BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 447—452 (1969)

# Association Involving Optically Active Ions. II. Association Constants of Tris(ethylenediamine)cobalt(III) and Tris(propylenediamine)-cobalt(III) Ions with Some Anions

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(Received June 30, 1968)

Association constants of $[Co\,en_3]^{3+}$ (en=ethylenediamine) and *d*- and *l*-$[Co\,d\text{-}pn_3]^{3+}$ (pn=propylenediamine; *d*- and *l*- refer to the sign of optical rotation at sodium D-line) with some anions have been determined spectrophotometrically. Values are as follows: $[Co\,en_3]^{3+}\cdot SO_4^{2-}$ 49, $[Co\,en_3]^{3+}$·glycollate$^-$ ~5, *d*-$[Co\,d\text{-}pn_3]^{3+}\cdot SO_4^{2-}$ 70, *d*-$[Co\,d\text{-}pn_3]^{3+}\cdot d\text{-tart}^{2-}$ ($\text{tart}^{2-}$=bivalent tartrate anion) 30, *d*-$[Co\,d\text{-}pn_3]^{3+}\cdot l\text{-tart}^{2-}$ 28, *l*-$[Co\,d\text{-}pn_3]^{3+}\cdot SO_4^{2-}$ 43, *l*-$[Co\,d\text{-}pn_3]^{3+}\cdot d\text{-tart}^{2-}$ ~7, *l*-$[Co\,d\text{-}pn_3]^{3+}\cdot l\text{-tart}^{2-}$ ~16. These association constants are discussed in terms of the microscopic interaction between the ions. The effect of outer-sphere association on the circular dichroism and optical rotatory dispersion is also discussed.

In the outer-sphere association, ionic charges and radii are considered to be of primary importance. It is also known that other effects such as dipole moment and polarizability exert influence. However, few investigations have been made on the effect of microscopic construction of individual ions on the outer-sphere association. In a previous paper,[1] it was shown that stereospecificity exists in the association between tris(ethylenediamine)-cobalt(III), $[Co\,en_3]^{3+}$, and tartrate ions. It can be interpreted only on the basis of microscopic interaction between ions. In order to obtain more distinct information on such an interaction, association involving diastereoisomers of tris(propylenediamine)cobalt(III) ions, *d*- and *l*-$[Co\,d\text{-}pn_3]^{3+}$ (*d*- and *l*- refer to the sign of the optical rotation at sodium D-line), is investigated in this paper. These systems are considered to be appropriate for the present purpose because the two isomers are different from each other only in the mutual orientation of bonds. Association constants of these complex ions with tartrate and with sulfate are determined spectrophotometrically and effects of association on the circular dichroism (CD) and optical rotatory dispersion (ORD) are investigated.

## Experimental

The complexes *d*-$[Co\,d\text{-}pn_3]I_3\cdot H_2O$ and *l*-$[Co\,d\text{-}pn_3]Cl\cdot d\text{-tart}\cdot 3H_2O$ ($\text{tart}^{2-}$ denotes bivalent tartrate anion) were prepared according to the method reported in the literature.[2] The complex *d*-$[Co\,d\text{-}pn_3]I_3\cdot H_2O$ was treated with $Na_3[Co(CN)_6]$. The precipitate was washed to be free from iodide and then converted into perchlorate by passing through a column of Dowex 1, X-8 in the perchlorate form. Found: C, 18.10; H, 5.29; N, 14.16%. Calcd for $[CoC_9H_{30}N_6](ClO_4)_3\cdot H_2O$: C, 18.12; H, 5.40; N, 14.09%. Molecular rotations at sodium D-line, and at peaks of ORD are as follows: $[M]_D=150°$, $[M]_{525}=2250°$ and $[M]_{468}=8000°$. The complex *l*-$[Co\,d\text{-}pn_3](ClO_4)_3$ was obtained by the addition of perchloric acid into the solution of *l*-$[Co\,d\text{-}pn_3]Cl\cdot d\text{-tart}\cdot 3H_2O$. Found: C, 18.92; H, 5.08; N, 14.45%. Calcd for $[CoC_9H_{30}N_6](ClO_4)_3$: C, 18.67; H, 5.22; N, 14.50%. $[M]_D=1500°$, $[M]_{515}=4500°$ and $[M]_{431}=5100°$. The preparation of *d*-$[Co\,en_3](ClO_4)_3$ was described in the previous paper.[1]

The electronic absorption spectra were measured with a Shimadzu QV-50 Spectrophotometer, and the ORD and CD spectra were obtained with a JASCO ORD/UV-5 Optical Rotatory Dispersion Recorder. All measurements were carried out at 25°C and $\mu=0.1$ ($NaClO_4$). The pH of the solution was adjusted so that tartrate ions are present as a bivalent anion in the solution. The concentration of the complexes was varied from 0.03 to 1.25 mM.

