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Association Involving Optically Active Ions. I. Association Constants of Tris(ethylenediamine)cobalt(III) and Tartrate Ions

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The enantiomer differentiation of an optically active metal complex through the presence of another kind of optically active ion in the solution is considered to be due to association. A mathematical treatment has been made of the equilibria which exist in solutions containing either or both antipodes of an optically active ion and optically active counter ions which do not racemize rapidly. The results have been applied to a system of $[\mathrm{Co\ en_3}]^{3+}$ (en=ethylenediamine) and *d*-tartrate ions. The increase in the optical absorbancy of $[\mathrm{Co\ en_3}]^{3+}$ in the charge transfer absorption region is not the same for *d*-, *l*- and *dl*-$[\mathrm{Co\ en_3}]^{3+}$. The association constants of *d*-$[\mathrm{Co\ en_3}]^{3+}\cdot$*d*-tartrate^{2-} and *l*-$[\mathrm{Co\ en_3}]^{3+}\cdot$*d*-tartrate^{2-} were found, by an analysis of the increase in the optical absorbancy, to be 26 and 21 respectively at $\mu=0.1$ at 25°C.

It is known that such properties as the rate of chemical reactions and diffusion of an optically active complex are not the same as those of the other antipode when another optically active compound is present in the solution.1) However, no quantitative analysis of the difference has yet been made.

Such a difference is considered to be due to association; the 1 : 1 association, for example, is expressed as

$$d\text{-}\mathrm{M}^{m+}+d\text{-}\mathrm{X}^{x-}(\text{or } l\text{-}\mathrm{X}^{x-}) \rightleftarrows d\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}(\text{or } d\text{-}\mathrm{M}^{m+}\cdot l\text{-}\mathrm{X}^{x-}) \qquad (1)$$

$$l\text{-}\mathrm{M}^{m+}+d\text{-}\mathrm{X}^{x-}(\text{or } l\text{-}\mathrm{X}^{x-}) \rightleftarrows l\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}(\text{or } l\text{-}\mathrm{M}^{m+}\cdot l\text{-}\mathrm{X}^{x-}) \qquad (2)$$

The difference accompanying association consists of two effects: a) the association constant of $d\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}$ is not necessarily the same as that of $l\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}$, and b) the molar contribution of $d\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}$ to the measured quantity is different from that of $l\text{-}\mathrm{M}^{m+}\cdot d\text{-}\mathrm{X}^{x-}$. These two effects can be distinguished only when the association constants are known, though no kind of association constant of an ion pair involving two optically active ions has yet been reported.

This paper will show that the association constant between *d*-$[\mathrm{Co\ en_3}]^{3+}$ (en=ethylenediamine) and *d*-tartrate ions differs from that between *l*-$[\mathrm{Co\ en_3}]^{3+}$ and *d*-tartrate ions.[*2] Further, a mathematical treatment will be made of the equilibrium which exists in solutions containing both antipodes of an optically active compound (racemate) and another optically active compound. The results will then be applied to the system of $[\mathrm{Co\ en_3}]^{3+}$ and *d*-tartrate ions.

Experimental

Racemic tris(ethylenediamine)cobalt(III) chloride2) and *d*- and *l*-tris(ethylenediamine)cobalt(III) iodide3)

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1) For example, N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954); V. Carassiti, *J. Inorg. Nucl. Chem.*, **8**, 227 (1958).

[*2] Notations *d*- and *l*- refer to the sign of the optical rotation at 589.3 mμ (sodium D-line).

2) J. B. Work, "Inorganic Syntheses," Vol. II, McGraw-Hill, New York (1946), p. 221.

3) J. A. Broomhead, F. P. Dwyer and J. W. Hogarth, *ibid.*, Vol. VI (1960), p. 183.

were prepared by the procedures given in the literature. These compound were then converted into the corresponding perchlorate by passing them through a column of anion exchange resin (Dowex 2, X-8) in the hydroxide form in the case of racemic chloride and one in the perchlorate form in the case of the optically active iodide, after which perchloric acid was added. The optical rotatory dispersion curve and the circular dichroism spectrum of d-[Co en$_3$](ClO$_4$)$_3$ were completely enantiomeric with those of l-[Co en$_3$](ClO$_4$)$_3$.

The electronic absorption spectra were measured with a Shimadzu QV-50 spectrophotometer at 25°C, in solutions containing 1.25 mM [Co en$_3$](ClO$_4$)$_3$, various amounts of sodium d-tartrate, sodium perchlorate to adjust the ionic strength to 0.1, and sodium hydroxide to adjust the pH to 8.

