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Circular Dichroism of Chromium(III) Complexes. II.[1] Correlation between Behavior in the Spin-forbidden Absorption Band Region and Absolute Configurations

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The absorption and circular dichroism (CD) spectra of twelve optically active chromium(III) complexes containing three bidentate ligands have been measured in the near-infrared to ultraviolet region. CD spectra in the spin-forbidden *d–d* absorption band region have been considered mainly in relation to the CD bands in the first spin-allowed *d–d* absorption band region. It has been concluded that the absolute configurations of chromium(III) complexes can be determined on the basis of the signs of the CD bands in the spin-forbidden band region. The splitting components of the CD bands in the spin-forbidden band region have been discussed considering the crystal field treatment by Macfarlane.

There have been a number of studies concerning the relationship between the absolute configurations of dissymmetric d^3 and d^6 metal complexes and their CD spectra in the region of *d–d* absorption bands.[2-5] In these cases, the absolute configurations have been assigned from a comparison of the signs of the CD bands in the spin-allowed *d–d* absorption band region with those of the electronically corresponding CD bands of a reference complex, *e. g.* $(+)_{546}$-$[Co(en)_3]^{3+}$, whose absolute configuration had been conclusively determined by an

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[1] Part I of this series: S. Kaizaki, J. Hidaka and Y. Shimura, This Bulletin, **42**, 988 (1969).

[2] A. J. McCaffery and S. F. Mason, *Trans. Faraday Soc.*, **59**, 1 (1963).

[3] A. J. McCaffery, S. F. Mason and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883.

[4] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

[5] S. F. Mason, Plenary Lecture presented at XII ICCC, Sydney (1969).

X-ray method.6) However, it was difficult to decide which band corresponded electronically to the key band of the reference complex. As a means to solve the problem the ion-pairing effect on the CD bands by selenite or phosphate ion in solutions has been proposed by Mason *et al.*

Kling and Woldbye7) obtained the rotatory dispersion of $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ and $(+)_{546}$-$[Cr(tn)_3]Cl_3$ in their spin-forbidden band region and found many inversive dispersions superimposed with each other. McCaffery and Mason2) reported the CD spectra of tris(L-tartrato)chromium(III) ion in the spin-forbidden band region. In the corresponding region, Mason8) found the splitting of the CD bands due to the ^2E_g transition of $(-)_{546}$-$[Cr_2(OH)_2(dip)_4]^{4+}$ and $(-)_{546}$-$[Cr_2(OH)_2(phen)_4]^{4+}$, and suggested the spin-spin coupling in these binuclear complexes. In a previous paper,1) we reported the CD spectra of three oxalato- and two L-tartratochromium(III) complexes in the spin-forbidden band region and proposed a tentative assignment of the sharp but weak CD bands observed.

In this paper, the CD and electronic absorption spectra of twelve optically active tris-chelate chromium(III) complexes, which belong to the types, $[Cr(N)_6]$, *cis*-$[Cr(O)_2(N)_4]$ and *cis*-$[Cr(O)_4(N)_2]$, will be reported and the assignment of the CD bands in the spin-forbidden band region will be confirmed on the basis of the ion-pairing effect on the CD bands of the tris-diamine chromium(III) complex ions. The correlation of the CD bands in the spin-forbidden band region with those in the spin-allowed absorption band region as well as with the exciton CD bands of tris- or bis-α-diimine metal complexes will be discussed in connection with the absolute configurations. Macfarlane's analysis9) using the crystal field model will be applied to the splitting components of the CD spectra in the spin-forbidden band region. The values for the electron repulsion parameter B and the trigonal parameter v and v' will be estimated and considered.

Experimental

Preparation and Optical Resolution. 1) $(+)_{546}$-$[Cr(ox)(en)_2]Cl$. This complex was prepared by Werner's method10) and resolved by the method of Vaughn and Walkwitz.11)

2) $(+)_{546}$-$[Cr(ox)(dip)_2]Cl$ and $(+)_{546}$-$[Cr(ox)(phen)_2]ClO_4\cdot 2.5H_2O$. These 2,2′-dipyridyl(=dip) and 1,10-phenanthroline(=phen) complexes were prepared and resolved by the method of Broomhead *et al.*12) The CD spectra of $(+)_{546}$-oxalatobis(dip)chromium(III) complex were measured after converting the diastereomer, $(+)_{546}$-$[Cr(ox)(dip)_2]\cdot(+)_{546}$-$[Cr(ox)_2(phen)]$, into the chloride with anion exchange resin of chloride type.

3) $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$. Trisethylenediaminechromium(III) perchlorate was prepared by the method of Linhard and Weigel13) and resolved by the method of Werner.14)

4) $(+)_{546}$-$[Cr(tn)_3](ClO_4)_3$. The preparation and optical resolution of this complex was performed by the method of Schläfer and Kling.15)

5) $(-)_{546}$-$[Cr(BH)_3]Cl_3$.[*1] The trisbiguanide complex was obtained by the reaction with potassium chromium(III) alum and biguanide sulfate in an alkaline solution.16) The optical resolution of this complex was carried out by Michelsen's method.17)

6) $(+)_{546}$-$[Cr(phen)_3](ClO_4)_3$. The synthesis of optically active tris(1,10-phenanthroline)chromium(III) complex was performed by the second order asymmetric process of Lee *et al.*18)

7) $(+)_{546}$-$K[Cr(ox)_2(dip)]\cdot 3H_2O$, $(+)_{546}$-$K[Cr(ox)_2(phen)]\cdot 4H_2O$, $(+)_{546}$-$K[Cr(ox)_2(en)]\cdot 2H_2O$, $Ba[Cr_2(\text{L-tart}_2H)(dip)_2]_2\cdot 9H_2O$ and $NH_4[Cr_2(\text{L-tart}_2H)(phen)_2]\cdot 6.5H_2O$. The preparation and optical resolution of these bisoxalato complexes and the syntheses of the L-tartrato complexes have been described in Part I of this series.1)

8) Sodium $(+)_{589}$-Nitrocamphoronate. The resolving agent with which $[Cr(en)_3]^{3+}$ and $[Cr(tn)_3]^{3+}$ were resolved was prepared from $(+)_{589}$-camphor.19) Preparation of $(+)_{589}$-bromocamphor as a starting material was carried out by treating $(+)_{589}$-camphor with bromine. The $(+)_{589}$-bromonitrocamphor was obtained by refluxing with nitric acid for about 50 hr. The resulting $(+)_{589}$-bromonitrocamphor was treated with sodium alcoholate and the crude product obtained was recrystallized from alcohol. The pure sodium $(+)_{589}$-nitrocamphoronate was obtained as pale yellow crystals.

