Study of Hydration and Association of Ions in Solution. II.[1] Complete Resolution of Tris(ethylenediamine)Cobalt(III), Chromium(III), and Rhodium(III) Complexes by Means of Paper Electrophoresis

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Complete resolution of racemic [M en_3]$^{3+}$ (M=Co^{III}, Cr^{III}, and Rh^{III}) by means of electrophoresis was achieved in a background solution of sodium *d*-tartrate and aluminum chloride. Electrophoretic data obtained under various conditions (various compositions, concentrations, and pH values of supporting electrolyte solutions) indicated that the separation of the enantiomers of [M en_3]$^{3+}$ complexes was accomplished not by the *d*-tartrate anion but by some aluminum *d*-tartrate complex anion.

Racemic mixtures of complex ions can be resolved by combining them with some optically-active counterions to form diastereoisomers which can be separated by the use of solubility differences. For example, $\Lambda(+)_{589}$-[Co en_3]Cl·*d*-tart·H_2O is easily separated as crystals, while $\Delta(-)_{589}$-[Co en_3]$^{3+}$ remains in solution. This suggests that the tendency of the Λ and Δ forms of the [Co en_3]$^{3+}$ complex cation towards association with the *d*-tartrate anion is different. In fact, Ogino and Saito[2] showed that the association constant of the $\Lambda(+)_{589}$-[Co en_3]$^{3+}$-*d*-tartrate^{2-} system differs from that of the $\Delta(-)_{589}$-[Co en_3]$^{3+}$-*d*-tartrate^{2-} system by analyzing the increase in the optical density of the charge-transfer absorption band.

On the other hand, the studies[3] of the electrophoretic behavior of complex salts revealed that the mobility of the complex depends largely on the type and concentration of the supporting electrolyte. This can be attributed to the different degrees of association between the complex ion and the counterion in a supporting electrolyte solution.

This leads to a possible method for resolution of the racemate into optically-active enantiomers by electrophoresis. That is, when the Λ and Δ forms of the complex ion have quite large difference in association tendency to some optically-active counterion, the Λ and Δ cations should have different mobilities. Therefore, under suitable conditions, complete resolution can be expected. With this idea in mind, Mazzei and Lederer[4] attempted to resolve racemic complex salts by electrophoresis in a chiral supporting electrolyte solution. However, they did not succeed in resolution. We also attempted the electrophoretic resolution and tried to resolve the racemic [Co en_3]$^{3+}$ complex by running it in sodium *d*-tartrate solutions. This also proved to be unsuccessful. However, we achieved complete resolution just by adding aluminum chloride to the sodium *d*-tartrate background solution.[5] Further, we achieved resolution of the racemic [Co en_3]$^{3+}$ by means of thin-layer chromatography[6] using a solution of a similar composition to that used in electrophoretic resolution.

In order to obtain a deeper insight into the mechanism of resolution, we carried out electrophoresis in various background solutions having various compositions, concentrations, and pH values. We also tried three other trisethylenediamine complexes and obtained similar resolution in the cases of [Cr en_3]$^{3+}$ and [Rh en_3]$^{3+}$, but not in the case of [Pt en_3]$^{4+}$.

Experimental

A migration apparatus with multicompartment cells was used, so that ten samples could be run at the same time. A paper strip was dipped uniformly in the background solution, and then the excess of the solution was removed by hanging the strip. After that about 5 μl of a sample solution was placed on the paper (Toyoroshi No. 51A, 2×40 cm).

Samples were run for 2—3 hr under a potential gradient 250 V/34 cm, keeping the temperature of the migrating box at 25°C (The box is filled with carbon tetrachloride in which the strips are immersed). In the case of the [Cr en_3]$^{3+}$ complex, the whole apparatus was covered with black cloth to prevent the photodecomposition.

The spot of cobalt, rhodium, and platinum complexes was detected by spraying with sodium sulfide solution, while in the case of the chromium complex, it could be easily detected by the red color which was developed after by exposure to daylight.