Consideration of the Equilibrium

Consider the association*3:

$$\mathrm{M}^{m+} + j\mathrm{X}^{x-} \rightleftarrows \mathrm{MX}_j^{(m-jx)+} \quad (j = 1,\ 2, \cdots,\ n) \tag{3}$$

where M^{m+} is either a free (hydrated) metal ion or a complex ion. The association constants are given by

$$K_j = [\mathrm{MX}_j]/([\mathrm{MX}_{j-1}][\mathrm{X}]) \tag{4}$$

$$\beta_j = [\mathrm{MX}_j]/([\mathrm{M}][\mathrm{X}]^j) \tag{5}$$

Association constants, especially outer-sphere association constants, are often determined by the measurement of such quantities as optical absorbancy, optical rotation, reaction rate, *etc.*, quantities which depend on the concentrations of several species in the solution, as in Eq. (6):

$$\Theta' = \theta_0[\mathrm{M}] + \sum_{j=1}^{n}\theta_j[\mathrm{MX}_j] + \theta_{\mathrm{X}}[\mathrm{X}] \tag{6}$$

where Θ' may be the optical absorbancy, the electrical conductivity, *etc.* For the Θ' of the optical absorbancy per unit of cell length, for example, θ_0, θ_j and θ_{X} are the molar extinction coefficients of M^{m+}, $\mathrm{MX}_j^{(m-jx)+}$ and X^{x-} respectively while for the Θ of circular dichroism per unit of cell length, the θ's indicate the molar circular dichroism. Provided that the value of $\theta_{\mathrm{X}}[\mathrm{X}]$ can be neglected or can be corrected for, the quantity given by Eq. (7) can be obtained experimentally.

$$\Theta = \theta_0[\mathrm{M}] + \sum_{j=1}^{n} \theta_j[\mathrm{MX}_j] \tag{7}$$

By introducing the definitions

$$\theta = \Theta/[\mathrm{M}]_t \tag{8}$$

$$[\mathrm{M}]_t = [\mathrm{M}] + \sum_{j=1}^{n} [\mathrm{MX}_j] \tag{9}$$

$$\Delta = \theta - \theta_0 \tag{10}$$

$$\Delta_j = \theta_j - \theta_0 \tag{11}$$

Eq. (12) is derived:

$$\Delta = \left(\sum_{j=1}^{n} \theta_j\beta_j[\mathrm{X}]^j\right)/\left(1 + \sum_{j=1}^{n} \beta_j[\mathrm{X}]^j\right) \tag{12}$$

In case only the 1 : 1 association takes place to a measurable extent, *i. e.*, when $n=1$,*4 Eq. (12) can be rearranged as

$$\frac{[\mathrm{X}]}{\Delta} = \frac{1}{K_1\Delta_1} + \frac{1}{\Delta_1}[\mathrm{X}] \tag{13}$$

Equation (13) shows that a plot of its left-hand side against [X] gives a straight line. The reciprocal slope of the straight line is equal to Δ_1, and the ratio of the slope to the intercept, to K_1, the association constant. By the use of an equation similar to Eq. (13), the association constants of sulfate and several complex ions were determined from the polarographic diffusion current.[4]

When both M^{m+} and X^{x-} have structures nonsuperimposable on their own mirror images, the associations given by Eqs. (1) and (2) can have different association constants:

$$\left.\begin{aligned} K_{dd} &= [d\text{-M}\cdot d\text{-X}]/([d\text{-M}][d\text{-X}]) \\ K_{ld} &= [l\text{-M}\cdot d\text{-X}]/([l\text{-M}][d\text{-X}]) \end{aligned}\right\} \tag{14}$$

It follows, from the viewpoint of symmetry, that

$$K_{dd} = K_{ll};\ K_{ld} = K_{dl} \tag{15}$$

The intensity factors in Eq. (7), θ's for d-M^{m+}, l-M^{m+}, d-$\mathrm{M}^{m+}\cdot d$-X^{x-} and l-$\mathrm{M}^{m+}\cdot d$-X^{x-} are denoted by θ_d, θ_l, θ_{dd} and θ_{ld} respectively, while Δ's are defined much as in Eq. (11):

$$\Delta_{dd} = \theta_{dd} - \theta_d;\ \Delta_{ld} = \theta_{ld} - \theta_l \tag{16}$$

The values of K_{dd} (or K_{ld}) and Δ_{dd} (or Δ_{ld}) can be obtained by the use of Eq. (13) from the Δ values obtained in solutions containing d-M^{m+} (or l-M^{m+}) and d-X^{x-} unless they racemize rapidly.

