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# Circular Dichroism of Chromium(III) Complexes. I. L-Tartrato Complexes. Their Stereospecific Formation and Spin-forbidden Absorption Bands

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Two novel mixed chromium(III) complexes containing L-tartrates and 2,2′-dipyridyl or 1,10-phenanthroline have been prepared, and their electronic absorption and circular dichroism spectra and the rotatory dispersion have been measured in the region of near-infrared to ultraviolet. From the construction of molecular models and from the comparison of the CD bands of the present complexes with those of the resolved oxalato complexes, $(-)_{546}$-K[Cr(ox)$_2$(dip)]$\cdot$3H$_2$O and $(-)_{546}$-K[Cr(ox)$_2$(phen)]$\cdot$4H$_2$O, it has been concluded that the present complexes have a binuclear structure in which two Cr(III) ions are bridged by two tetradentate L-tartrato ligands and that the absolute configuration of the binuclear complexes is $\Lambda(C_2)$-$\Lambda(C_2)$. Their formation is completely stereospecific and their formulae are represented by Ba[Cr$_2$(L-tart$_2$H)(dip)$_2$]$_2\cdot$9H$_2$O and NH$_4$[Cr$_2$(L-tart$_2$H)(phen)$_2$]$\cdot$6.5H$_2$O. The absolute configurations of several complexes which commonly belong to a general type, *cis*-[Cr(O)$_4$(N)$_2$] have been determined on the basis of circular dichroism studies of the present binuclear complexes. The circular dichroism in the spin-forbidden absorption band region have also been measured and discussed.

Much evidence has been obtained for the fact that an octahedral metal complex with two or three optically active bidentate ligands has been often stereospecifically formed or isolated; namely, only a limited number of its configurationally optically active isomers has been preferentially formed or isolated.[1] Naturally occuring L-tartrate is one of such bidentate ligands. A definite but not so marked stereospecific formation has been reported in a complex containing one L-tartrate($C_4H_4O_6{}^{2-}$) and two ethylenediamine ligands.[2] Moreover it is well known that L-tartrate forms various kinds of transition metal complexes which show the so-called anomalous rotatory dispersion in the visible region; most famous and historically important of these is believed to be the tris(L-tartrato)chromium(III) complex,[3] on which the so-called Cotton effect was first observed in 1896 by Cotton.[4] Recently, McCaffery and Mason[5] have shown from their studies using circular dichroism (CD) and rotatory dispersion (RD) techniques that one of the two possible configurationally optically active isomers has been produced in a solution of chromium(III) in 4M potassium L-tartrate at pH 12. That is, the stereospecificity is complete in this tris(L-tartrato) case. In the complexes mentioned above, the L-tartrate ligand is thought to be coordinated as a bidentate ligand, being free from the coordination of two of its four donor groups. Of course, no mononuclear complex which contains a tartrate ion as a tetradentate ligand seems to exist owing to its steric requirement. It has been shown by some X-ray analyses, however, that the tetradentate tartrato ligands exist in some binuclear complexes.[6,7] These binuclear complexes have a

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[1] F. P. Dwyer, F. L. Garvan and A. Schulman, *J. Am. Chem. Soc.* **81**, 290 (1959); R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

[2] H. B. Jonassen, J. C. Bailar, Jr., and E. H. Huffman, *J. Am. Chem. Soc.*, **70**, 756 (1948).

[3] J.-P. Mathieu, *Ann. Phys.*, [11] **3**, 371 (1935).

[4] A. Cotton, *Ann. Chim. Phys.*, [7] **8**, 347 (1896).

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

[6] J. G. Forrest and C. K. Prout, *J. Chem. Soc.*, *(A)*, **1967**, 1312; R. E. Tapscott, R. L. Belford and I. C. Paul, *Inorg. Chem.*, **7**, 356 (1968).

[7] G. A. Kiosse, N. I. Golovastikov and N. V. Belov, *Soviet Phys. Dokl.*, **9**, 198 (1964); G. A. Kiosse, N. L. Golovastikov, A. V. Ablov and N. V. Belov, *Dokl. Akad. Nauk SSSR*, **177**, 329 (1967); D. H. Templeton, A. Zalkin and T. Ueki, *Acta Cryst.*, **21**, A 154 (1966).

structure in which two five-coordinate metal ions, *i.e.*, antimony(III) or vanadium(IV), are bridged by two tetranegative tartrate anions.

