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Conductivity and Ion Association of Some Diastereoisomeric Salts in Water. II. Ion Association between the $\Delta(-)_{589}$- or $\Lambda(+)_{589}$-*cis*-Bis(ethylenediamine)dinitrocobalt(III) Ion and the $\Delta(+)_{589}$-(Ethylenediamine)bis(malonato)cobaltate(III) Ion and Its Temperature Dependence

Haruhiko Yokoyama* and Michio Nishimura
Department of Chemistry, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236

(Received October 6, 1984)

The electric conductivities of aqueous solutions of the diastereoisomeric salts, $\Delta(-)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{589}$-[Co$(mal)_2(en)$] and $\Lambda(+)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{589}$-[Co$(mal)_2(en)$](en=ethylenediamine and mal=malonate ion), have been measured at several temperatures from 15 to 35 °C. From the analysis of the conductivity data using the Pitts equation, it was found that the Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2]^+$ and Δ-[Co$(mal)_2(en)]^-$ ions are appreciably associated in spite of the large monovalent ions and that the ion association is almost nonstereoselective and is endothermic in contrast to the exothermic ion association between Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2]^+$ and Δ-[Co(edta)$]^-$ (edta=ethylenediaminetetraacetate ion). By considering the obtained values of thermodynamic parameters of ion association and the significantly large Stokes radius of Δ-[Co$(mal)_2(en)]^-$ compared to the effective radius estimated from its partial molar volume, this complex anion was presumed to have two hydration water molecules and to release one of them by associating with the complex cations. Possible short-range interactions between the complex ions were also discussed by considering the structures of the complex ions and the chemical properties of the ligands.

In a previous conductivity study[1)] of the diastereoisomeric salts, $\Delta(-)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{546}$-[Co(edta)] and $\Lambda(+)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{546}$-[Co(edta)], we have found that the Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2]^+$ and Δ-[Co(edta)$]^-$ ions are appreciably associated in water in spite of being large and monovalent. The ion association, though not stereoselective, was an exothermic reaction entirely unable to be explained by the usual electrostatic theories of ion association,[2—4)] suggesting the presence of short-range interactions which are operative on the surface of the complex ions and which are almost independent of the dielectric constant of the medium. Such interactions are considered to be of interest in connection with the problem of the stereoselectivity in the ion association of optically active complex ions, and of importance for the elucidation of the ion–ion and ion–solvent interactions in solutions containing complex ions and also for that of the mechanisms of various reactions of dissolved complex ions involving ion-pair formation in the reaction process.

In the present study, in order to accumulate information about the short-range interactions and make this nature clearer, the electric conductivities of aqueous solutions of the diastereoisomeric salts, $\Delta(-)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{589}$-[Co$(mal)_2(en)$] and $\Lambda(+)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{589}$-[Co$(mal)_2(en)$], were measured at several temperatures from 15 to 35 °C and the ion association between Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2]^+$ and Δ-[Co$(mal)_2(en)]^-$ was examined. The reasons for the use of these diastereoisomeric salts are as given below.

We can expect to obtain exact thermodynamic information about the short-range interactions, if present, between the complex ions, because such a system containing only monovalent complex ions of large size can be treated almost without considering the Bjerrum-type ion association[2—4)] and the usual Born-type hydration[5a)] of ions. The absolute configuration and structure of $\Delta(-)_{589}$-*cis*-[Co$(NO_2)_2(en)_2$]$\Delta(+)_{589}$-[Co$(mal)_2$-(en)], less soluble in water than the other diastereoisomeric salt, have been determined by an X-ray diffraction study.[6)] This can help the stereochemical consideration of the ion pairs formed. Further, it is of interest what differences are present between the ion associations of Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2]^+$ with Δ-[Co$(mal)_2(en)]^-$ and Δ-[Co(edta)$]^-$, since the Δ-[Co$(mal)_2(en)]^-$ ion is similar to Δ-[Co(edta)$]^-$ in having four carboxyl groups and two coordinated nitrogen atoms.