When a racemic salt of M^{m+}, which does not change the configuration rapidly, is added to the solution, the total concentrations of the two antipodes are equal; hence,

$$[\mathrm{M}]_t = 2[d\text{-M}]_t = 2[l\text{-M}]_t \tag{17}$$

and Θ is given by

$$\begin{aligned} \Theta = {} & \theta_d[d\text{-M}] + \theta_l[l\text{-M}] \\ & + \theta_{dd}[d\text{-M}\cdot d\text{-X}] + \theta_{ld}[l\text{-M}\cdot d\text{-X}] \end{aligned} \tag{18}$$

For such a quantity (Θ) as optical absorbancy, reaction rate, *etc.*,

$$\theta_d = \theta_l = \theta_0 \tag{19}$$

From Eqs. (8), (10), (14), and (16) to (19), the following equation is derived:

$$\frac{[d\text{-X}]}{\Delta} = a[d\text{-X}] + b - \frac{g}{[d\text{-X}]+f} \tag{20}$$

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*3 The word "association" includes both outer-sphere association and inner-sphere association.

*4 Cases involving the association of $n \geq 2$ will be discussed elsewhere.

[4] N. Tanaka, K. Ogino and G. Satô, This Bulletin, **39**, 366 (1966).

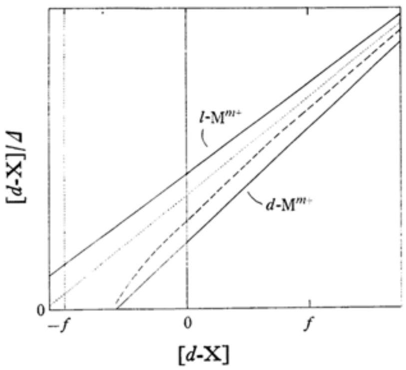


Fig. 1. Relationship between the straight lines of Eq. (13) for two optically active antipodes (——) and the curve of Eq. 20 for the racemate (- - - -). Dotted lines are asymptotes of the curve of Eq. (20). Here, it is assumed that $K_{dd}=2.5\ K_{ld}$ and $\Delta_{dd}=0.8\ \Delta_{ld}$.

where

$$\left.\begin{aligned} a &= 2/(\Delta_{dd}+\Delta_{ld}) \\ b &= \frac{2(K_{dd}\Delta_{ld}+K_{ld}\Delta_{dd})}{(\Delta_{dd}+\Delta_{ld})^2K_{dd}K_{ld}} \\ f &= \frac{K_{dd}\Delta_{dd}+K_{ld}\Delta_{ld}}{(\Delta_{dd}+\Delta_{ld})K_{dd}K_{ld}} \\ g &= \frac{2(K_{dd}-K_{ld})^2\Delta_{dd}\Delta_{ld}}{(\Delta_{dd}+\Delta_{ld})^3(K_{dd}K_{ld})^2} \end{aligned}\right\} \tag{21}$$

Figure 1 shows the schematic relationship between the curve of $[d\text{-X}]/\Delta$ *vs.* $[d\text{-X}]$ given by Eq. (20) and the straight lines given by Eq. (13) for solutions containing $d\text{-X}^{x-}$ and either of the antipodes of M^{m+}. The plot of Eq. (20) does not yield a straight line unless $K_{dd}=K_{ld}$; it yields a hyperbolic curve which lies between the two straight lines of $[d\text{-X}]/\Delta$ *vs.* $[d\text{-X}]$ for the *d*- and *l*-antipodes of M^{m+}.

The curve of Eq. (20) can be approximated as a straight line when its curvature is very small. An apparent association constant, K_{app}, can be obtained as the ratio of the slope to the intercept of the quasi-straight line. In case $af \gg g$,

$$K_{app} = \frac{K_{dd}\Delta_{dd}+K_{ld}\Delta_{ld}}{\Delta_{dd}+\Delta_{ld}} \tag{22}$$

while when $[d\text{-X}]$ is so great that the third term of Eq. (20) can be neglected,

$$\frac{1}{K_{app}} = \frac{(\Delta_{dd}/K_{dd})+(\Delta_{ld}/K_{ld})}{\Delta_{dd}+\Delta_{ld}} \tag{23}$$

and when $[d\text{-X}] \ll f$,

$$K_{app} = \frac{K_{dd}{}^2\Delta_{dd}+K_{ld}{}^2\Delta_{ld}}{K_{dd}\Delta_{dd}+K_{ld}\Delta_{ld}} \tag{24}$$

Equations (22) to (24) show that K_{app} is not a simple average of K_{dd} and K_{ld}, but that it depends on the relative magnitude of Δ_{dd} and Δ_{ld}.