Measurements. Absorption spectra were measured by a Beckman DU spectrophotometer. CD spectra were recorded with a Roussel-Jouan dichrograph. The CD spectra of $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ in the second spin-allowed *d-d* absorption band region were recorded with a Jasco Model ORD/UV-5 spectrophotometer. The concentrations of complexes for the CD measurements in the spin-forbidden absorption band region were 10^{-1}—10^{-2} F, and the cell lengths employed were 5 and 7 cm.

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6) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, This Bulletin, **30**, 158 (1957).

7) O. Kling and F. Woldbye, *Acta Chem. Scand.*, **15**, 704 (1961).

8) S.F. Mason and J.W. Wood, *Chem. Commun.*, **1968**, 1512; S. F. Mason, *Inorg. Chim. Acta, Rev.*, **2**, 89 (1968).

9) R. M. Macfarlane, *J. Chem. Phys.*, **39**, 3118 (1963).

10) A. Werner, *Ann.*, **406**, 286 (1914).

11) J. W. Vaughn and D. J. Walkwitz, *Inorg. Chem.*, **5**, 1082 (1966).

[*1] The abbreviation, BH, represents a biguanide.

12) J. A. Broomhead, M. Dwyer and N. A. P. Kane-Maguire, *Inorg. Chem.*, **7**, 1388 (1968).

13) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **271**, 115 (1952).

14) A. Werner, *Ber.*, **45**, 865 (1912).

15) H. L. Schläfer and O. Kling, *Z. Anorg. Allg. Chem.*, **302**, 1 (1959).

16) R. G. Rochow, *Inorg. Synth.*, **6**, 68 (1960).

17) K. Michelsen, *Acta Chem. Scand.*, **19**, 1175 (1965).

18) Ching S. Lee, E. M. Gorton, H. M. Neuman and H. R. Hunt, Jr., *Inorg. Chem.*, **5**, 1397 (1966).

19) V. Steele and T. M. Lowry, *J. Chem. Soc.*, **107**, 1038 (1915).

The CD measurements for the ion-pairing effect were made throughout the spin-forbidden and first spin-allowed absorption band region in solutions with the constant molar concentrations of both the complex perchlorates and sodium selenite, using cells with 7, 5, 2 and 1 cm path-length. The solvent employed was water for the complexes except $(+)_{546}$-$[Cr(ox)(phen)_2]ClO_4$. The absorption and CD spectra of this 1,10-phenanthroline complex were measured in 70% $HClO_4$, because of very small solubility in water to measure the CD spectrum in the spin-forbidden band region. In the first spin-allowed *d-d* absorption band region, the CD spectra in water show only one positive CD band, whereas the CD spectra in 70% $HClO_4$ show two CD bands, (−) and (+), listing from the longer wavelength side. In 70% $HClO_4$, however, the absorption spectra and the exciton CD bands in the ultraviolet region corresponding to the ligand transition (300—250 mμ) are similar to those in water. This fact indicates that the geometrical sturcture and absolute configuration are retained in 70% $HClO_4$ as they were in water.

Results and Discussion

General Features of the Spin-forbidden Bands. The absorption and CD spectra of the present complexes are shown in Figs. 1—8. Their characteristics are summarized in Table 1. In the spin-forbidden *d-d* absorption band region, the CD spectra of the complexes show a group of sharp and narrow peaks with weak intensity as may be seen in Figs. 1, 2 and 5—8. The intensities of the CD bands in this region are found to be one fraction of a few hundred times as weak as those in the first spin-allowed *d-d* absorption band region as shown in Table 1. The half-widths of these CD bands are found to be about 200 to 400 cm^{-1} with the exception of the case of $(-)_{546}$-$[Cr(BH)_3]Cl_3$, whose half-width is about 800 cm^{-1}. The experimental rotational strengths of the spin-forbidden transitions are found to be about 0.1% of that of the first spin-allowed transitions. This value is about one tenth of the value estimated for cobalt(III) complexes by Ballhausen.[20] The anisotropy factor, *g*, for the CD bands in the spin-forbidden band region is nearly equal to that of the CD bands in the first spin-allowed *d-d* absorption band region. This fact suggests that the rotational strength of the spin-forbidden transition originates from that of the first spin-allowed transition which is magnetically dipole allowed in O_h symmetry, rather than from that of the second spin-allowed transition which is magnetically dipole forbidden in O_h symmetry.

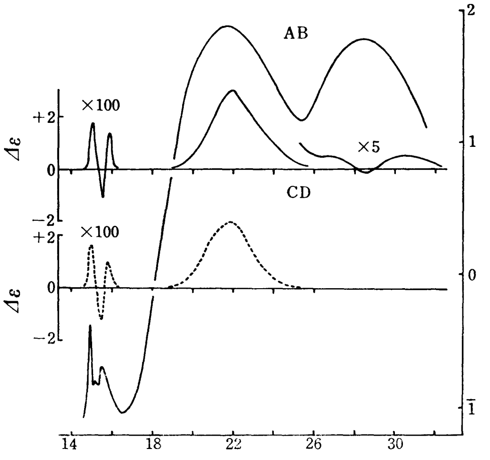

Fig. 1. Absorption (AB) and CD curves of $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ (———) in water and (·········) in 0.4F Na_2SeO_3 aqueous solution.