Experimental

Materials. Δ- *and* Λ-cis-*[Co$(NO_2)_2(en)_2$]X(X=Br and I)*: These salts were prepared in the manner described previously.[1)] The $[\alpha]_{589}$ values of Δ- and Λ-*cis*-[Co$(NO_2)_2(en)_2$]Br were −44°±1° and +44°±1° respectively, while those of the iodides of Δ- and Λ-complexes were −38°±1° and +39° ±1° respectively.

KΔ-[Co$(mal)_2(en)$]·$2H_2O$: This salt was prepared following the method of Dwyer *et al.*[7)] The recrystallization was effected from water by the addition of ethanol and repeated until a constant value of the optical rotation was reached. After air-drying at room temperature, the $[\alpha]_{589}$ and $[\alpha]_{546}$ values of the salt were +1530°±30° and +1260°±30° respectively.

Δ-cis-*[Co$(NO_2)_2(en)_2$]Δ-[Co$(mal)_2(en)$] and* Λ-cis-*[Co$(NO_2)_2$-$(en)_2$]Δ-[Co$(mal)_2(en)$]*: These diastereoisomeric salts were prepared as follows. The Δ- or Λ-*cis*-[Co$(NO_2)_2(en)_2$]I salt was transformed to the acetate by shaking silver acetate in warm water (*ca.* 40 °C). After the removal of the silver iodide, an equimolar amount of KΔ-[Co$(mal)_2(en)$]·$2H_2O$ was dissolved in the filtrate and ethanol was added to precipitate the diastereoisomeric salt. The recrystallization was carried out several times from water by the addition of ethanol. After air-drying, both salts were ascertained to be anhydrous by the use of an Abderhalden dryer and by the Kahl-Fischer method. The $[\alpha]_{589}$ and $[\alpha]_{546}$ values of Δ-*cis*-[Co-

$(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ were +1010°±20° and +780° ±20° respectively. The $[\alpha]_{589}$ and $[\alpha]_{546}$ values of Λ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ were +1060°±20° and +900° ±20° respectively.

ORD and Electronic Absorption Spectra of Diastereoisomeric Salts in Dilute Aqueous Solution. Measurements of the ORD and the absorption spectra were carried out with a JASCO ORD/UV-5 spectropolarimeter and a Hitachi 139 spectrophotometer. The molar rotation of Δ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ in water was identical with the sum of those of Δ-*cis*-$[Co(NO_2)_2(en)_2]Br$ and $K\Delta$-$[Co(mal)_2(en)]$ at any wavelength from about 370 to 700 nm, within the limits of experimental error. A similar additivity was observed for Λ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$. The absorption spectra of both diastereoisomeric salts in the same wavelength region as above agreed with each other and with the sum of those of *cis*-$[Co(NO_2)_2(en)_2]Br$ and $K[Co(mal)_2(en)]$, within the limits of experimental error.

Conductivity Measurements. Conductivity measurements were made at 15.0, 20.0, 25.0, 30.0, and 35.0 °C using a Fuso 360 linear-bridge conductometer in the manner described previously.[1)] The cell constant of the cell used in the present study was $0.11400\,cm^{-1}$.

The observed conductivity data were corrected for the conductivity of water, lower than $2.1\times10^{-7}\,S\,cm^{-1}$ at 25 °C, and for the minor conductivity change due to the aquation of *cis*-$[Co(NO_2)_2(en)_2]^+$.[8)] Each solution was completely measured within about 3.5 h after the preparation of the solution. Throughout the measurements, the solution was protected from light. The reproducibility of the conductivity measurements was about ±0.1%. The precision of the temperature measurements was ±0.003 °C.