For such a quantity of θ as optical rotation and circular dichroism, the signs of θ_d and θ_l are reversed:

$$\theta_d = -\theta_l \tag{25}$$

and, instead of Eq. (20), the following equation is obtained:

$$\frac{[d\text{-X}]}{\theta} = a[d\text{-X}] + b - \frac{g}{[d\text{-X}]+f} \tag{26}$$

where a, b, f and g are also given by Eq. (21) unless $\Delta_{dd}+\Delta_{ld}=0$. In case $\Delta_{dd}+\Delta_{ld}=0$,

$$\frac{[d\text{-X}]}{\theta} = \frac{1}{(K_{dd}-K_{ld})\Delta_{dd}}(K_{dd}[d\text{-X}]+1)(K_{ld}[d\text{-X}]+1) \tag{27}$$

Equations (26) and (27) indicate that a solution of a racemic compound may show optical rotation or circular dichrosim in the presence of another optically active compound*5 when $K_{dd} \neq K_{ld}$ and/or $\Delta_{dd}+\Delta_{ld} \neq 0$*6.

Results and Discussion

The addition of sodium *d*-tartrate to a solution of $[\text{Co en}_3](\text{ClO}_4)_3$ did not affect the spectrum in the *d-d* absorption region. However, in the charge transfer absorption region, the absorbancy increased in the presence of sodium *d*-tartrate. The increase was a little larger for $d\text{-[Co en}_3]^{3+}$ than for $l\text{-[Co-en}_3]^{3+}$, while that for the racemate was between those for the two optical antipodes, as is shown in Table 1. The solutions were prepared within

TABLE 1. VARIATION OF THE APPARENT EXTINCTION COEFFICIENT OF $[\text{Co en}_3]^{3+}$ AT 265mμ BY THE ADDITION OF SODIUM *d*-TARTRATE
$\mu=0.1(\text{NaClO}_4)$, 25°C

$[d\text{-tartrate}]_t$* M	Δ		
	$d\text{-[Co-en}_3]^{3+}$	$l\text{-[Co-en}_3]^{3+}$	$dl\text{-[Co-en}_3]^{3+}$
0.005	$36._8$	$33._6$	$36._3$
0.0075	$54._0$	$48._8$	$52._5$
0.010	$69._2$	$62._0$	$64._6$
0.0125	$80._8$	$74._1$	$79._9$
0.015	$94._3$	$86._2$	$89._0$
0.0175	$104._8$	$98._8$	$101._4$
0.020	$114._0$	$109._3$	$111._9$
0.0225	$125._0$	$117._4$	$121._2$
0.025	—	—	$129._3$

* $[d\text{-tartrate}]_t$ is the added concentration of sodium *d*-tartrate.

[*5] The contribution of $d\text{-X}^{x-}$ to the optical rotation or circular dichroism is not included in Θ, as has been postulated in the beginning of this section.

[*6] This phenomenon is not the so-called "Pfeiffer effect," since the absolute configuration of M^{m+} and X^{x-} is not assumed to change rapidly.

one day, and their absorbancies at a given wavelength were measured on the next day. The measured absorbancy was reproducible to 1% or less. The absorbancies of solutions of enantiomers with the same composition were measured alternately in order to avoid systematic errors. The differences in Δ's for *d*-, *l*- and *dl*-[Co en$_3$]$^{3+}$ were small, but were always observed unambiguously. Hence, they can be regarded as significant.

The values of [*d*-tartrate]/Δ were calculated; they are plotted against [*d*-tartrate] in Fig. 2. The concentration of unassociated *d*-tartrate ions, [*d*-tartrate], was calculated by successive approximation. From slopes and intercepts of the straight lines for *d*- and *l*-[Co en$_3$]$^{3+}$, the values of K_{dd}, K_{ld}, Δ_{dd} and Δ_{ld} were found to be as given in Table 2. By substituting these values into Eq. (20), the theoretical curve of [*d*-tartrate]/Δ *vs.* [*d*-tartrate] for *dl*-[Co en$_3$]$^{3+}$ was obtained; it is reproduced in Fig. 2 by a broken line. The open circecles indicate experimental values for *dl*-[Co en$_3$]$^{3+}$; these values are in good agreement with the theoretical curve.