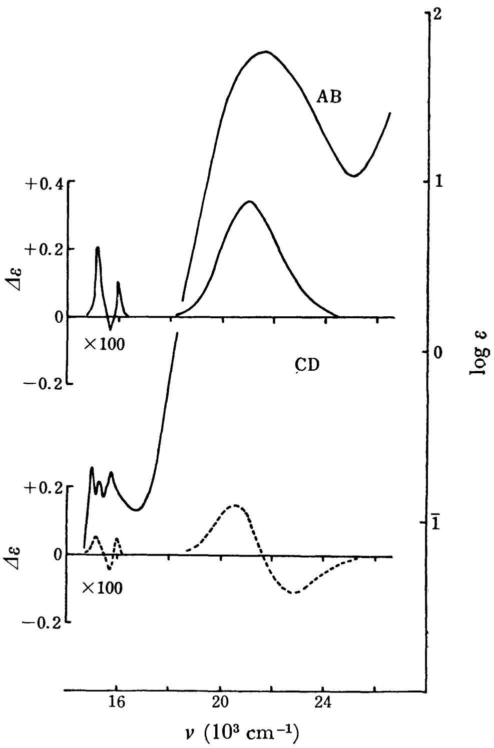

Fig. 2. Absorption (AB) and CD curves of $(+)_{546}$-$[Cr(tn)_3](ClO_4)_3$ (———) in water and (---------) in 0.6F Na_2SeO_3 aqueous solution.

The CD bands of trisoxalato- and trismalonatochromium(III) complexes were also observed in the spin-forbidden band region. However, the CD spectra of both complexes in this region are very complicated, because of the superposition upon the minor but broad CD band related to the longest wavelength component of the first spin-allowed absorption band.

According to the crystal field theory,[21] the

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[20] C. J. Ballhausen, *Mol. Phys.*, **5**, 461 (1963).

[21] Y. Tanabe, *Progr. Theor. Phys. Suppl.*, **14**, 17 (1960); H. Kamimura, S. Sugano and Y. Tanabe, "Ligand Field Theory and Its Applications," Syokabo Book Co., Tokyo (1969).

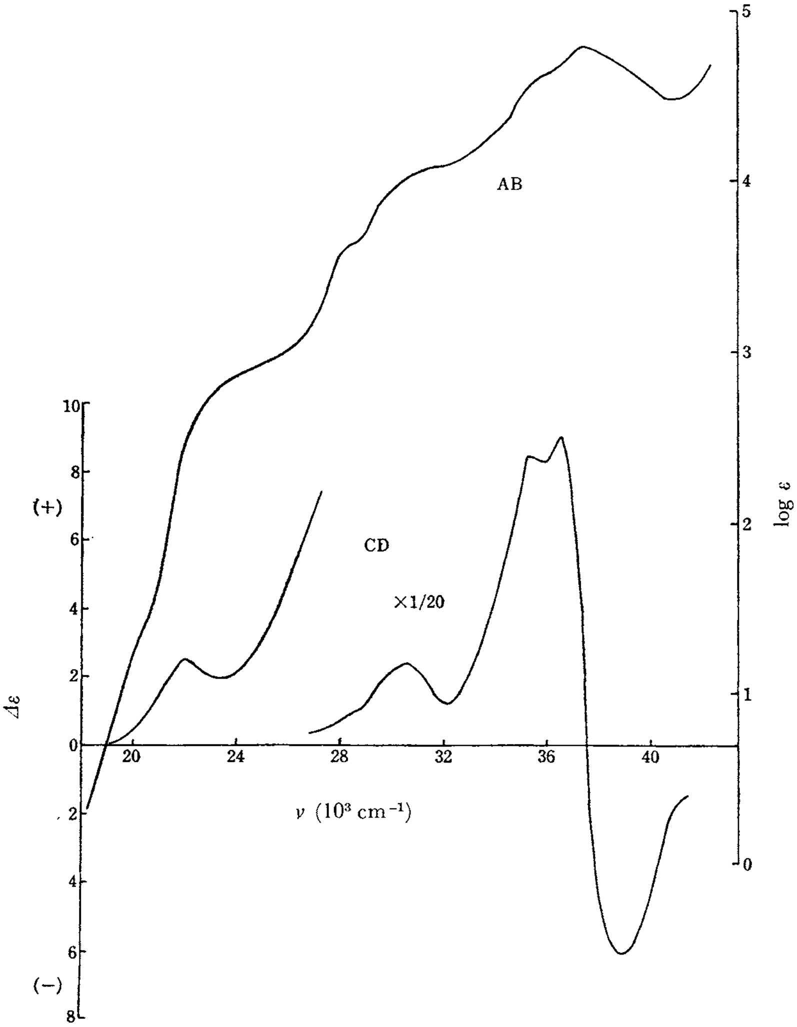

Fig. 3. Absorption (AB) and CD curves of $(+)_{546}$-$[Cr(phen)_3](ClO_4)_3$ in water.