Densities and Concentrations of Solutions. The solutions used for the conductivity measurements were made up by weight. The concentration, c, at each temperature was calculated from the molality, m, by the use of the density data. The densities, d, at (25.00±0.02) °C were measured for all solutions by using an Ostwald-type pycnometer with capacity of $50\,cm^3$. Approximately linear relationships were found between m and d (25 °C):

for Δ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$,

$$d(25°\,C)/g\,cm^{-3} = (0.99703\pm0.00002) + (0.284\pm0.003)m, \tag{1}$$

and for Λ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$,

$$d(25°\,C)/g\,cm^{-3} = (0.99704\pm0.00002) + (0.283\pm0.003)m. \tag{2}$$

The densities at the other temperature, t, were measured only for the most concentrated solution. The observed $d(t)$ values agreed, within the limits of experimental error, with those calculated by assuming:

$$d(t)/g\,cm^{-3} = d(H_2O,\,t) + pm, \tag{3}$$

where $d(H_2O,\,t)$ is the density of water and where p is identical with the coefficient of m given in Eq. 1 or 2. The $d(t)$ values of the other solutions were estimated by using Eq. 3.

The concentrations of solutions at the temperature, t, could be reproduced within the limits of experimental error by the use of the following equation:

$$c(t) = c(25°\,C) \times f, \tag{4}$$

where $c(t)$ and $c(25\,°C)$ are concentrations at t and 25 °C respectively and where f is equal to the ratio of $d(H_2O,\,t)/d(H_2O,\,25\,°C)$: f=1.00206, 1.00116, 0.99860, and 0.99698 for t=15, 20, 30, and 35 °C respectively.[9)]

Results and Discussion

Molar Conductivities of Diastereoisomeric Salts. The observed values of the molar conductivity, Λ(obsd), are summarized in Tables 1 and 2 and are plotted against $\sqrt{c}$ for each salt in Fig. 1. No appreciable difference in the plot is found between the two diastereoisomeric salts at any temperature. This relation is similar to that found between Δ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(edta)]$ and Λ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(edta)]$.[1)]

Analysis of Conductivity Data. The conductivity data were analyzed by assuming an ion association between Δ- or Λ- *cis*-$[Co(NO_2)_2(en)_2]^+$ and Δ-$[Co(mal)_2(en)]^-$. The analysis was made in terms of the Pitts conductivity equation,[10)] modified by considering the obstruction effect in the manner described previously.[1,11)]

The ion-association constant, K, and the limiting molar conductivity, Λ^∞, were calculated by the least-squares procedure minimizing $\sum[\Lambda(\text{obsd})-\Lambda(\text{calcd})]^2$. The values of the closest distance of approach of the ions, a, involved in the theoretical equations of conductivity and activity coefficient were estimated by considering the effective ionic radii of the dissolved complex ions to be reported in the following section.

Effective Ionic Radii of Complex Ions. The partial molar volume of a salt at an infinite dilution, V^∞(salt), can be estimated to be $176\pm2\,cm^3\,mol^{-1}$ for $K[Co(mal)_2(en)]$ according to the conventional manner[12)] from $d\,(0.008745\,mol\,dm^{-3},\,25\,°C)=0.99868\,g\,cm^{-3}$. The partial molar volume, V^∞(ion), for $[Co(mal)_2(en)]^-$ is, therefore, evaluated to be $172\pm2\,cm^3\,mol^{-1}$, taking $V^\infty(K^+,\,25\,°C)=3.6\,cm^3\,mol^{-1}$.[12,13)] By substituting the obtained value for V^∞(ion) into Glueckauf's expression of the partial molar volume of an ion,[1,12,14)] the ionic radius, r, corresponding to the crystallographic radius, can be estimated to be 3.5_9 Å for $[Co(mal)_2(en)]^-$ on the assumption that the shape of the complex ion is spherical.

The Λ^∞ values of Δ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ and Λ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ at 25 °C were determined to be 50.52±0.04 and 50.55±0.02 $S\,cm^2mol^{-1}$ respectively, from an analysis assuming that a=7.0 Å. Both values of Λ^∞, in accord with each other within the limits of experimental error, were almost independent of the assumed value of a. The limiting molar conductivity, Λ^∞(ion), for $[Co(mal)_2(en)]^-$ can be calculated to be $23.7\pm0.1\,S\,cm^2\,mol^{-1}$ by using $\Lambda^\infty(\text{ion})=26.8\pm0.1\,S\,cm^2mol^{-1}$ for *cis*-$[Co(NO_2)_2(en)_2]^+$.[1)] The Stokes radius, r_s, is thus obtained to be 3.8_9 Å for $[Co(mal)_2(en)]^-$.