## Results and Discussion

The absorbancy, CD and ORD of many complex ions are affected by the outer-sphere association, which is expressed by

$$M^{m+} + jX^{x-} \rightleftarrows MX_j^{(m-jx)+} \quad (j=1, 2, \cdots, n) \qquad (1)$$

where $M^{m+}$ and $X^{x-}$ correspond to the complex ion and the counter ion, respectively. Association constants are defined by

$$K = [MX^{(m-x)+}]/([M^{m+}][X^{x-}]) \qquad (2)$$

$$\beta_j = [MX_j^{(m-jx)+}]/([M^{m+}][X^{x-}]^j) \qquad (3)$$

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[1] K. Ogino and U. Saito, This Bulletin, **40**, 826 (1967).

[2] F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

In the previous paper,[1)] the relation between the association constants and the change of a partial molar quantity on association, $\Delta$, was given in a generalized form (Eq. (12) in Ref. 1):

$$\Delta=\sum_{j=1}^{n}\Delta_{\mathrm{MX}_j}\beta_j[\mathrm{X}^{x-}]^j/(1+\sum_{j=1}^{n}\beta_j[\mathrm{X}^{x-}]^j) \tag{4}$$

which is valid for any property that is additive for $\mathrm{MX}_j{}^{(m-jx)+}$, *e. g.*, absorbancy, electrical conductivity, *etc.* In the case of absorbancy, $\Delta$ and $\Delta_{\mathrm{MX}_j}$ are defined by

$$\Delta=\varepsilon_{app}-\varepsilon_0 \tag{5}$$

and

$$\Delta_{\mathrm{MX}_j}=\varepsilon_{\mathrm{MX}_j}-\varepsilon_0 \tag{6}$$

respectively, where $\varepsilon_0$ and $\varepsilon_{\mathrm{MX}_j}$ are molar extinction coefficients of $\mathrm{M}^{m+}$ and $\mathrm{MX}^{(m-jx)+}$, and $\varepsilon_{app}$ is the apparent extinction coefficient of the solution:

$$\varepsilon_{app}=(\text{absorbancy})/([\mathrm{M}^{m+}]+\sum_{j=1}^{n}[\mathrm{MX}_j{}^{(m-jx)+}]) \tag{7}$$

In the case of CD and ORD, $\Delta$ and $\Delta_{\mathrm{MX}_j}$ are defined similarly as in Eqs. (5) and (6):

$$\Delta=(\varepsilon_l-\varepsilon_r)_{app}-(\varepsilon_l-\varepsilon_0)_0 \tag{8}$$

$$\Delta_{\mathrm{MX}_j}=(\varepsilon_l-\varepsilon_r)_{\mathrm{MX}_j}-(\varepsilon_l-\varepsilon_r)_0 \tag{9}$$

for CD and

$$\Delta=[M]_{app}-[M]_0 \tag{10}$$

$$\Delta_{\mathrm{MX}_j}=[M]_{\mathrm{MX}_j}-[M]_0 \tag{11}$$

for ORD, where the subscripts *app*, 0 and $\mathrm{MX}_j$ have the same meanings as in Eqs. (5) and (6).

