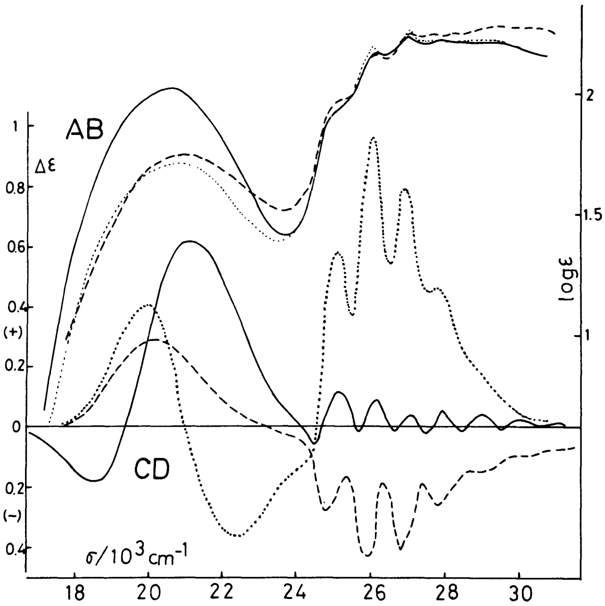


Fig. 1. Absorption(AB) and CD spectra of Λ-*cis*-$[Cr(ONO)_2(en)_2]^+$(——), *trans*-$[Cr(ONO)_2(R\text{-pn})_2]^+$(----), and *trans*-$[Cr(ONO)_2(R,R\text{-ptn})_2]^+$(····) in DMF.

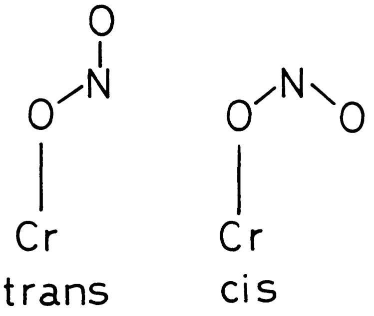
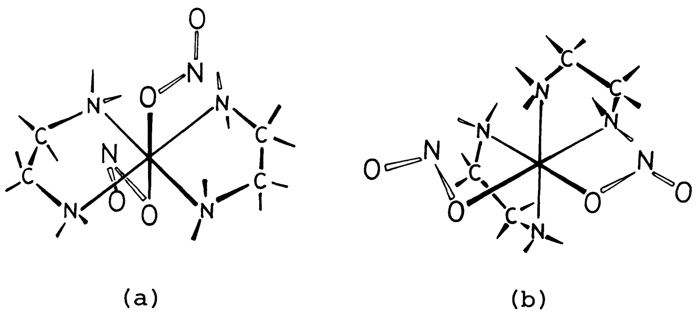


Fig. 2. Possible coordination modes for unidentate nitrito ligands.

In this case, the congestion of the diamine chelate rings seems to be released in the neighbourhood of the amino nitrogen atom on the side of the equatorial NH protons, where the rotation of nitrito ligands is fixed. From the fact that the intensity of the intraligand CD band in KBr disk of *trans* *R*-pn complex perchlorate is about ten times as strong as that in the first d-d absorption band region, it can be supposed that in the solid state of this complex two nitrito ligands are arranged in such a way that the nitrito nitrogen atoms are located in the neighbourhood of the amino nitrogen atoms on the side of the equatorial NH protons of *R*-pn and that such an arrangement results in configurational chirality as shown in Fig. 3. Thus, it is expected that the pronounced enhancement of the CD intensities occurs in the intraligand band region. The CD intensities in KBr disk of *trans* *R*-pn complex tetraphenylborate and *trans* *R,R*-ptn complex perchlorate in the corresponding region are found to be as weak as those in the first band region. Therefore, it appears that the chiral configuration of two ligand rotamers is disordered in these complexes and that the rigid configurational arrangement results accidentally for *trans* *R*-pn complex perchlorate, probably due to the intra- and intermolecular interactions in solid state. Assuming the similar situation for the *cis* complex with the stable $\Lambda(\delta\delta)lel_2$ conformation, the location of the nitrito nitrogen atoms in the neighbourhood of the amino nitrogen atom on the side of the equatorial NH protons of ethylenediamine gives rise to achiral configuration in which two nitrito ligands lie in the same plane as shown in Fig. 3. The weak CD intensity in KBr disk of Λ-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$ suggests the proposed rotamer conformation.



(a) (b)

Fig. 3. Proposed configurations due to rotamer conformations of two nitrito ligands in (a) *trans*-$[Cr(ONO)_2(R\text{-pn})_2]ClO_4$ and (b) Λ-*cis*-$[Cr(ONO)_2(en)_2]ClO_4$. The methyl groups of *R*-pn and all hydrogen atoms are omitted for clarity.