narrow and sharp absorption bands of chromium(III) complexes appearing at 800—600 mμ are considered to be due to the spin-forbidden transitions within the t_{2g} shell and to be assigned to the $^4A_{2g}$–^2E_g and $^4A_{2g}$–$^2T_{1g}$ transitions in O_h symmetry. Furthermore, the ^2E_g state seems to occur at the longer wavelength side and to be of stronger intensity than the $^2T_{1g}$ state.[21] On the other hand, Schläfer *et al.*[22–24] have extensively studied the phosphorescence spectra of a number of chromium(III) complexes. It has been revealed that the relatively intense spin-forbidden absorption band lying at the longest wavelength side are the zero-zero band of the ^2E_g transition and the remaining bands are due to the vibrational transitions associated with the electronic transition to the ^2E_g state rather than the electronic transitions to the $^2T_{1g}$ state. Now, in D_3 symmetry, to which most of the present complexes belong, the T_{1g} state breaks down into the E_b and A_2 states and the E_g state remains as the E_a one. Accordingly, from the fact that most of the complexes studied here exhibit a close correspondence between the positions of the lowest frequency CD band and those of the absorption and phosphorescence bands in the spin-forbidden band region,[22–24] the lowest frequency CD band may be assigned to the ^2E_a transition. Assuming that the remaining CD bands are due to the electronic transitions to the $^2T_{1g}$ state in O_h symmetry, these CD bands may be tentatively assigned to the $^2A_2$ and ^2E_b states in D_3 symmetry.[1] However,

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[22] G. B. Porter and H. L. Schläfer, *Z. Phys. Chem.*, **38**, 227 (1963); G. B. Porter and H. L. Schläfer, *ibid.*, **40**, 280 (1964).

[23] J.L. Laver and P.W. Smith, *Chem. Commun.*, **1968**, 769.

[24] K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1403 (1963).

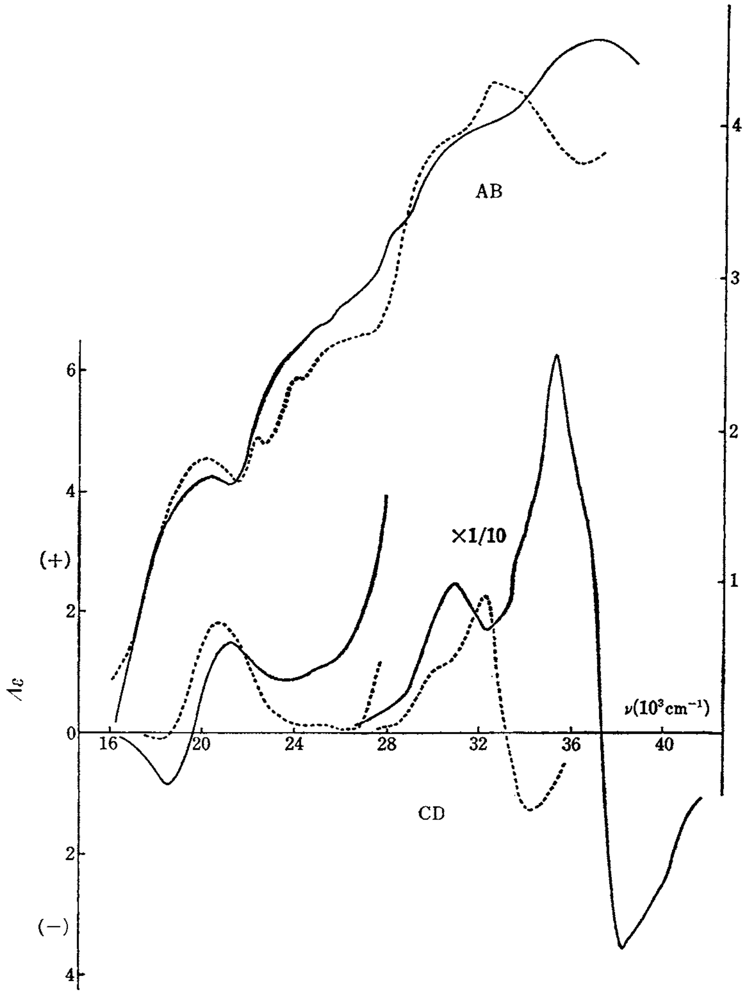

Fig. 4. Absorption (AB) and CD curves of (+)$_{546}$-[Cr(ox)(phen)$_2$]ClO$_4$ (———) in 70% HClO$_4$ and(+)$_{546}$-[Cr(ox)(dip)$_2$]Cl (·········) in water.

it is difficult to determine whether these CD bands are due to the vibrational transitions associated with the electronic transitions to the $^2E_g(O_h)$ state or to the electronic transitions to the $^2T_{1g}(O_h)$ state from the following reasons. Firstly, the ^2E_g and $^2T_{1g}$ states with $(t_{2g})^3$ configuration are theoretically expected to be split neither to the first order by means of the spin-orbit coupling nor in terms of lowering of symmetry.[21] Secondly, these CD bands in the spin-forbidden band region show rather simpler patterns than the corresponding absorption bands.

(+)$_{546}$-[Cr(en)$_3$](ClO$_4$)$_3$ and (+)$_{546}$-[Cr(tn)$_3$]-(ClO$_4$)$_3$. The absorption spectra of trisethylenediamine- and tristrimethylenediaminechromium(III) complexes coincide with those reported.[15] The CD spectra of (+)$_{546}$-trisethylenediamine complex in the first spin-allowed *d–d* absorption band region coincide with those reported by Mathieu.[25] In the second spin-allowed *d–d* absorption band region, however, the CD spectra of the complex obtained here are quite different from those reported by Mathieu.[25] According to the present measurement, three weak CD peaks, (+), (−) and (+) listing from the longer wavelength side, are evidently observed in the corresponding region as may be seen in Fig. 1. This result is inconsistent with the theory[26] that the d^3 or d^6 complex with D_3 symmetry should give only one CD component in the second absorption band region.

Mason *et al.*[27–29] have intensively studied the

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[25] J.-P. Mathieu, *J. Chim. Phys.*, **33**, 78 (1936).

[26] W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

[27] S. F. Mason and B. J. Norman, *J. Chem. Soc.*, *A*, **1966**, 307.

[28] P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).

[29] J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, **1968**, 689.