The values of r and r_s for *cis*-$[Co(NO_2)_2(en)_2]^+$ and $[Co(edta)]^-$ were as follows: $r=3.3_7$ Å and $r_s=3.4_4$ Å for the former ion and $r=3.6_3$ Å and $r_s=3.5_2$ Å for the latter

TABLE 1. MOLAR CONDUCTIVITIES OF Δ-*cis*-[$Co(NO_2)_2(en)_2$]Δ-[$Co(mal)_2(en)$] IN WATER

c(25 °C)[a]	Λ(obsd)/S cm^2 mol^{-1}				
10^{-3} mol dm^{-3}	at 15 °C	at 20 °C	at 25 °C	at 30 °C	at 35 °C
0.9929	37.72	42.85	48.19	53.67	59.35
1.5072	37.37	42.40	47.63	53.07	58.65
2.0019	36.93	41.91	47.11	52.51	58.04
2.4931	36.64	41.58	46.73	52.08	57.56
2.9687	36.43	41.34	46.46	51.75	57.22
3.9217	35.94	40.78	45.78	51.03	56.40
5.0278	35.46	40.25	45.18	50.32	55.61
6.4901	34.92	39.61	44.48	49.52	54.74
8.0476	34.35	38.97	43.71	48.71	53.79
9.9821	33.77	38.30	43.01	47.84	52.85

a) Concentrations at the other temperatures can be obtained by using Eq. 4.

TABLE 2. MOLAR CONDUCTIVITIES OF Λ-*cis*-[$Co(NO_2)_2(en)_2$]Δ-[$Co(mal)_2(en)$] IN WATER

c(25 °C)[a]	Λ(obsd)/S cm^2 mol^{-1}				
10^{-3} mol dm^{-3}	at 15 °C	at 20 °C	at 25 °C	at 30 °C	at 35 °C
1.4976	37.38	42.43	47.66	53.11	58.68
2.0156	37.01	41.98	47.19	52.54	58.07
2.4942	36.74	41.66	46.81	52.14	57.64
2.9824	36.40	41.30	46.42	51.68	57.11
3.9840	35.91	40.75	45.80	50.98	56.35
4.9958	35.46	40.22	45.18	50.30	55.59
6.4758	34.91	39.59	44.46	49.52	54.72
7.9951	34.40	39.01	43.81	48.76	53.86
9.9628	33.80	38.33	43.05	47.88	52.86

a) Concentrations at the other temperatures can be obtained by using Eq. 4.

ion.[1] It is obvious that the r and r_s values are close to each other for these complex ions. On the other hand, a significant difference is found between the r and r_s values for [$Co(mal)_2(en)$]$^-$. Considering the closeness between the r values of [$Co(mal)_2(en)$]$^-$ and [$Co(edta)$]$^-$, the r_s value of the former complex ion seems to be significantly large. This may imply that the [$Co(mal)_2(en)$]$^-$ ion is hydrated. That is, the Stokes radius of [$Co(mal)_2(en)$]$^-$ can be well explained by assuming that this complex ion has two hydration water molecules, because an r value of 3.8_5 Å close to that of 3.8_9 Å for r_s, can be obtained for the hydrated complex ion from its partial molar volume, $\overline{V}^\infty$([$Co(mal)_2(en)$]$^-\cdot 2H_2O$)=208±2 cm^3 mol^{-1}, where the molar volume of the hydration water molecule was assumed to be 18.1 cm^3 mol^{-1}, equal to the partial molar volume of water.[9] Further discussion about the hydration of [$Co(mal)_2(en)$]$^-$ will be made later.[15]

In a previous study,[1] the value of a between *cis*-[$Co(NO_2)_2(en)_2$]$^+$ and [$Co(edta)$]$^-$ was taken to be 7.0 Å, equal to the sum of the r or r_s values of the complex ions. The sums of the ionic radii of *cis*-[$Co(NO_2)_2(en)_2$]$^+$ and [$Co(mal)_2(en)$]$^-$ become 7.0 Å with r and 7.3 Å with r_s. The results obtained by assuming both a=7.0 Å and a=7.3 Å will be discussed below.