In the present paper, two new examples of such binuclear complexes will be reported, in which the two central metal ions have octahedral coordination. These are chromium(III) complexes of L-tartrate ($C_4H_2O_6{}^{4-}$=tart) and 2,2′-dipyridyl (=dip) or 1,10-phenanthroline (=phen), namely, Ba[$Cr_2$(L-$tart_2$H)-$(dip)_2]_2\cdot 9H_2O$ and $NH_4[Cr_2$(L-$tart_2$H)$(phen)_2]\cdot 6.5H_2O$. A preliminary short communication[8] has already been reported for the stereospecific formation of these complexes. The electronic absorption, and CD spectra and RD of these binuclear complexes will be discussed in comparison with those of the corresponding mononuclear complexes, $(-)_{546}$-K[Cr$(ox)_2$(dip)]$\cdot 3H_2O$ and $(-)_{546}$-K[Cr$(ox)_2$-(phen)]$\cdot 4H_2O$.

## Experimental

**Preparation.** 1) Ba[$Cr_2$(L-$tart_2$H)$(dip)_2]_2\cdot 9H_2O$: To a solution containing 2.3 g of sodium L-tartrate dihydrate (L-$Na_2H_2$tart$\cdot 2H_2O$) in 30 m*l* of a boiling dmf water*1 mixture (1 : 1), 3.88 g of [$CrCl_3$(dmf)-(dip)] was added. The reaction mixture was heated at about 120°C for a few minutes in an oil bath. After the color of the solution changed to dark red, the resulting solution was filtered and 1.2 g of $BaCl_2\cdot 2H_2O$ was added to the filtrate. When the solution was cooled in an ice bath, the desired dark crystals began to separate. The crude product was recrystallized from hot water. The pure crystals were filtered off and washed with a little ice water, ethanol and then with ether.

Found: C, 43.51; H, 3.03; N, 7.33; Ba, 9.98%*2. Calcd for $C_{56}H_{42}N_8O_{24}BaCr_4$=Ba[$Cr_2$(L-$tart_2$H)$(dip)_2]_2$: C, 43.21; H, 2.73; N, 7.20; Ba, 8.83%. Found: $H_2O$, 9.24%. Calcd for Ba[$Cr_2$(L-$tart_2$H)$(dip)_2]_2\cdot 9H_2O$: 9.44%.

2) $NH_4[Cr_2$(L-$tart_2$H)$(phen)_2]\cdot 6.5H_2O$: A solution containing 7.7 g of [$CrCl_3$(dmf)(phen)] and 3.45 g of ammonium L-tartrate (L-$(NH_4)_2H_2$tart) in 50 m*l* of a dmf-water mixture (1 : 1) was heated at about 120°C in an oil bath for a few minutes, while the color of the solution changed to dark red and the brown complex began to precipitate. It was allowed to stand at room temperature. The product was filtered off, and recrystallized from a hot dmf-water mixture (1 : 1). The pure crystals obtained were washed with a dmf-water mixture, ethanol and then with ether. This complex is sparingly soluble in water, but soluble in a dmf-water mixture (1 : 1).

Found: C, 49.26; H, 3.41; N, 8.46%. Calcd for $C_{32}H_{25}N_5O_{12}Cr_2$: C, 49.55; H, 3.26; N, 9.03%. Found: $H_2O$, 13.38%. Calcd for the 6.5 hydrate: $H_2O$, 13.09%.

3) [$CrCl_3$(dmf)(dip)]: This starting complex was prepared by Dwyer's method.[9] The hygroscopic anhydrous chromium(III) chloride, which was used instead of sublimated chromium(III) chloride, was completely dissolved in dry dmf without a trace of zinc dust.[10] To a hot solution of 5 g of chromium(III) chloride in 50 m*l* of dry dmf was added 5 g of 2,2′-dipyridyl. After refluxing the resulting solution for a few minutes, the greenish material began to separate. The reaction mixture was allowed to cool to room temperature. The product was filtered off and washed with cold dmf and then with ether.

4) [$CrCl_3$(dmf)(phen)]: This complex was obtained by the same method as that used for the 2,2′-dipyridyl complex, using 1,10-phenanthroline instead of 2,2′-dipyridyl.