Results and Discussion

Table 1 shows the mobilities of four kinds of trisethylenediamine complexes in background solutions of stepwise concentrations which contain only sodium *d*-tartrate as a supporting electrolyte. In this study, the mobility of a complex is defined as a migration distance relative to that of the [Co en_3]$^{3+}$ complex in 0.1 M NaCl solution. The data clearly indicate the effect of ionic association, because the mobility of these complexes goes down with the increase in the background tartrate concentration. However, the migrat-

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Table 1. The mobilities of four kinds of racemic trisethylenediamine complexes in sodium *d*-tartrate solutions. (250 V, 2.5 hr., 25°C)

Na_2*d*-tart	pH	[Co en_3]Cl_3	[Cr en_3]Cl_3	[Rh en_3]Cl_3	[Pt en_3]Cl_4
0.72M	7.90	0.34	0.30	0.31	0.43
0.36M	7.60	0.40	0.35	0.35	0.49
0.18M	7.52	0.42	0.39	0.40	0.62
0.12M	7.50	0.44	0.46	0.45	0.69
0.09M	7.30	0.48	0.51	0.48	0.73
0.06M	7.20	0.55	0.63	0.54	0.83
0.03M	7.10	0.73	0.80	0.76	0.98

ing racemic species appeared always in one spot, irrespective of the concentration of sodium *d*-tartrate. This means that the difference in the degree of ionic association between the Λ-complex-*d*-tartrate and the Δ-complex-*d*-tartrate combinations is too small to be observed in electrophoresis.

However, the addition of the aluminum salt caused a marvellous effect as reported in the earlier communication.[5] In this paper, the extended work is presented in Table 2. Here the mole ratio between Al^{3+} and *d*-tartrate was fixed at 2: 3, and the concentration of the tartrate was increased stepwise just as in Table 1.

To facilitate the understanding of general features, the data concerning the [Co en_3]$^{3+}$ complex are shown in Fig. 1. As is clearly seen in this figure, the addition of Al^{3+} causes the separation of two spots in a wide concentration range of the background solution (from 0.06M up to 0.36M *d*-tartrate).

Table 2. The mobilities of four kinds of racemic trisethylenediamine complexes in sodium *d*-tartrate–aluminum chloride mixed solutions. (250 V, 2.5 hr., 25°C)

Na_2*d*-tart $AlCl_3$	pH	[Co en_3]$^{3+}$	[Cr en_3]$^{3+}$	[Rh en_3]$^{3+}$	[Pt en_3]$^{4+}$
0.72M 0.48M	1.65	0.29	0.22	0.25	0.29
0.36M 0.24M	2.00	0.14—0.31 0.45	0.11—0.29 0.39	0.09—0.23 0.40	0.45
0.18M 0.12M	2.23	0.14—0.32 0.60	0.12—0.32 0.59	0.11—0.32 0.61	0.61
0.12M 0.08M	2.50	0.11—0.32 0.63	0.15—0.28 0.61	0.18—0.38 0.63	0.64
0.09M 0.06M	2.60	0.14—0.33 0.69	0.15—0.31 0.64	0.18—0.38 0.65	0.70
0.06M 0.04M	2.71	0.16—0.35 0.69	0.12—0.35 0.68	0.41—0.62 0.68	0.85
0.03M 0.02M	2.79	1.03	1.03	1.03	1.12

This can be regarded as resolution, because the Λ or Δ form of the complex showed only either one of these two spots in the background solution having the same composition (The Λ form corresponds to the spot of longer migration, the Δ form to that of shorter migration).

Here it must be noted that the background solutions are fairly acidic due to the presence of aluminum chloride. To see the effect of pH variation upon resolution, a sample was migrated in several background solutions of different pH values which were prepared by adding a small amount of HCl or NaOH to the original solution containing 0.18M Na_2 *d*-tartrate and 0.12M $AlCl_3$. The result is shown in Fig. 2. It is easily understood that no resolution was achieved in the solution of pH 1. In such a solution, the tartrate is protonated and becomes a neutral molecule. However, it was a surprise to find that resolution was successful only within a limited acidic pH range of the solution. Even in a neutral background (pH 7), it was worth noting that resolution is incomplete.

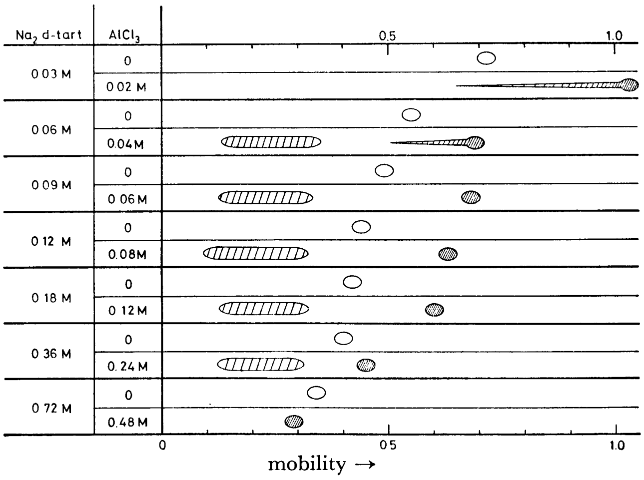

Fig. 1. Electrophoresis pattern of the racemic [Co en_3]$^{3+}$ complex in sodium *d*-tartrate solution with and without aluminum chloride.