Assuming that only the species $\mathrm{MX}^{(m-x)+}$ is formed and higher association is absent, Eq. (12) is obtained instead of Eq. (4).

$$\Delta=\Delta_{\mathrm{MX}}K[\mathrm{X}^{x-}]/(1+K[\mathrm{X}^{x-}]) \tag{12}$$

$$\Delta_{\mathrm{MX}}=\varepsilon_{\mathrm{MX}}-\varepsilon_0 \tag{13}$$

As has been explained in the previous paper,[1)] the association constant $K$ can be determined by use of Eq. (14).

$$[\mathrm{X}^{x-}]/\Delta=[\mathrm{X}^{x-}]/\Delta_{\mathrm{MX}}+1/(K\Delta_{\mathrm{MX}}) \tag{14}$$

By plotting $[\mathrm{X}^{x-}]/\Delta$ against $[\mathrm{X}^{x-}]$, $K$ is obtained as the ratio of slope to intercept of the resulting straight line. If other species, $\mathrm{MX}_2{}^{(m-2x)+},\cdots$, $\mathrm{MX}_n{}^{(m-nx)+}$ were also formed, the plot of $[\mathrm{X}^{x-}]/\Delta$ *vs.* $[\mathrm{X}^{x-}]$ would not give a straight line, but give a curve dependent on the relative magnitude of $\Delta_{\mathrm{MX}_j}$ and $\beta_j$. Whenever the curvature of the plot is small and can be approximated to be a straight line, an apparent 1 : 1 association constant can be obtained by use of Eq. (14). However, such an apparent constant should be a function of the ratio $\Delta_{\mathrm{MX}_j}/\Delta_{\mathrm{MX}}$, and since the ratio is expected to depend on the wavelength at which the absorbancy is measured, the apparent constant obtained at different wavelengths will not give a constant value.

Equation (14) was applied to the change of absorbancy of $[\mathrm{Co\,en_3}]^{3+}$ on addition of sulfate, and the association constants were obtained to be 49, 47 and 50 from absorbancies at 260, 262 and 265 mμ, respectively. The small deviation of these values suggests that 1 : 1 association occurs predominantly.

The absence of higher association was also examined by the following procedure. When the change of absorbancy, CD or ODR at two concentrations $[\mathrm{X}^{x-}]_1$ and $[\mathrm{X}^{x-}]_2$ are measured to be $\Delta_1$ and $\Delta_2$ respectively, the ratio $\Delta_1/\Delta_2$ is given by

$$\frac{\Delta_1}{\Delta_2}=\frac{(\sum_{j=1}^{n}\Delta_{\mathrm{MX}_j}[\mathrm{X}^{x-}]_1{}^j)(1+\sum_{j=1}^{n}\beta_j[\mathrm{X}^{x-}]_2{}^j)}{(\sum_{j=1}^{n}\Delta_{\mathrm{MX}_j}[\mathrm{X}^{x-}]_2{}^j)(1+\sum_{j=1}^{n}\beta_j[\mathrm{X}^{x-}]_1{}^j)} \tag{15}$$

It is a function of the ratio $\Delta_{\mathrm{MX}_j}/\Delta_{\mathrm{MX}}$. When only 1 : 1 association takes place, Eq. (15) is simplified as

$$\frac{\Delta_1}{\Delta_2}=\frac{[\mathrm{X}^{x-}]_1(1+K[\mathrm{X}^{x-}]_2)}{[\mathrm{X}^{x-}]_2(1+K[\mathrm{X}^{x-}]_1)} \tag{16}$$

which does not contain $\Delta_{\mathrm{MX}}$, hence $\Delta_1/\Delta_2$ should be constant for any properties that are affected by association. This equation was applied to the changes of the absorbancy, ORD and CD of the system *d*-$[\mathrm{Co\,en_3}]^{3+}$ and sulfate in the wavelengths where the changes caused by the addition of sulfate could be measured most accurately (*cf.* Figs. 4 and 5). The result for the absorbancy is shown in Table 1. At $[\mathrm{X}^{x-}]_1=0.025$ M and $[\mathrm{X}^{x-}]_2=0.01$ M, the value of $\Delta_1/\Delta_2$ is calculated to be 1.68 by use of Eq. (16) and $K=49$. The values in Table 1 agree with it. The ratio for the change of ORD at 360—410 mμ and that for CD at 435—470 mμ were also found to agree with the calculated value within the experimental error.