5) K[Cr$(ox)_2$(dip)]$\cdot 3H_2O$ and K[Cr$(ox)_2$(phen)]$\cdot 4H_2O$: The preparation and optical resolution of these complexes were carried out by Broomhead's method.[11] The electronic absorption and rotatory dispersion of these complexes obtained coincided with those reported by Bürer.[12]

6) K[Cr$(ox)_2$(en)]$\cdot 2H_2O$: This was prepared by Werner's method,[13] and resolved by the method of Bushra and Johnson.[14]

**Measurements.** The electronic absorption spectra Were measured by a Beckman DU spectrophotometer. The CD spectra were recorded with a Roussel-Jouan dichrographe, while the RD curves were obtained with a Yanagimoto Recording spectropolarimeter model-185. The solvent employed for $(-)_{546}$-K[Cr-$(ox)_2$(dip)]$\cdot 3H_2O$, Ba[$Cr_2$(L-$tart_2$H)$(dip)_2]_2\cdot 9H_2O$ and $(+)_{546}$-K[Cr$(ox)_2$(en)]$\cdot 2H_2O$ was water, and for $(-)_{546}$-K[Cr$(ox)_2$(phen)]$\cdot 4H_2O$ and $NH_4[Cr_2$(L-$tart_2$H)$(phen)_2]\cdot 6.5H_2O$ a dmf-water mixture (1 : 1). Because the oxalato complexes racemize at moderate rates in aqueous solutions,[11] the measurement for these complexes were made as rapidly as possible using solutions freshly prepared in turn.

## Results and Discussion

**Spectra of the Visible and Ultraviolet Region.** The absorption and CD spectra, and RD of the complexes studied are shown in Figs. 1, 2, 4 and 5, and their characteristics are summarized in Table 1. The data of $(-)_{546}$-K[Cr$(ox)_2$(phen)]$\cdot 4H_2O$ and of $NH_4[Cr_2$(L-$tart_2$H)$(phen)_2]\cdot 6.5H_2O$ were obtained in a dmf-water mixture (1 : 1), since the L-tartrato complex is sparingly soluble in water. From a comparison of the absorption and CD spectra of $(-)_{546}$-K[Cr$(ox)_2$(phen)]$\cdot 4H_2O$ in water and in a dmf-water mixture (1 : 1), it was confirmed that the solvent dependence of the spectra of the 1,10-phenanthroline complex is negligibly small.

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[8] S. Kaizaki, J. Hidaka and Y. Shimura, This Bulletin, **40**, 2207 (1967).

*1 The abbreviation, dmf, represents dimethylformamide.

*2 The content of Ba was determined semi-quantitatively by flame spectrophotometry.

[9] F. P. Dwyer and J. A. Broomhead, *Austral. J. Chem.*, **14**, 250 (1961).

[10] A. R. Pray, *Inorg. Synth.*, **5**, 153 (1957).

[11] J. A. Broomhead, *Austral. J. Chem.*, **15**, 228 (1962).

[12] Th. Bürer, *Helv. Chim. Acta*, **46**, 242 (1963).

[13] A. Werner, *Ann.*, **406**, 286 (1914).

[14] E. Bushra and C. H. Johnson, *J. Chem. Soc.*, **1939**, 1937.

TABLE 1. ABSORPTION (AB) AND CD MAXIMUM DATA OF *cis*-$[Cr(O)_4(N)_2]$ TYPE COMPLEXES (The wave numbers are given in $10^3\ cm^{-1}$)

| $K[Cr(ox)_2(dip)]$ | | $Ba[Cr_2(L\text{-}tart_2H)(dip)_2]_2$* | |
|---|---|---|---|
| AB (log $\varepsilon_{\max}$) | CD ($\Delta\varepsilon_{ext}$) of $(-)_{546}$-isomer | AB (log $\varepsilon_{\max}$) | CD ($\Delta\varepsilon_{ext}$) |
| 13.9 ($\bar{1}.84$) | 13.8 ($<-0.004_5$) | | |
| *ca.* 14.4 ($\bar{1}.80$) | 14.3 ($>+0.005_4$) | | |
| | 14.5 ($>+0.006_6$) | | |
| *ca.* 14.7 (0.06) | 14.8 ($<-0.001_7$) | | |
| | 17.0 ($>+0.12$) | | 15.7 (+0.14) |
| 18.3 (1.87) | 19.5 ($<-2.22$) | 18.3 (2.09) | 18.3 (−5.10) |
| *ca.* 22.5 (1.63) | | *ca.* 22.7 (2.10) | |
| *ca.* 24.2 (2.10) | | *ca.* 24.4 (2.36) | |
| 25.6 (2.21) | 25.3 ($>+0.53$) | *ca.* 25.7 (2.50) | 25.1 (+0.95) |
| | | | 28.5 (−0.78) |
| 32.9 (4.01) | | 33.1 (4.29) | 33.6 (+15.0) |