If the resolution were due to the different degrees of association of the *d*-tartrate to the Λ and Δ forms of the complex cation, resolution should take place in neutral and alkaline solutions. However, this is not the case, which implies that the mechanism is more complicated than considered before.[6] In connection with this discussion, one thing must be pointed out. That is, the addition of aluminum chloride effects the migration of the Λ and Δ forms of the complex in opposite directions. As is seen in Fig. 1, the one component of the separated two spots in the presence of aluminum ions appears

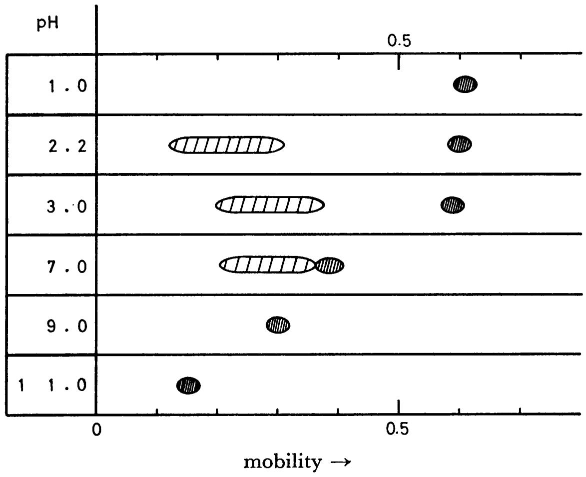

Fig. 2. Effect of pH upon the electrophoretic resolution of the racemic [Co en_3]$^{3+}$ complex.
(The background solution contains 0.18M Na_2*d*-tratrate and 0.12M $AlCl_3$ in all cases).

TABLE 3. THE MOBILITIES OF THE $[\mathrm{Coen}_3]^{3+}$ ION IN *d*-TARTRATE, *meso*-TARTRATE, AND *l*-MALATE SOLUTIONS WITH AND WITHOUT ALUMINUM CHLORIDE.
(The *meso*-trartrate and malate solutions were prepared by neutralizing the free acids with sodium carbonate)

	Conc.	pH	Mobility	$AlCl_3$ conc.	pH	Mobility
Na_2*d*-tart	0.36M	7.60	0.42	0.24M	2.00	0.14—0.31, 0.45
	0.18M	7.52	0.44	0.12M	2.23	0.14—0.32, 0.60
	0.09M	7.30	0.50	0.06M	2.50	0.14—0.33, 0.69
Na_2*meso*-trartrate	0.36M	6.70	0.37	0.24M	2.10	0.44
	0.18M	6.60	0.41	0.12M	2.50	0.60
	0.09M	5.59	0.51	0.06M	2.90	0.65
Na_2*l*-malate	0.36M	6.00	0.44	0.24M	2.40	0.64
	0.18M	5.95	0.56	0.12M	2.50	0.67
	0.09M	6.00	0.62	0.06M	2.90	0.76

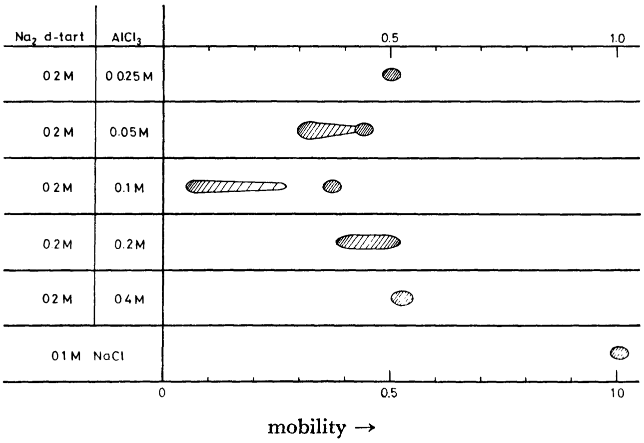

Fig. 3. Effect of the addition of aluminum chloride upon the electrophoretic resolution of the racemic $[\mathrm{Co\ en}_3]^{3+}$ complex.

behind and the other component ahead of the original spot observed in the absence of aluminum ions. If the role of aluminum ions is simply dehydration of the complex ion, the split two spots should be both behind of the original spot due to increased ionic association. Therefore it is more reasonable to assume that the aluminum ion forms the *d*-tartrate complex anion which can select the Λ and Δ form of the $[\mathrm{Co\ en}_3]^{3+}$ complex.