TABLE 1. THE RATIO $\Delta_1/\Delta_2$ AT $[\mathrm{X}^{x-}]_1=0.025$ M AND $[\mathrm{X}^{x-}]_2=0.010$ M FOR ABSORBANCY OF THE SYSTEM, $[\mathrm{Co\,en_3}]^{3+}$ AND SULFATE

| mμ | $\Delta_1/\Delta_2$ | mμ | $\Delta_1/\Delta_2$ | mμ | $\Delta_1/\Delta_2$ |
|---|---|---|---|---|---|
| 267.5 | $1.7_0$ | 257.5 | $1.6_4$ | 216 | 1.7 |
| 265 | $1.6_4$ | 255 | $1.6_8$ | 210 | 1.7 |
| 262.5 | $1.6_7$ | 225 | 1.6 | 206 | 1.6 |
| 260 | $1.6_8$ | 220 | 1.7 | | |

From above observations it may be concluded that only the species $[\mathrm{Co\,en_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$ are formed predominantly by the association under the experimental condition. Larsson[3)] reported the evidence of higher association between $[\mathrm{Co\,en_3}]^{3+}$ and sulfate ions. This difference may be due to the differences in sulfate concentrations and ionic strength: In the study by Larsson, sulfate concentration was varied from 0.015 to 1 M and other electrolytes were not added in solution, while in this study the

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[3)] R. Larsson, *Acta Chem. Scand.*, **16**, 2267 (1962).

maximum sulfate concentration was 0.025 M and ionic strength was kept to be 0.1 with sodium perchlorate.

The absorbancy, CD and ORD of [Co *d*-pn$_3$]$^{3+}$ also changed on the addition of sulfate and tartrate. In Figs. 1 and 2 are shown the changes in the apparent extinction coefficient (*cf.* Eq. (5)) at 265 m$\mu$. The changes are neither the same for *d*- and *l*-tartrate, nor for *d*- and *l*-[Co *d*-pn$_3$]$^{3+}$. From these plots association constants were determined by use of Eq. (14). In Table 2 the constants obtained are given. Using these association constants, the changes of CD and ORD spectra of *d*- and *l*-[Co *d*-pn$_3$]$^{3+}$ on the addition of sulfate could be explained by Eq. (16). This equation was also applied to the system *d*-[Co *d*-pn$_3$]$^{3+}$ and tartrate, but was not applied to the system *l*-[Co *d*-pn$_3$]$^{3+}$ and tartrate because of the limited accuracy of association constants and the small change of CD caused by the addition of tartrate (*cf.* Fig. 9).

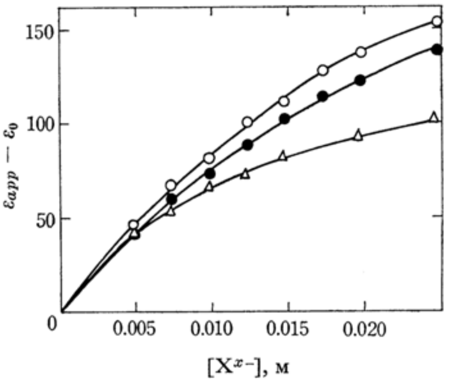

Fig. 1. Variation of the apparent extinction coefficient of *d*-[Co *d*-pn$_3$]$^{3+}$ at 265 m$\mu$ as a function of anion concentration, [X$^{x-}$], $\mu$=0.1, 25°C.
—○—: X$^{x-}$=*d*-tart$^{2-}$, —●—: X$^{x-}$=*l*-tart$^{2-}$,
—△—: X$^{x-}$=SO$_4{}^{2-}$

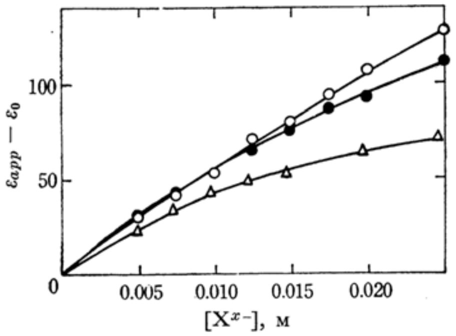

Fig. 2. Variation of the apparent extinction coefficient of *l*-[Co *d*-pn$_3$]$^{3+}$ at 265 m$\mu$ as a function of anion concentration, [X$^{x-}$], $\mu$=0.1, 25°C.
—○—: X$^{x-}$=*d*-tart$^{2-}$, —●—: X$^{x-}$=*l*-tart$^{2-}$,
—△—: X$^{x-}$=SO$_4{}^{2-}$