| $K[Cr(ox)_2(phen)]$ | | $NH_4[Cr_2(L\text{-}tart_2H)(phen)_2]$ | |
|---|---|---|---|
| AB (log $\varepsilon_{\max}$) | CD ($\Delta\varepsilon_{ext}$) of $(-)_{546}$-isomer | AB (log $\varepsilon_{\max}$) | CD ($\Delta\varepsilon_{ext}$) |
| 14.1 (0.42) | 13.9 ($<-0.03_2$) | | |
| | 14.4 ($>+0.003$) | | |
| *ca.* 14.7 (0.5) | 14.7 ($<-0.02_7$) | | |
| | 16.4 ($>+0.13$) | | 15.5 (+0.15) |
| 18.5 (1.89) | 19.0 ($<-2.46$) | 18.3 (2.16) | 18.3 (−8.11) |
| 24.8 (2.12) | 25.6 ($>+0.44$) | 24.7 (2.56) | 24.5 (+1.21) |
| 28.8 (2.89) | | 28.0 (3.20) | 28.3 (−1.20) |
| *ca.* 30.0 (3.10) | | *ca.* 30.3 (3.48) | |
| 33.4 (3.90) | | 33.6 (4.29) | 33.6 (+6.00) |
| 36.1 (4.43) | | 36.0 (4.74) | 37.3 (+41.8) |

| $K[Cr(ox)_2(en)]$ | |
|---|---|
| AB (log $\varepsilon_{\max}$) | CD ($\Delta\varepsilon_{ext}$) of $(+)_{546}$-isomer |
| 14.5 (0.19) | 14.5 ($>+0.007_5$) |
| *ca.* 14.9 (0.2) | 14.9 ($<-0.010_3$) |
| | 15.3 ($>+0.011_3$) |
| | 16.8 ($<-0.05$) |
| 18.8 (1.96) | 19.4 ($>+2.00$) |
| 25.3 (2.00) | 25.3 ($<-0.35$) |

* The intensities are given per one complex ion, *i.e.*, per two chromium(III) ions.

The absorption curves of the L-tartrato and oxalato complexes resemble each other on the whole. It is possible to point out that the new L-tartrato complexes have a geometrical structure similar to that of $[Cr(ox)_2(dip)]^-$ and $[Cr(ox)_2(phen)]^-$. As may be seen in Fig. 1 and Table 1, the 2, 2′-dipyridyl complexes show three narrow inflections in the second spin-allowed absorption band region. In the corresponding region, a few small inversive dispersions are also observed.

The CD spectra and RD of the oxalato and L-tartrato complexes are also similar to each other (Figs. 1 and 2). That is, both the complexes show two CD bands, one positive at about 600 mμ and the other negative at about 520 mμ, in the first spin-allowed d→d absorption band region, and a weak positive CD band (at about 400 mμ) in the second spin-allowed d→d absorption band region. The CD band of the L-tartrato complexes are shifted to longer wavelengths than those of the oxalato complexes in the first spin-allowed absorption band region. Furthermore, the negative CD bands of these complexes are much higher in intensity than the positive one. These facts resemble those of the optically active tris(oxalato) and tris(L-tartrato) chromium(III) complexes in the corresponding region.[5] Assuming that the complexes employed here belong to pseudo $D_3$ symmetry, the negative CD bands are assigned to the ${}^4A_2 \rightarrow {}^4E_a$ transition and the positive ones to the ${}^4A_2 \rightarrow {}^4A_1$ transition as in $(-)_{546}$-[Cr-