Ion Association. In Table 3, the ion-association constants (K) and the limiting molar conductivities (Λ^∞) obtained by assuming a=7.0 and 7.3 Å are summarized, together with the standard deviations, σ.[16] The values of Λ^∞ are almost the same between a=7.0 and 7.3 Å at a given temperature, while those of K are

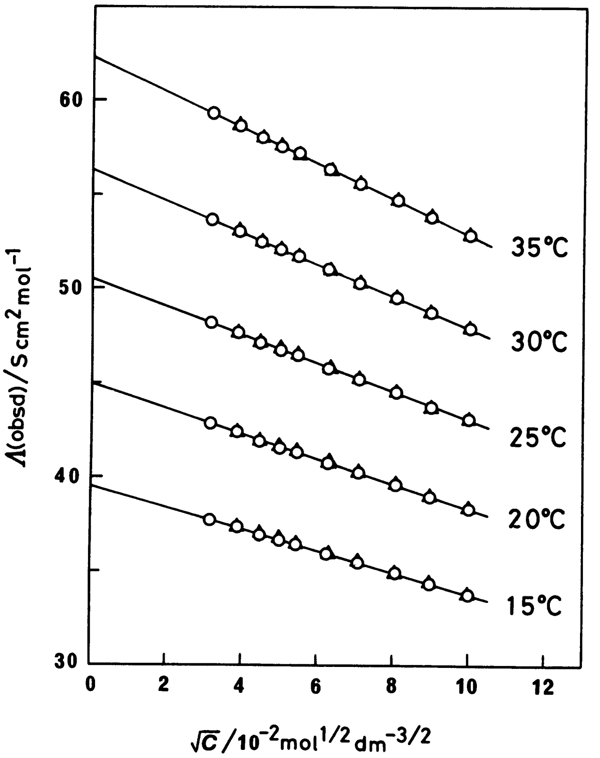

Fig. 1. Plot of Λ(obsd) against $\sqrt{c}$.
○: Δ-*cis*-[$Co(NO_2)_2(en)_2$] Δ-[$Co(mal)_2(en)$], △: Λ-*cis*-[$Co(NO_2)_2(en)_2$] Δ-[$Co(mal)_2(en)$].
Solid lines are theoretical curves reproduced with the Λ^∞ and K values given in Table 3; the curves at a given temperature are close and overlapped to each other between the two diastereoisomeric salts and between a=7.0 and 7.3 Å.

TABLE 3. Λ^∞ AND K VALUES OBTAINED FOR THE DIASTEREOISOMERIC SALTS BY ASSUMING a=7.0 AND 7.3 Å WITH THE PITTS EQUATION

Temp	a=7.0 Å			a=7.3 Å		
	Λ^∞	K	σ	Λ^∞	K	σ
°C	S cm^2 mol^{-1}	dm^3 mol^{-1}	S cm^2 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	S cm^2 mol^{-1}
			Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)]			
15	39.55±0.04	5.4±0.6	0.0332	39.55±0.04	5.5±0.6	0.0331
20	44.92±0.04	5.5±0.4	0.0326	44.92±0.04	5.6±0.4	0.0325
25	50.52±0.04	5.8±0.4	0.0351	50.51±0.04	5.9±0.4	0.0351
30	56.31±0.03	5.9±0.3	0.0274	56.31±0.03	6.0±0.3	0.0271
35	62.27±0.05	6.0±0.3	0.0404	62.27±0.04	6.1±0.3	0.0401
			Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)]			
15	39.62±0.02	5.6±0.2	0.0204	39.62±0.02	5.7±0.2	0.0206
20	44.97±0.02	5.7±0.2	0.0200	44.96±0.02	5.8±0.2	0.0202
25	50.55±0.02	5.8±0.2	0.0206	50.55±0.02	5.9±0.2	0.0208
30	56.33±0.03	6.0±0.2	0.0254	56.33±0.03	6.1±0.2	0.0256
35	62.30±0.03	6.1±0.2	0.0279	62.30±0.03	6.2±0.2	0.0279