It was shown by the X-ray analyses that the absolute configurations of *d*- and *l*-[Co *d*-pn$_3$]$^{3+}$ are $\Delta$(C$_2$)[5] and $\Delta$(C$_2$)[6],[*1] respectively, and *d*- and *l*-[Co *d*-pn$_3$]$^{3+}$ correspond to the "*lel*" type and the "*ob*" type according to Corey and Bailar's notation.[7] In the *lel* conformation, two sets of three N–H bonds are nearly parallel to the C$_3$ axis of the complex ion,[8] and the anion in the ion pair can be located along the direction of the C$_3$ axis so as to form hydrogen bonding with N–H hydrogen. On the other hand, in the *ob* conformation orientations of the N–H bonds are not the same to one another. As is seen in Table 2, the association constants for *lel*-$\Delta$(C$_2$)-[Co *d*-pn$_3$]$^{3+}$ are substantially larger than those for the *ob*-$\Lambda$(C$_2$)-isomer. Such a difference will be attributable to the difference in the orientation of N–H bonds in *lel* and *ob* isomer.

TABLE 2. ASSOCIATION CONSTANTS AT $\mu$=0.1 AND 25°C

| | Absolute configuration | *d*-tart$^{2-}$ | *l*-tart$^{2-}$ | SO$_4{}^{2-}$ | glycolate$^-$ |
|---|---|---|---|---|---|
| *d*-[Co en$_3$]$^{3+}$ | $\Delta$(C$_2$)[4] | 26±2[1] | | 49±2 | 5±2 |
| *l*-[Co en$_3$]$^{3+}$ | $\Lambda$(C$_2$) | 21±2[1] | | | |
| *d*-[Co *d*-pn$_3$]$^{3+}$ | $\Delta$(C$_2$)[5] | 30±2 | 28±2 | 70±2 | |
| *l*-[Co *d*-pn$_3$]$^{3+}$ | $\Lambda$(C$_2$)[6] | 7±2 | 16±2 | 43±3 | |

The conformations of [Co en$_3$]$^{3+}$ in the solution are predominantly *lel*. Association constants in Table 2 show that those for [Co en$_3$]$^{3+}$ are a little smaller than those for *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$,[*2] contrary

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4) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, This Bulletin, **30**, 795 (1957); *Acta Cryst.*, **8**, 729 (1955).

5) H. Iwasaki and Y. Saito, This Bulletin, **39**, 92 (1966).

6) Y. Saito, Structures and Absolute Configurations of Cobalt(III) Complexes, Plenary Lecture, Xth I.C.C.C., *Pure Appl. Chem.*, IUPAC, to be published.

[*1] The complex *l*-[Co *d*-pn$_3$]$^{3+}$ used in this study is the same sample that was used in the X-ray analysis by Y. Saito *et al.*

7) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

8) S. F. Mason and B. J. Norman, *J. Chem. Soc.*, *A*, **1966**, 307.

[*2] According to the potential energy difference calculated by Corey and Bailar,[7] *ca.* 64% of the total complex in the solution of tris(diamine)cobalt(III), is in the *lel* conformation, *ca.* 3% in the *ob* conformation, and the rest of the complex is in the intermediate conformations between *lel* and *ob*. The result of the calculation was supported by the experiments by Dwyer *et al.*[9] When it is assumed that the association constant between sulfate and [Co en$_3$]$^{3+}$ in conformations other than *lel* is about 43/70 (ratio of association constants of *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$·SO$_4{}^{2-}$ and *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$·SO$_4{}^{2-}$) of that of [Co en$_3$]$^{3+}$ in the *lel* conformation, the hypothetical association constant of *lel*-[Co en$_3$]$^{3+}$·SO$_4{}^{2-}$ is calculated to be 58, which is still smaller than the association constant of *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$·SO$_4{}^{2-}$.

9) F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963); F. P. Dwyer, A. M. Sargeson and L. B. James, *ibid.*, **86**, 590 (1964).

to the expectation from the electrostatic theory that the larger ions should have smaller association constants. This indicates that the steric hindrance of the methyl group of propylenediamine is not significant in the association with sulfate and with tartrate. It may be because the methyl groups have trigonal orientation nearly perpendicular to the $C_3$ axis and do not interfere with the approach of anions along the direction of the $C_3$ axis.