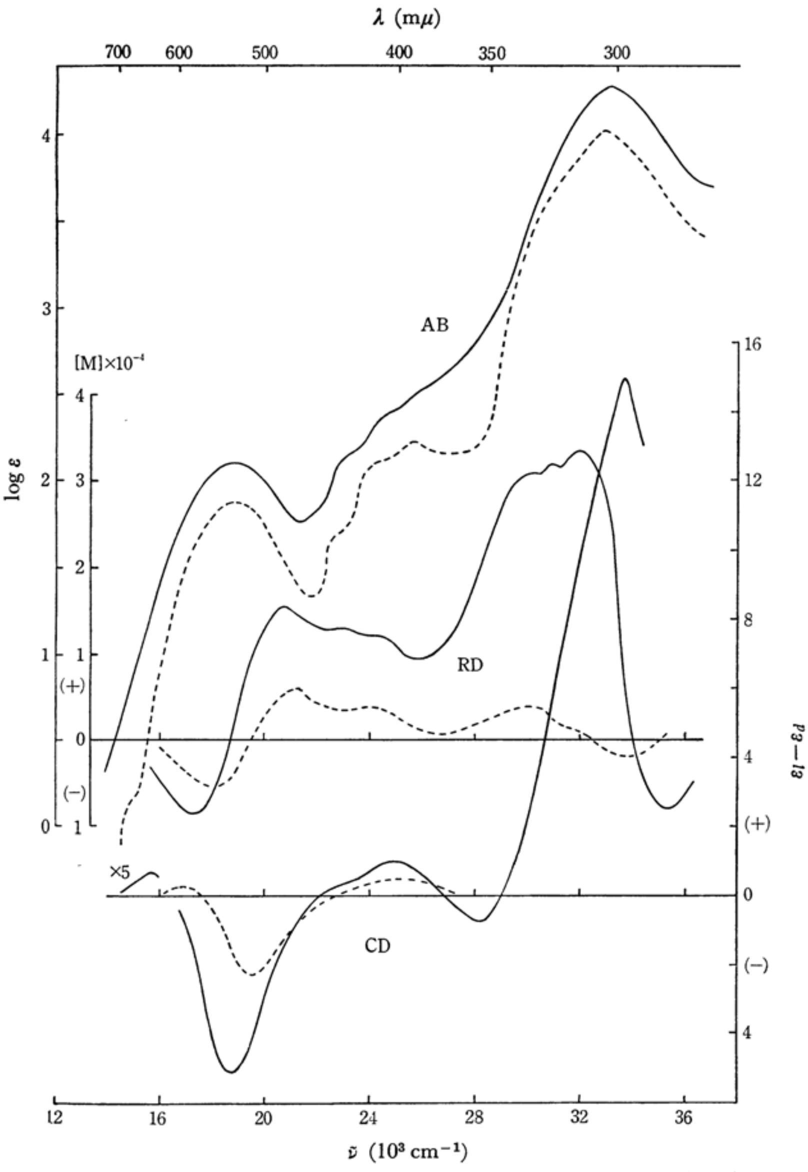

Fig. 1. Absorption (AB), CD and RD curves of, —— [Cr$_2$(L-tart$_2$H)(dip)$_2$]$^-$ and ---- (−)$_{546}$-[Cr(ox)$_2$(dip)]$^-$. (AB curves of mononuclear complex was measured for the racemic one.)

(ox)$_3$]$^{3-}$.[5,15)]

From a comparison with the data for the other complexes containing 2,2′-dipyridyl or 1,10-phenanthroline,[16,17)] the intense absorption bands at about 300 mμ are assigned to the π→π* transition originating from the coordinated 2,2′-dipyridyl or 1,10-phenanthroline ligand (Figs. 1 and 2).

**Stereospecificity of the L-Tartrato Complexes.** The L-tartrato complexes obtained by the reaction of [CrCl$_3$(dmf)(dip)] or [CrCl$_3$(dmf)-(phen)] with L-tartrate have rather complicated formulae, but the similarity between these complexes and the oxalato complexes are evident. An L-tartrate ion can not span four coordination sites around one metal ion, and the elemental analysis data exclude any possibilities of mononuclear structures for these L-tartrato complexes. It is clear that the optical activity of the L-tartrato complexes is due to a kind of configurational dissymmetry rather

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15) A. J. McCaffery, S. F. Mason and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883.

16) N. Matsuoka, Y. Shimura and R. Tsuchida, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 1637 (1961).

17) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964).