In solution, the solvent effect on the distribution of the rotamers of different conformations must be taken into consideration, for the CD spectra of the present complexes vary with solvent in the intraligand band region. The fine structure of the CD spectra in the corresponding region becomes more resolved, sharper and more amplified in the order of H_2O, formamide, N-methylformamide(NMF), DMF, and dimethylacetamide(DMA) as shown in Figs. 4 and 5. The above order for the CD variation is in accord with the order derived from the solvent-dependent CD study of cobalt(III) complexes.[6)]
This finding suggests that the solvation between achiral solvents and chiral solutes is responsible for the variation of the intraligand CD spectra with solvent. The broadening of the vibronic CD components in protic solvents such as water, formamide, and NMF seems to be due to the hydrogen bonding between nitrito ligands and protons of the

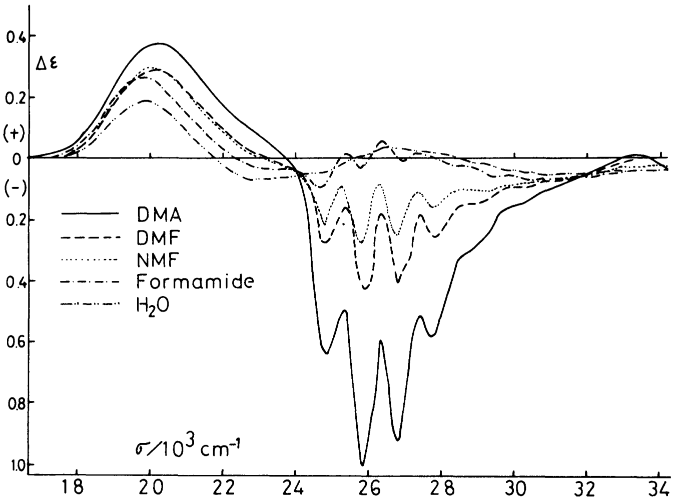


Fig. 4. CD spectra of *trans* *R*-pn complex in solvents.

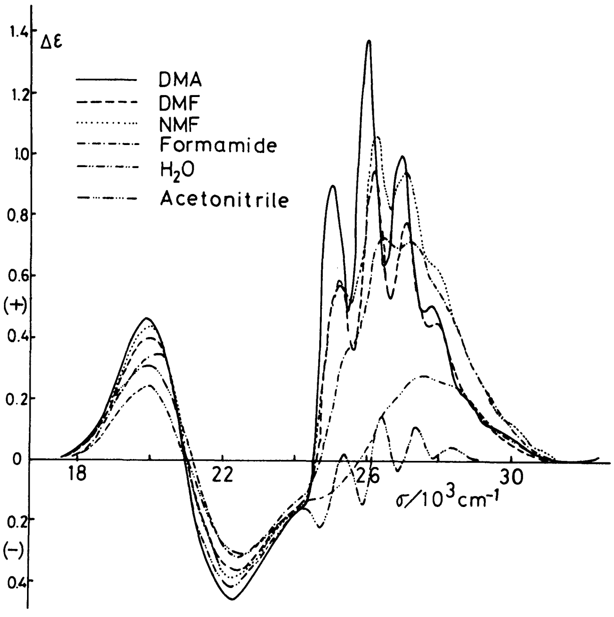


Fig. 5. CD spectra of *trans* *R,R*-ptn complex in solvents.

solvents. In aprotic solvents such as DMF and DMA, it has been revealed that the solvation of the complex cation involves the preferential hydrogen bonding between the donor atom of solvents and equatorial NH protons of the diamines.$^{6)}$ Such a stereoselective solvation between the cation and aprotic solvents assists the rotational restriction of nitrito ligands in forming the predominant rotamer conformations. As a result, optical activity may be enhanced in the intraligand band region. This is compatible with the CD behaviour of the *trans* complexes. In acetonitrile, the intraligand CD spectra of *trans* *R*-pn complex are similar to those in DMF, whereas *trans* *R,R*-ptn complex gives a quite different pattern in this solvent from that in DMF as in Fig. 5. This fact together with the opposite signs of the intraligand CD bands of *R*-pn and *R,R*-ptn complexes as noted before reflects the subtle difference of the stereochemical circumstance including the first solvation sphere around the nitrito ligands between *trans* *R*-pn and *R,R*-ptn complexes. Judging from the relatively weak CD intensities of the Λ-*cis* complex in solution, the proportions of the rotamer conformations must be such that almost perfect compensation is accomplished, in other words, nitrito ligands rotate almost completely freely in this complex.

References

1) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, 14, 828(1975).
2) C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Am. Chem. Soc.*, 85, 2835(1963).
3) W. W. Fee, C. S. Garner, and J. MacB. Harrowfield, *Inorg. Chem.*, 6, 87(1967).
4) S. Kaizaki and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 48, 3611(1975).
5) M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 1964, 363.
6) C. J. Hawkins, G. A. Lawrance, and R. M. Peachey, *Aust. J. Chem.*, 30, 2115(1977).

(Received September 18, 1978)