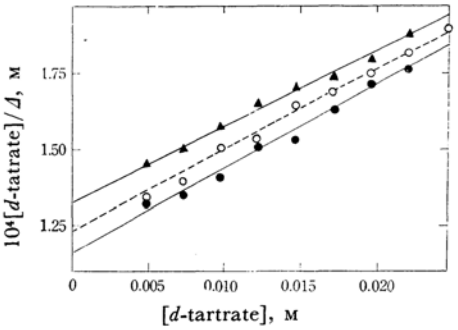
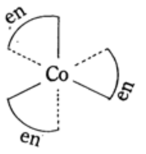


Fig. 2. Plots of [*d*-tartrate]/Δ *vs.* [*d*-tartrate] for *d*-[Co en$_3$]$^{3+}$ (-●-), *l*-[Co en$_3$]$^{3+}$ (-▲-) and *dl*-[Co en$_3$]$^{3+}$ (○) at 265mμ.

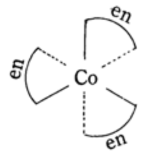
TABLE 2. VALUES OF K_{dd}, K_{ld}, Δ_{dd} AND Δ_{ld} FOR THE ASSOCIATION OF [Co en$_3$]$^{3+}$ AND *d*-TARTRATE IONS μ=0.1, 25°C

Wavelength mμ	θ_0	Δ_{dd}	Δ_{ld}	K_{dd}	K_{ld}
265	158	358	397	24	19
262	268	430	460	27	22

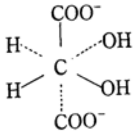
The association constants of ion pairs involving [Co en$_3$]$^{3+}$ are collected in Table 3. The association constants between [Co en$_3$]$^{3+}$ and *d*-tartrate ions are about one-half of that between [Co en$_3$]$^{3+}$ and sulfate ions at ionic strength 0.1 at 25°C. A comparison of the association constants of [Co-en$_3$]$^{3+}$·*d*-tartrate^{2-} and those in Table 3 suggest that two carboxyl groups in a tartrate ion take part simultaneously in the association. Structures I, II, and III show the absolute configurations of *d*-[Co en$_3$]$^{3+}$ ⁷⁾, *l*-[Co en$_3$]$^{3+}$, and *d*-tartrate ions respectively.



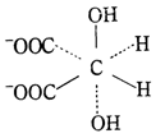
I



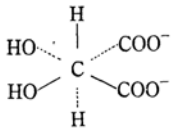
II



IIIa



IIIb



IIIc

For a *d*-tartrate ion, three conformations are possible, as is shown by Structures IIIa to IIIc. The two carboxyl groups are *trans* in Structure IIIa and *gauche* in Structures IIIb and IIIc. In Structure IIIb, the $^-$OOC–C–C–COO$^-$ bonds are arranged as a right-handed screw form, while in Structure IIIc they are arranged as a left-handed screw form. The association constant of *d*-[Co en$_3$]$^{3+}$·*d*-tartrate^{2-} is larger than that of *l*-[Co en$_3$]$^{3+}$·*d*-tartrate^{2-} by about 20%, as Table 2 shows. From a consideration with the aid of appropriate molecular models, it may tentatively be supposed that the difference in K_{dd} and K_{ld} is related to the relative configuration of the $^-$OOC–C–C–COO$^-$ screw and [Co en$_3$]$^{3+}$, and to the relative stability of the two *gauche* forms, IIIb and IIIC.

The authors wish to thank Professor Kazuo Saito and Dr. Junnosuke Fujita for their useful discussions.

TABLE 3. ASSOCIATION CONSTANTS OF ION-PAIRS INVOLVING [Co en$_3$]$^{3+}$ AT 25°C

X^{x-}	*K*	Ionic strength	Method	Investigator
SO$_4$$^{2-}$	4.9 ×10	0.1(NaClO$_4$)	Spectrophotometry	Ogino⁵⁾
SO$_4$$^{2-}$	2.82×10³	→0	Conductivity	Jenkins and Monk⁶⁾
Cl$^-$	5.3 ×10	→0	Conductivity	Jenkins and Monk⁶⁾

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5) K. Ogino, unpublished.

6) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

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