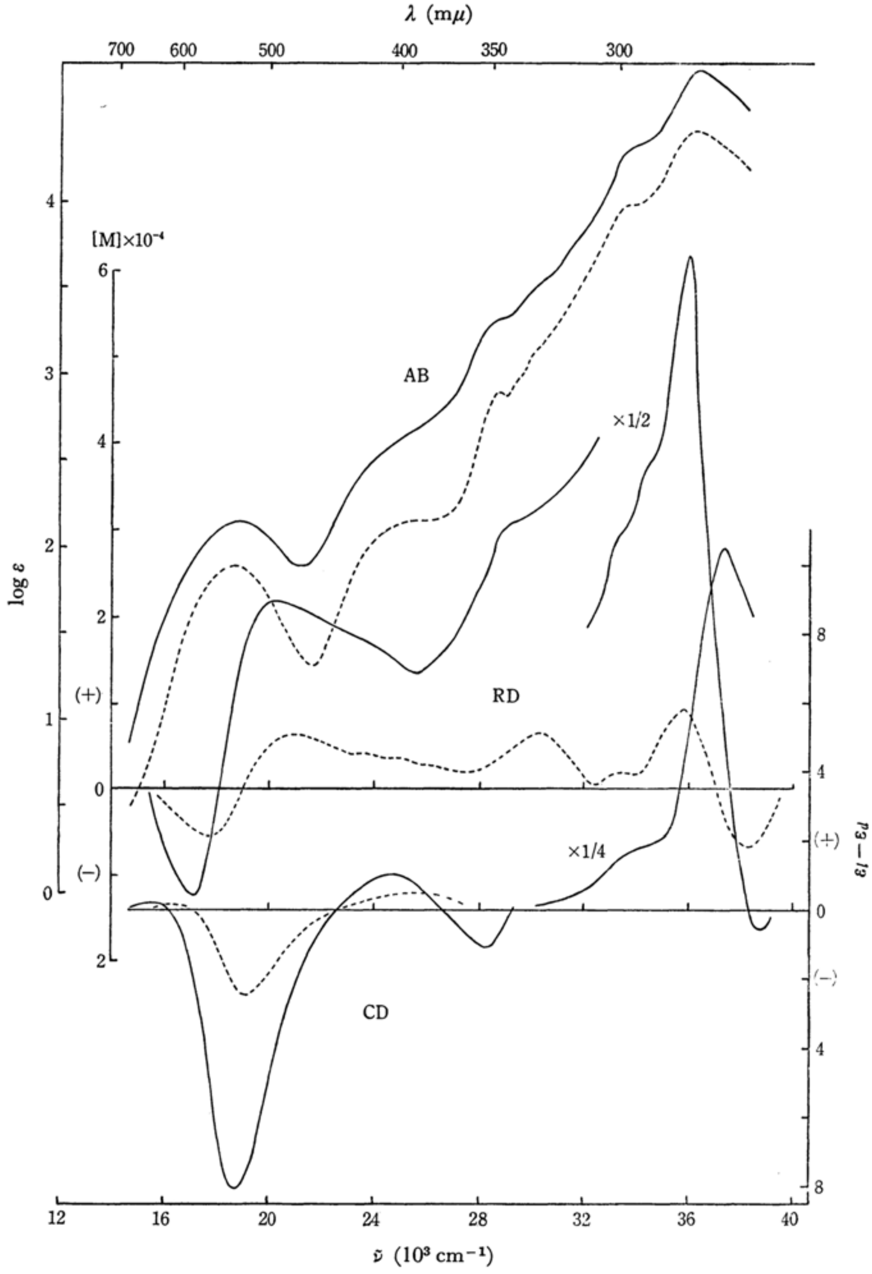

Fig. 2. Absorption (AB), CD and RD curves of, —— $[Cr_2(L\text{-tart}_2H)(phen)_2]^-$, and ---- $(-)_{546}$-$[Cr(ox)_2(phen)]^-$. (AB curve of the mononuclear complex was measured for the racemic one.)

than vicinal contribution of the coordinated L-tartrate ions from following reasons. Firstly, the absorption spectrum, CD and RD of the L-tartrato complexes in the visible region, if calculated per Cr(III) ion, have just the same or stronger intensities than those of the corresponding oxalato complexes. It has been known that the oxalato complexes easily racemize in aqueous solutions with half-lives of about 50 min.[11] On the other hand, the L-tartrato complexes do not racemize at all. Secondly, according to the construction of molecular models, the most probable structure for the experimental formula obtained is a binuclear one in which two chromium (III) ions are bridged by two tetradentate L-tartrate ions, as may be seen in Fig. 3. In this structure, the stereospecificity due to the two dissymmetric ligands is perfect; namely, as far as the L-tartrate is used, the binuclear complex which has an absolute configuration $\Lambda(C_2)$-$\Lambda(C_2)$ about the two tris-chelate type octahedra is the only one possible to be con-

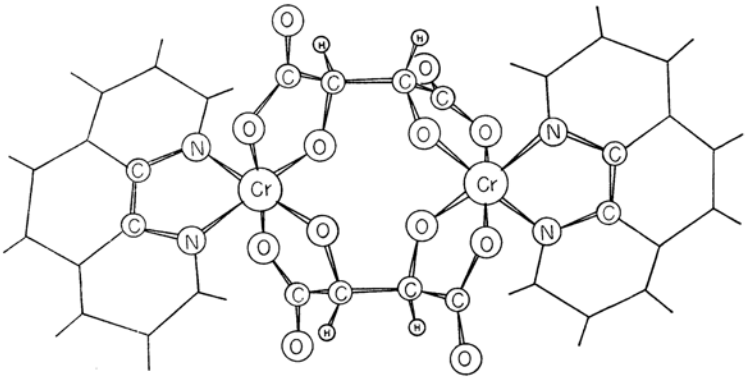

Fig. 3. Proposed structure of the L-tartrato phenanthroline complex (one proton not shown).