TABLE 4. THERMODYNAMIC PARAMETERS OF ION ASSOCIATION, $\Delta G°$, $\Delta H°$, AND $\Delta S°$, AT 25 °C OBTAINED BY ASSUMING a=7.0 Å WITH THE PITTS EQUATION

Salt	$\Delta G°$	$\Delta H°$	$\Delta S°$
	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)]	−4.35±0.15	4.0±1.0	28±4
Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)]	−4.36±0.07	3.2±0.7	25±3
Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)]	−6.13±0.13[a]	−5.7±0.3[a]	1.4±1.4[a]
Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)]	−6.17±0.12[a]	−5.3±0.7[a]	3.0±2.8[a]

a) Cited from Ref. 1.

slightly changed, depending on the assumed value of a, but still within the limits of experimental error.

No appreciable difference in the obtained K values is found between Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)] and Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)] at any temperature, considering the experimental error. A similar relation has also been obtained between Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)] and Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(edta)]. The ion-association constants of these diastereoisomeric salts were as follows: K/dm^3 mol^{-1}= 12.9±0.4 (15 °C), 11.9±0.6 (25 °C), and 11.1±0.8 (35 °C) for the former salt and 13.2±0.7 (15 °C), 12.0±0.5 (25 °C), and 11.4±0.5 (35 °C) for the latter.[1]

The K values obtained in the present study are about half of those for the ion association between *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$. However, they are considerably larger than the previously reported theoretical ion-association constants: K (25 °C, a=7.0 Å)/dm^3 mol^{-1}=0 (by Bjerrum[2]), 2.41 (by Fuoss[3]), and 0.24 (by Ebeling[17] and Yokoyama-Yamatera[4]).[1] This implies that interactions other than the simple electrostatic one are also present between *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(mal)$_2$(en)]$^-$.

The ion association of *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ with [Co(mal)$_2$(en)]$^-$ is endothermic, since the K value increases with an increase in the temperature, as is shown in Table 3. This temperature dependence is the opposite of that observed for the ion association of this complex cation with [Co(edta)]$^-$,[1] but it is seemingly similar to that observed for such 2:2 electrolytes as MgSO$_4$[18] or that predicted from the ion-association theories.[1,3,4,17]

The standard enthalpy and entropy of ion association, $\Delta H°$ and $\Delta S°$, were estimated from the temperature dependence of the ion-association constant. The values of $\Delta H°$, $\Delta S°$, and the standard Gibbs free energy, $\Delta G°$, at 25 °C are shown in Table 4 with a=7.0 Å; the $\Delta H°$ and $\Delta S°$ values obtained with a=7.3 Å were the same as those given in Table 4 within 1%. Slight differences in the $\Delta H°$ and $\Delta S°$ values might seem to be present between Δ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)] and Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Δ-[Co(mal)$_2$(en)], but the situation is ambiguous because of the experimental error.

In Table 4, the $\Delta H°$ and $\Delta S°$ values are also shown for the ion association between Δ- or Λ-*cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and Δ-[Co(edta)]$^-$. In the previous paper,[1] by considering the small $\Delta S°$ value to be close to zero and the $\Delta H°$ value to be negative, these ion associations were interpreted as being caused by short-range interactions between the complex ions, almost independent of the dielectric constant of the medium, and to be performed without any release of hydration water molecules. The last argument was consistent with the presumption, based on the likeness between the r and r_s values, that the ions of both *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(edta)]$^-$ are not appreciably hydrated.

The $\Delta H°$ and $\Delta S°$ values for the ion association between *cis*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and [Co(mal)$_2$(en)]$^-$ are in contrast with those between this complex cation and [Co(edta)]$^-$, as is to be expected from the temperature dependence of the ion-association constant. The present results can be explained well by assuming that the $[Co(mal)_2(en)]^-$ ion is hydrated. That is, the large positive ΔS° value implies that the ion association is accomplished by the release of hydration water molecules of the complex anion. The positive ΔH° value is considered to result from the energy requirement for the release of hydration water molecules. The assumption of the hydration of $[Co(mal)_2(en)]^-$ is consistent with the presumption from its Stokes radius described in the preceding section.