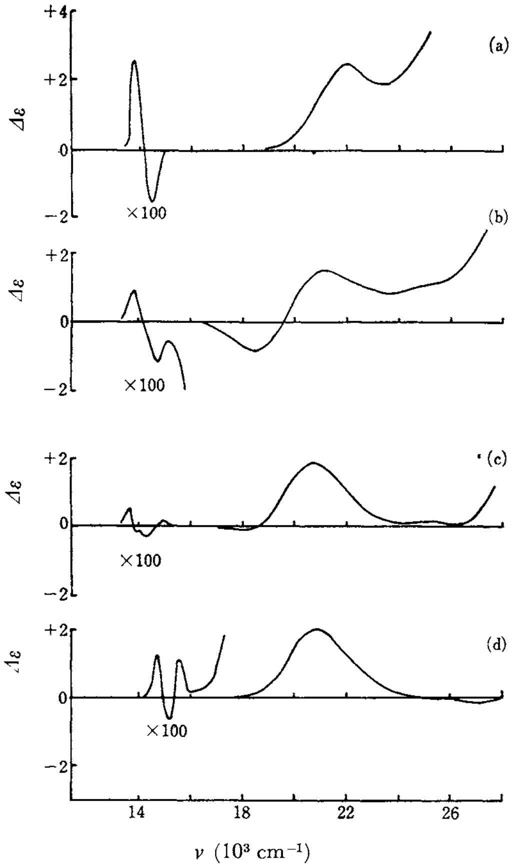

Fig. 5. CD curves of tris(phen) and *cis*-$[Cr(O)_2(N)_4]$ type complexes in the *d–d* absorption band region.

(a) $(+)_{546}$-$[Cr(phen)_3](ClO_4)_3$ in water
(b) $(+)_{546}$-$[Cr(ox)(phen)_2]ClO_4$ in 70% $HClO_4$
(c) $(+)_{546}$-$[Cr(ox)(dip)_2]Cl$ in water
(d) $(+)_{546}$-$[Cr(ox)(en)_2]Cl$ in water

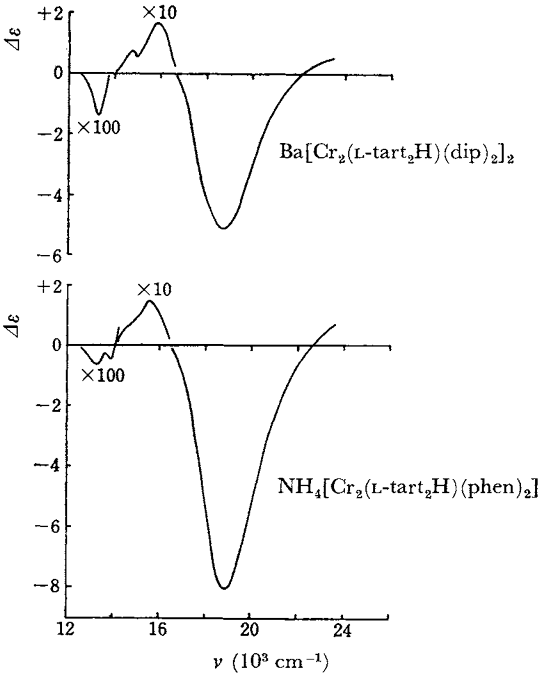

Fig. 6. CD curves of the two L-tartrato complexes in the *d–d* absorption band region. (The intensities are given per one complex, *i.e.*, per two chromium(III) ion.)

ion-pairing effect on the CD spectra of trisdiamine metal complexes. It has been reported that the diminution or increase of the intensity of the CD bands by the ion-pairing effect are observed in the first spin-allowed absorption band region, and it has been proposed that the diminished CD band is assigned in the case of chromium(III) complexes to the ^4E component and the increased CD band to the $^4A_1$ in D_3 symmetry. In the first spin-allowed *d–d* absorption band region, the intensity of the positive CD band of $(+)_{546}$-trisethylenediaminechromium(III) complex is diminished with the addition of sodium selenite to the solution as may be seen in Fig. 1 and Table 1.[27] Since the diminished positive CD band is due to the ^4E component, the $(+)_{546}$-isomer of trisethylenediamine complex seems likely to have a $\Delta(C_2)$ absolute configuration. The same CD behavior due to the ion-pairing effect is also more markedly observed for the $(+)_{546}$-tristrimethylenediamine complex as seen in Fig. 2. In this complex, the intensity of a positive CD band at 477 mμ is diminished and a new CD band appears at 435 mμ with the addition of sodium selenite to the solution.[28] Thus, the diminished positive band is assigned to the ^4E component and the newly appearing negative band to the $^4A_1$ component.[28] From this fact, the $(+)_{546}$-tristrimethylenediaminechromium(III) complex was determined to have a $\Delta(C_2)$ absolute configuration. The CD spectra in the region corresponding to the spin-forbidden transitions for the $(+)_{546}$-trisethylenediamine- and tristrimethylenediaminechromium(III) complexes with a $\Delta(C_2)$ configuration show three sharp and narrow peaks, (+), (−) and (+). For the $(+)_{546}$-trisethylenediamine complex, the CD intensity of the positive component at the longest wavelength side is diminished by the ion-pairing effect as shown in Table 1. The CD behavior in the corresponding region for the tristrimethylenediamine complex is similar to that for the ethylenediamine complex. That is, the CD intensity of the positive band due to the ^2E_a transition of the trimethylenediamine complex is markedly reduced with the addition of sodium selenite as shown in Fig. 2 and Table 1. From this parallel reduction in the CD intensity by the ion-pairing effect between the ^4E and ^2E_a transitions and from the above-mentioned anisotropy factor, it is suggested that the excited doublet and quartet states with the same orbital symmetry are mixed with