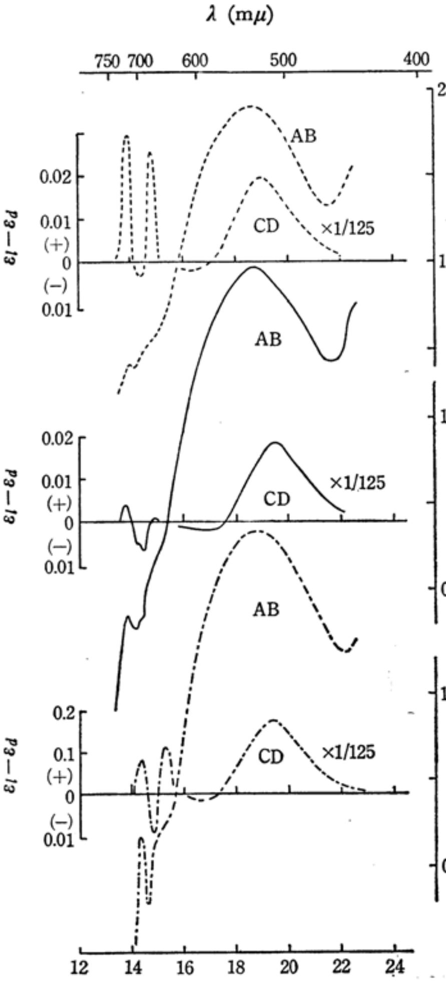

Fig. 4. Absorption (AB) and CD curves of
---- $(+)_{546}$-$[Cr(ox)_2(phen)]^-$,
—— $(+)_{546}$-$[Cr(ox)_2(dip)]^-$,
·—· $(+)_{546}$-$[Cr(ox)_2(en)]^-$.

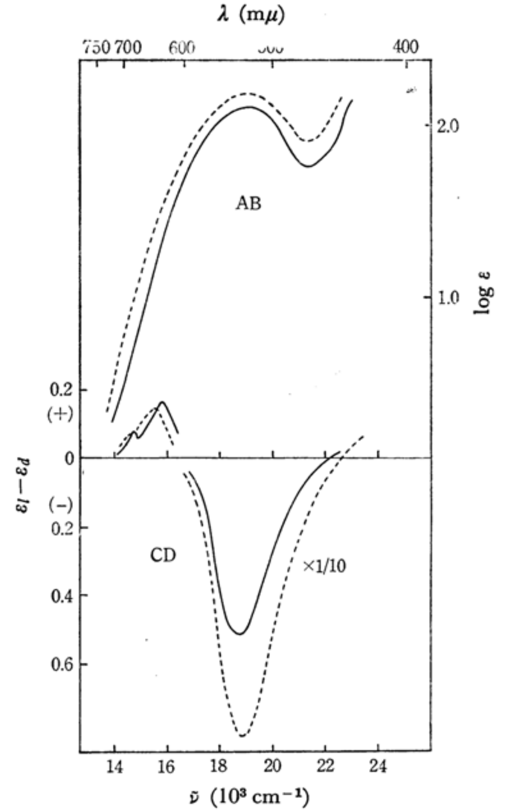

Fig. 5. Absorption (AB) and CD curves of
---- $[Cr_2(L\text{-}tart_2H)(phen)_2]^-$,
—— $[Cr_2(L\text{-}tart_2H)(dip)_2]^-$.

structed. A similar structure has been revealed for the vanadyl tartrato complexes by the X-ray analyses.[6] In the vanadyl tartrato complexes, the tartrates are tetranegative and tetradentate ligands. On the contrary, it seems likely that in the present chromium(III) complexes, one proton remains undissociated per two tetranegative L-tartrates. Nevertheless, all the L-tartrates seems to be acting as tetradentate ligands. A question remains to be answered about the exact position of this proton or its role in the binuclear structure.