The most effective short-range interaction of *cis*-$[Co(NO_2)_2(en)_2]^+$ with $[Co(edta)]^-$ was considered to be hydrogen-bonding between the amino group in the complex cation and the carboxyl group in the complex anion.[1] The ion association of *cis*-$[Co(NO_2)_2(en)_2]^+$ with $[Co(mal)_2(en)]^-$ may also be caused mainly by the hydrogen-bonding between the above two groups as well as by that between the nitro ion in the complex cation and the amino group in the complex anion. The possibility of the presence of the former hydrogen-bonding between the complex cation and anion in the Δ-*cis*-$[Co(NO_2)_2(en)_2]\Delta$-$[Co(mal)_2(en)]$ crystal has been revealed by an X-ray diffraction study.[6]

The hydration of $[Co(mal)_2(en)]^-$ is thought to be due to specific interactions of the complex ion with water molecules, since the usual Born-type hydration[5a] of such a large monovalent complex ion is considered to be very weak. The most effective interaction is probably also hydrogen-bonding. Both the carboxyl and amino groups of $[Co(mal)_2(en)]^-$ can contribute to the hydrogen bonding with water molecules. Especially, the amino groups may play an important part, together with the carboxyl groups, considering the difference in the degree of hydration between $[Co(mal)_2(en)]^-$ and $[Co(edta)]^-$. The two hydration water molecules of the former anion, estimated from the deviation between the r and r_s values, may be related to the fact that this complex anion has two amino groups. From the structural point of view, two spaces favorable for accepting such water molecules exist on the surface of $[Co(mal)_2(en)]^-$. Each space is adjacent to an amino group of the ethylenediamine and two coordinated oxygen atoms of different malonate ions, and is located on the side opposite another one across the central cobalt(III) ion.

The entropies of ion association between *cis*-$[Co(NO_2)_2(en)_2]^+$ and $[Co(mal)_2(en)]^-$ were more positive by about 20—30 J mol^{-1}K^{-1} than those between this complex cation and $[Co(edta)]^-$, as is shown in Table 4. Assuming that the difference in the entropy is mainly attributable to that in the number of hydration water molecules released on the ion association, and that the entropy of hydration is to be regarded as -25 J mol^{-1}K^{-1}, according to Ulich's treatment,[19] the difference in the number of released hydration water molecules can be estimated to be about one. Since the *cis*-$[Co(NO_2)_2(en)_2]^+$ and $[Co(edta)]^-$ ions probably have no hydration water molecule, only one of the two hydration water molecules of $[Co(mal)_2(en)]^-$ comes to be released on the ion association of this complex anion with *cis*-$[Co(NO_2)_2(en)_2]^+$. This is conceivable, because it is geometrically difficult for the associated *cis*-$[Co(NO_2)_2(en)_2]^+$ ion to occupy simultaneously the two spaces situated apart from each other on the surface of $[Co(mal)_2(en)]^-$, described above, by removing the two hydration water molecules from these spaces. In other words, this implies that the occupation of one of the two spaces by *cis*-$[Co(NO_2)_2(en)_2]^+$ is required for the short-range interactions between these complex ions.

The stereoselectivity in the formation of the diastereoisomeric ion pairs, Δ-*cis*-$[Co(NO_2)_2(en)_2]^+\Delta$-$[Co(mal)_2(en)]^-$ and Λ-*cis*-$[Co(NO_2)_2(en)_2]^+\Delta$-$[Co(mal)_2(en)]^-$, seemed to be absent or slight, if present, with respect to the thermodynamic parameters of ion association given in Tables 3 and 4. This implies that the ease of approaching the complex cation and anion to interact and the strength of the interactions are not so very different between the two diastereoisomeric ion pairs.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 564197) from the Ministry of Education, Science and Culture.

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