Association constants of $[\mathrm{Co\,en_3}]^{3+}$ with tartrate ions were discussed briefly in the previous paper.[1] They are about one half of that with sulfate but much larger than that with univalent glycollate. It suggests that the two carboxylate groups in a tartrate ion take part simultaneously in association. Therefore the two carboxylates in a tartrate ion should not be oriented trans to each other. Between the two gauche conformations of a *d*-tartrate ion in Fig. 3, I is considered to be more stable because two hydroxyl groups are trans to each other and hydrogen bonding is possible between $-\mathrm{COO^-}$ and $-\mathrm{OH}$. Thus, the bond $^-\mathrm{OOC{-}C{-}C{-}COO^-}$ in a *d*-tartrate ion is arranged as a right handed screw in an ion-pair, while in an *l*-tartrate ion it is arranged as a left handed screw. The difference in the association constants of *lel*-$\Delta$- and *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$ with *d*- and *l*-tartrate ions is supposed to be related to the relative configuration of the

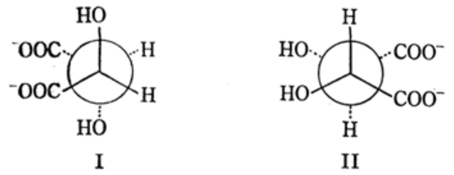

Fig. 3. Conformations of a *d*-tartrate ion viewed along the direction of the bond between two asymmetric carbon atoms.

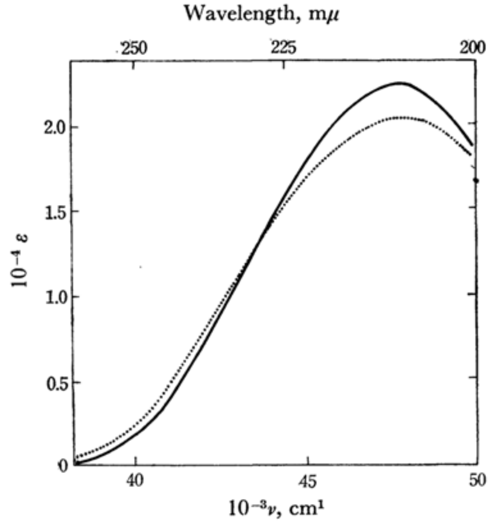

Fig. 4. Electronic absorption spectra in the charge transfer region.
——: $[\mathrm{Co\,en_3}]^{3+}$, ……: $[\mathrm{Co\,en_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$

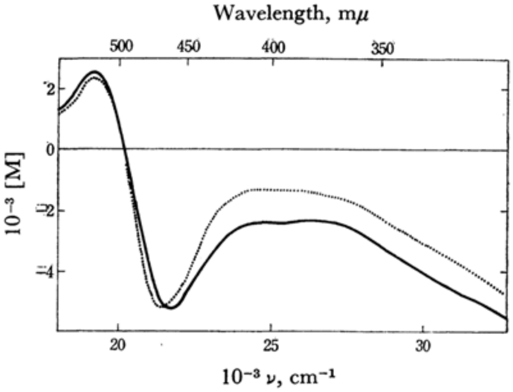

Fig. 5. Optical rotatory dispersion curves.
——: $[\mathrm{Co\,en_3}]^{3+}$, ……: $[\mathrm{Co\,en_3}]^{3+}\cdot\mathrm{SO_4}^{2-}$