On the basis that the L-tartrato complexes have the absolute configuration $\Lambda(C_2)$-$\Lambda(C_2)$, it is possible to determine the absolute configurations of the mononuclear complexes which belong to a general type, *cis*-$[Cr(O)_4(N)_2]$, because the similarity of the CD or RD curves between the L-tartrato and the oxalato complexes is quite good. Namely, it can be concluded that $(-)_{546}$-$K[Cr(ox)_2(dip)]\cdot 3H_2O$ and $(+)_{546}$-$K[Cr(ox)_2(phen)]\cdot 4H_2O$, both of which were obtained from the less soluble diastereomers with $(-)_{546}$-$[Co(ox)(en)_2]^+$, have the $\Lambda(C_2)$ and $\Delta(C_2)$ configurations respectively, and that the ethylenediamine complex, $(+)_{546}$-$K[Cr(ox)_2(en)]\cdot 2H_2O$, forming the less soluble diastereomer with brucinium ion, has the $\Delta(C_2)$ configuration.

The $\Lambda(C_2)$ isomers of both the 2,2′-dipyridyl and 1,10-phenanthroline complexes, including the present binuclear complexes show a positive CD band in their ligand $\pi\rightarrow\pi^*$ absorption band region (280—300 mμ). This is also true for another mono-phen-Co(III) complex, $(-)_{546}$-$[Co(en)_2(phen)]I_3$, which shows an intense positive CD band at about 280 mμ and a negative CD band in its first d→d absorption band region.[17]

**Spin-forbidden Bands.** A few reports have been made on the CD or RD in the region of the spin-forbidden absorption bands of chromium(III) complexes. Kling and Woldbye[18] measured the RD of $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ and $(+)_{546}$-$[Cr(tn)_3]Cl_3$ in their spin-forbidden bands, and found many sharp inversive dispersions superimposed with each other. McCaffery and Mason[5] measured the CD of tris(L-tartrato)chromium(III) ion in the corresponding region and found a CD band of weak intensity. As may be seen in Figs. 4 and 5, all of the oxalato complexes, $(+)_{546}$-$K[Cr(ox)_2(dip)]\cdot 3H_2O$, $(+)_{546}$-$K[Cr(ox)_2(phen)]\cdot 4H_2O$, and $(+)_{546}$-$K[Cr(ox)_2(en)]\cdot 2H_2O$, show a group of weak CD bands in the spin-forbidden absorption bands. The L-tartrato complexes, $Ba[Cr_2$(L-tart$_2$H)$(dip)_2]_2\cdot 9H_2O$ and $NH_4[Cr_2$(L-tart$_2$H)$(phen)_2]\cdot 6.5H_2O$, also show an apparently positive weak CD band (at about 690 mμ) superposed on the positive CD component (at about 640 mμ) of the first spin-allowed absorption band. Each of the oxalato complexes with the $\Delta(C_2)$ configuration shows three sharp CD peaks, (+), (−), (+) listing from the side of the long wavelengths, though the negative CD peak (at about 690 mμ) of $(+)_{546}$-$K[Cr(ox)_2(dip)]$ splits into two components. The CD intensities of the spin-forbidden bands are one over a few hundred as weak as those of the spin-allowed ones.

The spin-forbidden d→d transition bands which appear in the longer wavelength region than the spin-allowed transition bands should be assigned to the ${}^4A_{2g}\rightarrow{}^2E_g$ and ${}^4A_{2g}\rightarrow{}^2T_{1g}$ in a complex of octahedral symmetry. But it seems that the exact assignments of these bands of various chromium(III) complexes are still difficult.[19] The CD band which appears at longest wavelengths for the present complexes may be assigned to the ${}^4A_{2g}\rightarrow{}^2E_g$ transition under $O_h$ symmetry. In $D_3$ symmetry, the $T_{1g}$ state breaks down into the E and $A_2$ states and the $E_g$ state remains as the E state. Since these spin-forbidden transitions acquire their rotational strengths only by borrowing the electric and magnetic moments from the upper quartet state of the same symmetry,[20] the spin-forbidden transitions must have the same sign of the CD bands with that of the spin-allowed transition to the state with the same symmetry. Now, assuming that the present complexes belong to pseudo $D_3$ symmetry, two positive CD bands of their $(+)_{546}$-isomers may be assigned to the ${}^2E$ state and the negative one to the ${}^2A_2$ state, because the ${}^4E_a$ components of the first spin-allowed bands of these complexes have the positive CD sign. However, from the fact that the negative orbitally nondegenerate ${}^2A_2$ state of $(+)_{546}$-$K[Cr(ox)_2(dip)]$ splits into two CD components, it seems likely that the spin-orbit coupling or vibrational structures must be taken into consideration.

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[19] H. L. Schläfer, *Z. Phys. Chem. N. F.*, **11**, 65 (1957). C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., New York (1962), p. 236.

[20] S. F. Mason, *Quart. Rev.*, **27**, 20 (1963).