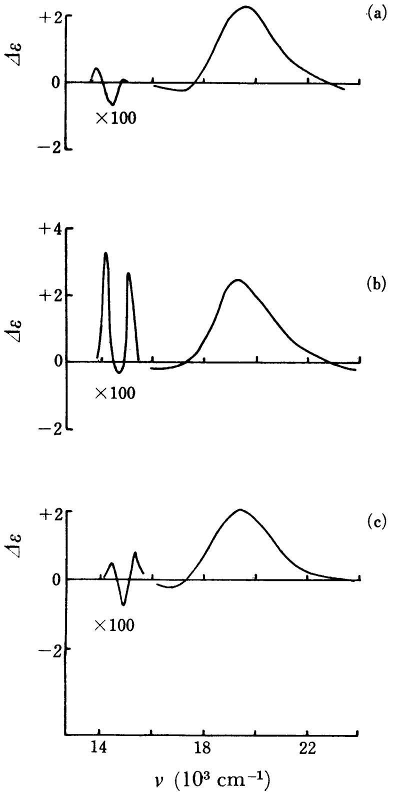

Fig. 7. CD curves of *cis*-$[Cr(O)_4(N)_2]$ type complexes in the *d–d* absorption band region.
(a) $(+)_{546}$-K$[Cr(ox)_2(dip)]$
(b) $(+)_{546}$-K$[Cr(ox)_2(phen)]$
(c) $(+)_{546}$-K$[Cr(ox)_2(en)]$

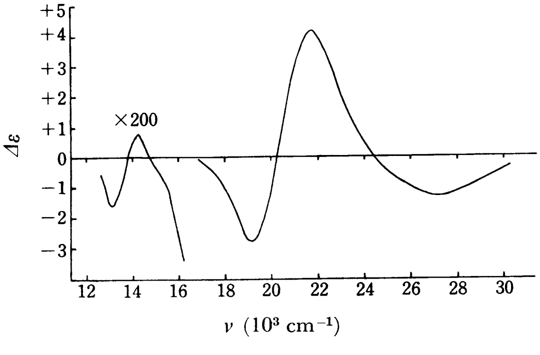

Fig. 8. CD curve of $(-)_{546}$-$[Cr(BH)_3]Cl_3$ in water.

each other by means of the spin-orbit coupling, which allows the ^2E_a transition to acquire a rotational strength by borrowing both the magnetic and electric transition dipole moments from the upper ^4E transition and to have the same sign of rotational strength as that of the ^4E transition. The central negative and the highest frequency positive CD bands in the spin-forbidden band region may be tentatively assigned to the $^2A_2$ and ^2E_b transition with octahedral $^2T_{1g}$ parentage, respectively, though for the $^4A_2$–$^2A_2$ transition the corresponding spin-allowed transition ($^4A_2$–$^4A_2$) is both electrically and magnetically dipole forbidden. From this consideration, it can be proposed that chromium(III) complexes with the positive ^4E CD band of the first spin-allowed *d–d* transition exhibit the positive ^2E_a CD band and have a $\Delta(C_2)$ configuration. This proposal is consistent with the result from the determination of absolute configurations on the basis of the exciton CD bands and of stereospecificity as will be mentioned below.

1,10-Phenanthroline and 2,2′-Dipyridyl Complexes. Mason *et al.*[30–32] and Bosnich[33] have developed the nonempirical method for determining the absolute configurations of tris- or bis-α-diimine metal complexes on the basis of CD spectra in the ultraviolet region, where long-axis-polarized π–π^* ligand transition occurs. According to their consideration, the simple electrostatic treatment of the exciton theory neglecting the central metal ion predicts that tris- or bis-α-diimine metal complexes should take a $\Delta(C_2)$ configuration, if these complexes show a positive and a negative CD band at the longer and shorter wavelength side, respectively, in the exciton band region. This prediction has been recently confirmed by X-ray determination[34] of the absolute configuration of $(-)_{589}$-$[Fe(phen)_3]^{2+}$ and has been shown to be consistent with the result of the empirical method on the basis of the CD bands in the first spin-allowed *d–d* absorption band region.[8,31] In the region from 300 mμ to 250 mμ, the CD spectra of tris- or bis-1,10-phenanthroline- and bis-2,2′-dipyridylchromium(III) complexes studied show two large typical exciton bands, which have signs opposite each other and are of nearly equal intensity. As may be seen in Figs. 3 and 4, $(+)_{546}$-$[Cr(phen)_3](ClO_4)_3$, $(+)_{546}$-$[Cr(ox)(phen)_2]ClO_4$ and $(+)_{546}$-$[Cr(ox)(dip)_2]Cl$ give two exciton CD bands, namely, (+) and (−) bands, and a positive major CD band in the first spin-allowed *d–d* absorption band region.[8,35] Consequently, on the basis of the CD bands, the absolute configuration of these phen and dip complexes

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30) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, **1963**, 211; A. J. McCaffery and S. F. Mason, *ibid.*, **1964**, 259; E. Larsen, S. F. Mason and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966); J. Mason and S. F. Mason, *Tetrahedron*, **23**, 1919 (1967).

31) S. F. Mason and B. J. Norman, *Inorg. Nucl. Chem. Lett.*, **3**, 285 (1967).

32) A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, *A*, **1969**, 1428; S. F. Mason and B. J. Norman, *ibid.*, **1969**, 1442.

33) B. Bosnich, *Inorg. Chem.*, **7**, 178 (1968); B. Bosnich, *ibid.*, **7**, 2379 (1968).

34) D. M. Templeton, A. Zalkin and T. Ueki, *Acta Crystallogr.*, **21**, A 154 (1966).

35) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).

TABLE 1. CD DATA OF THE CHROMIUM(III) COMPLEXES IN THE d–d ABSORPTION BAND REGION
(The wave numbers are given in 10^3 cm^{-1}, and the intensities, $(\varepsilon_l - \varepsilon_d)$, in parentheses.)