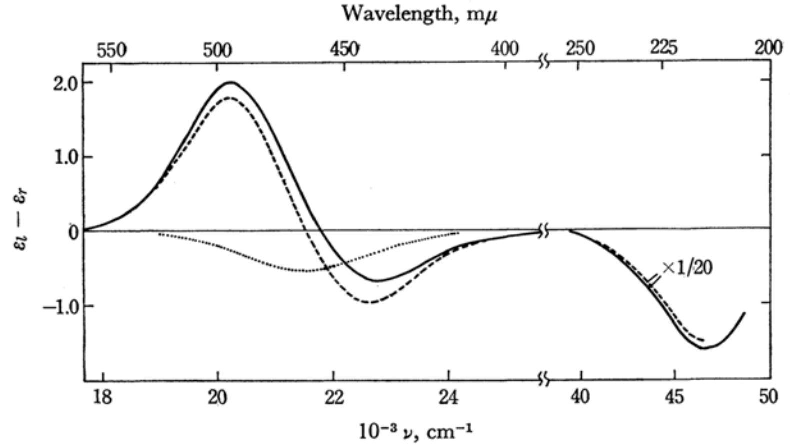

Fig. 6. Effect of sulfate on the circular dichroism curve of $\Delta$-[Co *d*-pn$_3$](ClO$_4$)$_3\cdot$H$_2$O, $\mu=0.1$(NaClO$_4$), 25°C.
——: CD in solution without sulfate, ------: CD in 0.025 M $\mathrm{Na_2SO_4}$ solution,
……: Difference between CD curves of $\Delta$-[Co *d*-pn$_3$]$^{3+}\cdot\mathrm{SO_4}^{2-}$ and $\Delta$-[Co *d*-pn$_3$]$^{3+}$ (*cf.* Eq. (17)).

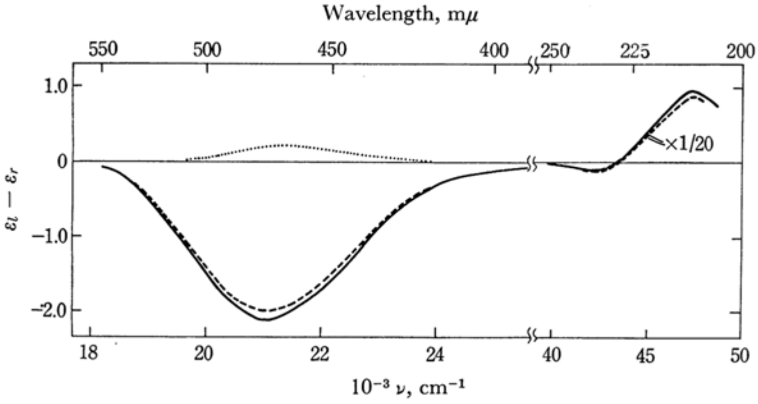

Fig. 7. Effect of sulfate on the circular dichroism curve of $\Lambda$-$[Co\,d\text{-}pn_3](ClO_4)_3$, $\mu=0.1(NaClO_4)$, 25°C.
——: CD in solution without sulfate, ------: CD in 0.025 M $Na_2SO_4$ solution,
……: Difference between CD curves of $\Lambda$-$[Co\,d\text{-}pn_3]^{3+}\cdot SO_4^{2-}$ and $\Lambda$-$[Co\,d\text{-}pn_3]^{3+}$ (*cf.* Eq. (17)).

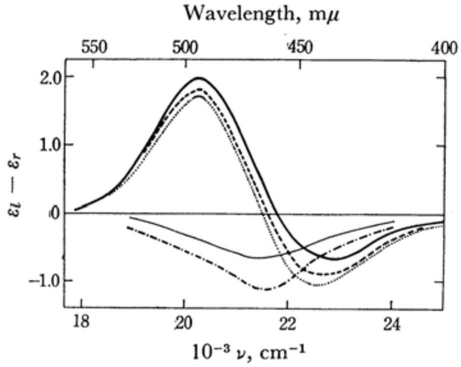

Fig. 8. Effect of tartrate on the circular dichroism spectrum of $\Delta$-$[Co\,d\text{-}pn_3](ClO_4)_3\cdot H_2O$, $\mu=0.1$ $(NaClO_4)$, 25°C.
——: CD in solution without tartrate
……: CD in 0.025 M $Na_2$*d*-tart solution
------: CD in 0.025 M $Na_2$ *l*-tart solution
-·-·-: Difference between CD curves of $\Delta$-$[Co\,d\text{-}pn_3]^{3+}\cdot d\text{-}tart^{2-}$ and $\Delta$-$[Co\,d\text{-}pn_3]^{3+}$
——: Difference between CD curves of $\Delta$-$[Co\,d\text{-}pn_3]^{3+}\cdot l\text{-}tart^{2-}$ and $\Delta$-$[Co\,d\text{-}pn_3]^{3+}$