To find the favorable concentration of aluminum chloride for resolution, five supporting electrolyte solutions, each of which contains 0.2M sodium *d*-tartrate and various concentrations of aluminum chloride, were tested as shown in Fig. 3.

Thus it was revealed that the mole ratio between the aluminum ion and the tartrate for successful resolution was also confined to a certain limited range.

As shown in Table 2, the resolution of $[\mathrm{Cr\ en}_3]^{3+}$ and $[\mathrm{Rh\ en}_3]^{3+}$ was achieved in the same way as the resolution of $[\mathrm{Co\ en}_3]^{3+}$. The small difference in their ionic weight did not cause any practical difference in migration distance. However, the quadrivalent $[\mathrm{Pt\ en}_3]^{4+}$ ion could not be resolved in the same way. This is probably because the complex is more highly hydrated than the tervalent complex, and the situation of ionic association concerning this complex may be quite different from that in the case of tervalent complexes.

With regard to the mechanism of resolution, we can obtain information from the data obtained using the *meso*-tartrate and *l*-malate as a supporting electrolyte. Since the *meso*-tartrate is not optically-active, no resolution is expected even in the presence of aluminum ions. Nevertheless, it is worthwhile to see whether the spot appears near the longer migrating component or near the shorter migrating component in the case of the aluminum-*d*-tartrate system. Actually, the mobility in the aluminum-*meso*-tartrate system is almost the same as that of the longer migrating component in the corresponding aluminum-*d*-tartrate system (See Table 3). Although the *l*-malate is optically active, no resolution was achieved in the aluminum-*l*-malate system, and the mobility of the complex is even higher than those in the corresponding aluminum-*d*-tartrate and aluminum-*meso*-tartrate systems.

These findings can be interpreted in the following way. While the *d*- and *l*-tartrates are constructed with two *d* and two *l* moieties, respectively, the *meso*-tartrate consists of one *d* and one *l* moiety. Suppose two or three *d*-tartrate anions are coordinated to the aluminum ion to form a complex, they use their *d* moiety for coordination and leave the other *d* moiety free. When two or three optically active ligands are coordinated in the metal ion, the complex produced takes as a whole one type of enantiomeric form, say D or L. Thus if we represent the *d*-tartrate as *d*-*d*, we may represent the aluminum *d*-tartrate complex with D-*d*-*d*. Usually there is no L-*d*-*d*. On the other hand, the aluminum-*meso*-tartrate complex can exist in two enantiomeric forms D-*d*-*l* and L-*l*-*d*. Although there are four possible combinations between the aluminum-*meso*-tartrate complex (D-*d*-*l* and L-*l*-*d*) and the racemic $[\mathrm{Co\ en}_3]^{3+}$ complex (*d* and *l*) ion, we obtained only one spot corresponding to the spot of longer migration distance in the case of the aluminum-*d*-tartrate (D-*d*-*d*) system.

Thus, it was revealed that among these three aluminum-tartrate systems D-*d*-*d*, D-*d*-*l*, and L-*l*-*d*, only D-*d*-*d* shows a strong interaction with the $\Delta(-)_{589}$-$[\mathrm{Co\ en}_3]^{3+}$ complex. This interaction is therefore stereospecific.

In addition, the aluminum-*l*-malate system gives even longer migration than the component of longer migration in the D-*d*-*d* system. Therefore, it is presumed that cooperation of the OH and COO^- groups is necessary for such a stereospecific interaction.

Finally, we wish to go further to the discussion of the probable structure of D-*d*-*d*. Since it attracts the complex cation, it must be an anion. Thus, we have two possible aluminum tartrate complex anions, $[Al(d\text{-tart})_3]^{3-}$ and $[Al(H_2O)_2(d\text{-tart})_2]^-$. The possibility of $[Al(d\text{-tart})_3]^{3-}$ can be excluded, because this should also give resolution in neutral and alkaline solution, contrary to the observations. Therefore, we may presume that the most probable D-*d*-*d* is $[Al(H_2O)_2(d\text{-tart})_2]^-$.

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