Complex	Solvent	CD peaks in the region of spin-forbidden band	CD peaks in the region of spin-allowed band
$(+)_{546}$-$[Cr(en)_3](ClO_4)_3$	water	15.0 $(+8.85\times10^{-3})$ 15.5 (-5.70×10^{-3}) 15.8 $(+6.75\times10^{-3})$	21.9 (+1.49) 26.5 (+0.55) 28.5 (−0.08) 30.4 (+0.58)
	0.4F Na_2SeO_3 solution	15.0 $(+7.80\times10^{-3})$ 15.5 (-6.00×10^{-3}) 15.8 $(+4.50\times10^{-3})$	21.9 (+1.28)
$(+)_{546}$-$[Cr(tn)_3](ClO_4)_3$	water	15.1 $(+2.08\times10^{-3})$ 15.6 (-0.45×10^{-3}) 15.9 $(+1.04\times10^{-3})$	20.9 (+0.34)
	0.6F Na_2SeO_3 solution	15.1 $(+0.50\times10^{-3})$ 15.7 (-0.36×10^{-3}) 16.0 $(+0.54\times10^{-3})$	20.5 (+0.14) 22.9 (−0.11)
$(+)_{546}$-$[Cr(phen)_3](ClO_4)_3$	water	13.8 $(+12.4\times10^{-3})$ 14.5 (-7.50×10^{-3})	21.9 (+2.48)
$(+)_{546}$-$[Cr(ox)(phen)_2]ClO_4$	70% $HClO_4$	13.8 $(+4.50\times10^{-3})$ 14.8 (-6.00×10^{-3})	18.4(−0.83) 21.2(+1.50)
$(+)_{546}$-$[Cr(ox)(dip)_2]Cl$	water	13.6 $(+5.48\times10^{-3})$ 14.0 (-1.63×10^{-3}) 14.3 (-2.96×10^{-3}) 14.9 $(+1.92\times10^{-3})$	17.8(−0.06) 20.6 (+1.40)
$(+)_{546}$-$[Cr(ox)(en)_2]Cl$	water	14.7 $(+12.9\times10^{-3})$ 15.2 (-6.40×10^{-3}) 15.5 $(+11.4\times10^{-3})$	20.8 (+1.97) 26.9 (−0.14)
$Ba_{0.5}$ $[Cr_2(L\text{-}tart_2H)(dip)_2]$	water	13.3 (-14.2×10^{-3})	15.7 (+0.14) 18.3 (−5.10)
$NH_4[Cr_2(L\text{-}tart_2H)(phen)_2]$	dmf-water mixture	13.3 (-6.40×10^{-3}) 13.9 (-4.60×10^{-3})	15.5 (+0.15) 18.3 (−8.11)
$(+)_{546}$-$K[Cr(ox)_2(dip)]$	water	13.8 $(>+4.50\times10^{-3})$ 14.3 $(<-5.40\times10^{-3})$ 14.5 $(<-6.60\times10^{-3})$ 14.8 $(>+1.70\times10^{-3})$	17.0 (<-0.12) 19.5 $(>+2.22)$
$(+)_{546}$-$K[Cr(ox)_2(phen)]$	water	13.9 $(>+32.0\times10^{-3})$ 14.4 $(<-3.00\times10^{-3})$ 14.7 $(>+27.0\times10^{-3})$	16.4 (<-0.13) 19.0 $(>+2.46)$
$(+)_{546}$-$K[Cr(ox)_2(en)]$	water	14.5 $(>+7.50\times10^{-3})$ 14.9 $(<-10.3\times10^{-3})$ 15.3 $(>+11.3\times10^{-3})$	16.8 (<-0.05) 19.4 $(>+2.00)$
$(-)_{546}$-$[Cr(BH)_3]Cl_3$	water	13.1 (-7.77×10^{-3}) 14.3 $(+3.89\times10^{-3})$	19.2 (−2.78) 21.7 (+4.16)

will be determined to be a $\Delta(C_2)$ configuration.[*2] The CD spectra in the spin-forbidden band region show two peaks, (+) and (−), for $(+)_{546}$-$[Cr(phen)_3]^{3+}$ and $(+)_{546}$-$[Cr(ox)(phen)_2]^+$ and four peaks, (+), (−), (−) and (+), for $(+)_{546}$-$[Cr(ox)(dip)_2]^+$, listing from the longer wavelength side as may be seen in Fig. 5. That is, the sign of the lowest frequency CD band due to the ^2E_a transition for the phen and dip complexes having the $\Delta(C_2)$ absolute configuration is always positive. In the case of $(+)_{546}$-$[Cr(ox)(en)_2]Cl$, which has a *cis*-$[Cr(O)_2(N)_4]$ type structure similar to that of bis(phen)- and bis(dip)oxalato complexes, the CD band in the region of the spin-forbidden band is also related to that in the first spin-allowed absorption band region. Namely, the CD spectra of $(+)_{546}$-$[Cr(ox)(en)_2]Cl$ show a positive band in the first absorption band region and three sharp peaks, (+), (−) and (+), in the spin-forbidden band region, as seen in Fig. 5. Thus, it can be determined that $(+)_{546}$-$[Cr(ox)(en)_2]Cl$ giving the positive ^4E and ^2E_a CD components take a $\Delta(C_2)$ configuration.