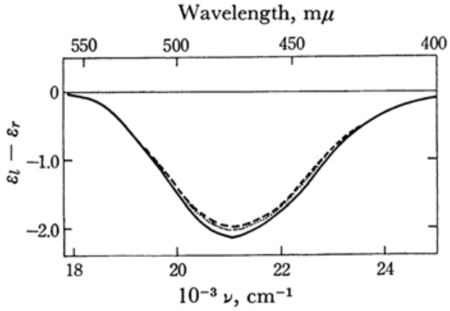

Fig. 9. Effect of tartrate on the circular dichroism spectrum of $\Lambda$-$[Co\,d\text{-}pn_3](ClO_4)_3$, $\mu=0.1(NaClO_4)$, 25°C.
——: CD in solution without tartrate
……: CD in 0.025 M $Na_2$ *d*-tart solution
------: CD in 0.025 M $Na_2$ *l*-tart solution

complex ion and the $^-OOC$–C–C–$COO^-$ screw in the tartrate ion. A consideration with the aid of molecular models reveals that association of *d*-tartrate ion with complex ions of $\Delta(C_2)$ configuration is more preferable to that with complex ions of $\Lambda(C_2)$ configuration. This assumption is in accord with the results in Table 2. The difference in the association constants of tartrate ions with *lel*-$\Delta$- and *ob*-$\Lambda$-$[Co\,d\text{-}pn_3]^{3+}$, which have the same charge and nearly the same size, shows the importance of the microscopic construction of ions in the outer-sphere association.

Using the association constant in Table 2, absorption and CD spectra of $[Co\,en_3]^{3+}$ and $[Co\,d\text{-}pn_3]^{3+}$ were analyzed in terms of 1 : 1 association by use of Eq. (12). In Figs. 4 and 5 are shown the absorption spectrum and the ORD curve of the ion-pair $[Co\,en_3]^{3+}\cdot SO_4^{2-}$. The absorbancy increases by association at wavelengths 270—230 mμ, but it decreases at shorter wavelengths. The absorbancy of *lel*-$\Delta$- and *ob*-$\Lambda$-$[Co\,d\text{-}pn_3]^{3+}$ change similarly by the association with sulfate as that of $[Co\,en_3]^{3+}$.

Figures 6 and 7 show CD spectra of *lel*-$\Delta$- and *ob*-$\Lambda$-$[Co\,d\text{-}pn_3]^{3+}$ in the absence and in the presence of 0.025 M sodium sulfate. The CD bands of these complexes in the absence of sulfate were discussed in a seperate paper.[10] As can be seen in

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[10] K. Ogino, K. Murano and J. Fujita, *Inorg. Nucl. Chem. Letters,* **4,** 351 (1968).

Figs. 6 and 7 the sign of the change on addition of sulfate (*cf.* Eq. (8)) is negative in the *d–d* abosprtion region and positive in the charge transfer region for *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$, while the sign of the change is reversed for *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$. Figures 8 and 9 are CD spectra of *lel*-$\Delta$- and *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$ in 0.025 M *d*- and *l*-tartrate solutions. The changes in CD produced by the addition of sulfate and tartrate are larger for *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$ than for *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$. As can be seen from Eq. (12) such a difference is attributable to differences of both $K$ and $\Delta_{MX}$ which is defined by

$$\Delta_{MX} = (\varepsilon_l - \varepsilon_r)_{MX} - (\varepsilon_l - \varepsilon_r)_0 \qquad (17)$$

$(\varepsilon_l - \varepsilon_r)_{MX}$ being the circular dichroism of the ion-pair. Vales of $\Delta_{MX}$ were obtained at each wavelength and are also given in Figs. 6 and 7. It is seen that the larger change of CD of *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$ than that of *ob*-$\Lambda$-[Co *d*-pn$_3$]$^{3+}$ caused by the addition of the same amount of sulfate is due to larger values of both $K$ and $\Delta_{MX}$ of the *lel*-$\Delta$(C$_2$)-isomer. Values of $\Delta_{MX}$ were obtained also for the association of *lel*-$\Delta$-[Co *d*-pn$_3$]$^{3+}$ with tartrate (Fig. 8). The difference of $\Delta_{MX}$ values for *lel*-$\Delta$(C$_2$)- and *ob*-$\Lambda$(C$_2$)-isomer and for *d*- and *l*-tartrate may be related to the different structure in the outer-sphere association due to different conformations.

The author wishes to thank Professor Kazuo Saito and Dr. Junnosuke Fujita for their helpful advice and encouragement, and Mr. Hide Saito from whom the complex *l*-[Co *d*-pn$_3$]Cl·*d*-tart·3H$_2$O was obtained.