L-Tartrato and Oxalato Complexes. We have revealed that the L-tartratochromium(III) (1:1)-complexes, $Ba[Cr_2(L\text{-}tart_2H)(dip)_2]_2 \cdot 9H_2O$ and $NH_4[Cr(L\text{-}tart_2H)(phen)_2] \cdot 6.5H_2O$, are formed completely stereospecifically to have a bis(L-tartrato)-bridged binuclear structure with a $\Lambda(C_2)$–$\Lambda(C_2)$ configuration. The L-tartrato complexes gave apparently positive weak CD bands in the spin-forbidden band region superimposing on the positive CD component related to the first spin-allowed absorption band.[1] Upon detailed remeasurements, however, another sharp but weak negative CD bands are observed at longer wavelengths in the spin-forbidden band region as shown in Fig. 6. It is evident that the L-tartrato complexes with the $\Lambda(C_2)$ absolute configuration give the negative CD peaks at the longest wavelength side in the spin-forbidden band region and the negative major CD band in the first spin-allowed *d–d* absorption band region. The L-tartrato complex containing 1,10-phenanthroline exhibits splitting of the negative CD band of the spin-forbidden transition (Fig. 6). This fact suggests the existence of the spin-spin coupling between the two chromium(III) ions also in this binuclear complex as reported by Mason[8] in the case of $(-)_{546}$-$[Cr_2(OH)_2(dip)_4]^{4+}$ and $(-)_{546}$-$[Cr_2(OH)_2(phen)_4]^{4+}$. For the oxalato complexes, $(+)_{546}$-$K[Cr(ox)_2(dip)]$, $(+)_{546}$-$K[Cr(ox)_2(phen)]$ and $(+)_{546}$-$K[Cr(ox)_2(en)]$, which have the geometrical structure identical to that of the L-tartrato complex, *cis*-$[Cr(O)_4(N)_2]$ type, the major CD band in the first spin-allowed absorption band region and the lowest frequency CD band in the spin-forbidden band region have a positive sign, as seen in Fig. 7. Thus, the oxalato complexes take a $\Delta(C_2)$ absolute configuration.

Trisbiguanide Complex. The biguanide complex, $(-)_{546}$-$[Cr(BH)_3]Cl_3$, shows two intense CD bands in the first spin-allowed absorption band region, (+) one at 460 mμ and (−) one at 520 mμ.[17] In the region of the spin-forbidden band, this complex gives two weak and broad CD bands, (−) and (+), as seen in Fig. 8. The absolute configuration of this complex may be assumed to be a $\Delta(C_2)$ one on the basis of the sign of the major CD band in the first spin-allowed band region.[17] On the contrary, a $\Lambda(C_2)$ configuration may be assumed from the theory that the ^2E_a CD component is at the longest wavelength side. However, this contradiction may be solved as follows. Since a biguanide forms a six membered chelate ring, the energy ordering of the trigonal splitting for this complex is assumed to be similar to that of tristrimethylenediamine complex with six membered chelate rings. Thus, the positive major CD component at the shorter wavelength side may be assigned to the $^4A_1$ and the negative minor CD component at the longer wavelength side to the ^4E component. Therefore, the ^4E CD component has a negative sign similar to the ^2E_a CD component. It is thus concluded that the $(-)_{546}$-trisbiguanidechromium(III) complex has a $\Lambda(C_2)$ absolute configuration.

It is concluded that the absolute configurations of tris-chelate chromium(III) complexes can be determined on the basis of the sign of the lowest frequency CD component corresponding to the ^2E_a transition derived from the octahedral ^2E_g parentage. Namely, if the ^2E_a CD component show a positive sign, the absolute configuration of the complexes can be determined to be a $\Delta(C_2)$.

Analysis of the CD Bands. On analysis of the spectra of d^3 ions in a trigonal field in terms of the weak field perturbation, Macfarlane[9] has estimated the contribution of the ligand field parameter Δ, the trigonal parameters v and v', and the electronic repulsion parameters B and C, to the transition energies of the doublet states as shown in Table 2.

[*2] When the metal-ligand and ligand-ligand bonding are taken into consideration, the relative energies of the exciton splitting are affected by the central metal ion and also by the kind of conjugated ligand. According to Ferguson *et al.*,[35] the sign of the exciton splitting has been experimentally determined on the basis of analysis of the ligand absorption bands and it has been found that the sign for $(+)_{546}$-$[Cr(ox)(dip)_2]^+$ is opposite that of $(+)_{546}$-$[Cr(ox)(phen)_2]^+$.

In consequence, it has been concluded that the two $(+)_{546}$-isomers have been assigned to have opposite configurations to each other. It is doubtful, however, that the difference in the π-bonding between 2,2′-dipyridyl and 1,10-phenanthroline gives rise to such drastic modification of the relative energies of the exciton splitting, because the contributions of the metal-ligand or ligand-ligand bonding to the exciton splitting are expected to be small and almost the same for the dip and phen chromium(III) complexes.[8,32] Therefore, the simple dipole-dipole interaction theory may be adopted here as a good approximation.

Table 2. Representation of the transition energies of the doublet states

$$\nu(^2E_a)=0.0317\varDelta-0.241v-0.178v'+6.54B+3.06C$$
$$\nu(^2A_2)=0.0250\varDelta-0.217v'+7.63B+3.00C$$
$$\nu(^2E_b)=0.0176\varDelta-0.052v-0.109v'+7.81B+3.01C$$

Table 3. Values for the parameters (cm^{-1})

Complexes	B	v	v'
$[Cr(en)_3]^{3+}$	772	+104	+912
$[Cr(tn)_3]^{3+}$	776	+303	+862

A similar treatment neglecting the spin-orbit coupling was applied for the trisdiamine complexes on the basis of the above-mentioned assignment for three CD peaks observed in the spin-forbidden band region, on the assumption that the ligand field splitting $\varDelta$ equals the energy of the first absorption band maximum and that the Racah parameter C is equal to 4B. The values of the parameters B, v and v' obtained are given in Table 3. The values obtained for the parameter B are so reasonable that they are closer to those from Schäffer's treatment[36] including the non-diagonal elements rather than values from strong field approximation with only diagonal elements.[23] The sign of the trigonal parameter v of $[Cr(tn)_3]^{3+}$ obtained is in agreement with the result from the CD measurement. However, the sign for $[Cr(en)_3]^{3+}$ is opposite that from the polarized crystal spectra.[37]

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