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Effect of Lattice Anions on the Racemization of Optically Active Metal Chelate Salts in the Solid State. 2.[1)] $[Co(phen)_3]X_3$, $[Co(phen)_2(en)]X_3$, and $[Co(phen)(en)_2]X_3$, Where $X^-=Cl^-$, Br^-, or I^-

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The kinetics of racemization of the anhydrous complexes (−)-$[Co(phen)_3]X_3$, (+)-$[Co(phen)_2(en)]X_3$, and (−)-$[Co(phen)(en)_2]X_3$, where phen=1,10-phenanthroline, en=ethylenediamine, and $X^-=Cl^-$, Br^-, or I^-, have been examined in the solid state. A rapid initial loss of optical activity and a subsequent first-order racemization were observed for the complex salts. Enthalpies and entropies of activation, ΔH^* and ΔS^*, were evaluated for the first-order process of $[Co(phen)_3]X_3$ and $[Co(phen)_2(en)]X_3$. It was found that for $[Co(phen)_3]X_3$ the chloride salt racemizes more rapidly than the bromide salt and that ΔH^* and ΔS^* decrease with the lattice anion in the order $X^-=Br^->Cl^-$. On the other hand, the reverse sequence in ΔH^* and ΔS^*, $X^-=Br^-<Cl^-$, was observed for $[Co(phen)_2(en)]X_3$. Moreover, the rate of racemization of $[Co(phen)(en)_2]X_3$ was found to decrease with the lattice anion in the order $X^-=I^->Br^->Cl^-$. These anion effects for the series were successfully interpreted in terms of the chemical interactions due to donicity and hydrogen bonding ability of anions, but not in terms of the physical factor, lattice energy. Thermal decomposition studies of the complexes lend support to the interpretation of the racemization kinetic data.

In our previous study of the solid-state racemization of halide salts of tris-complexes of 1,10-phenanthroline and 2,2′-bipyridine with iron and nickel ions,[1)] a difference in racemization mechanism between the iron and nickel complexes was reported as it is in solution.[2,3)] The operation of only a twist process without any nucleophilic interaction of lattice anions is postulated for the iron complexes as in solution.[3,4)] On the other hand, ΔH^* and ΔS^* values for the nickel complexes were found to decrease with the lattice anion in the order $X^-=ClO_4^->I^->Br^->Cl^-$. Then, we have pointed out that the trend is attributed to the donicity of the anions[5)] to stabilize a 7-coordinate transition state which is generated by attack of the lattice anion on the central metal as proposed for solutions.[6,7)] Kutal and Bailar found that the rate of racemization of the complex salt, $[Co(en_3)]X_3\cdot nH_2O$, increases in the order of anions $Cl^-<NCS^-<Br^-<I^-$ for the anhydrous compounds, and it was presumed that hydrogen bonding of the type N-H···X was responsible for the rate differences in the series.[8)] On the other hand, activation energies or enthalpies for the dehydration of the series of compounds $[M(NH_3)_5(H_2O)]X_3$ in the solid state[9,10)] (where M=Cr, Co, or Ru) were found to decrease with the anion in the order $X^-=I^->Br^->Cl^-$ and an S_N2-type mechanism was proposed for the reaction.

However, a different mechanism from them was proposed recently by House[11)] for the solid-state reactions in which the generation of a point defect is considered to be the origin of the transition state. The intramolecular racemization of $[Co(en)_3]X_3$ has been shown to be consistent with the substituted ion type of defect, while the dehydration of $[M(NH_3)_5(H_2O)]X_3$ is consistent with the formation of a Frenkel type of defect. Then, energy of the formation of the transition state is discussed in terms of lattice energy and ionic radii. However, we pointed out in previous paper[12)] that the anion effects on the racemization of the iron and nickel complexes cannot be accounted for in terms of House's model or the physical factor alone, lattice energy.

In view of these studies, it is of interest to explore the role of the factors which facilitate or retard the solid-state racemization of the series of homo- and heterochelated tris-complexes of 1,10-phenanthroline and ethylenediamine, $[Co(phen)_3]X_3$, $[Co(phen)_2(en)]X_3$, and $[Co(phen)(en)_2]X_3$. An attempt was made to isolate the optically active complex, (−)-$[Co(phen)_3]^{3+}$, as the halide salts by a conventional method, namely, by addition of an excess of sodium halide solutions to aqueous solutions of the active complex. However, we failed to obtain the active halide salts because the complex racemizes very rapidly in halide-containing solutions.[13)] Recently by a freeze-drying method, we successfully isolated the optically active chloride and bromide salts of the complex.[14)] In addition to the kinetic data, the results of studies on the thermal decomposition of these complexes were incorporated into the analysis of the effect of lattice anions on the transition state for the solid-state racemization.

Experimental

Materials. The bromide and chloride salts of the optical isomer of $[Co(phen)_3]^{3+}$ isolated in our previous study[14)] were employed here. The preparation and resolution of $[Co(phen)_2(en)]^{3+}$ were performed according to the method of Gillard *et al.*[15)] The complex, $K_3[(+)_{589}$-Co(L-cysu)$_3$] [cysu=cysteinesulfinato(2−)-*SN**], prepared by a previously reported method,[16)] was used as the resolving agent. The diastereoisomer with $(+)_{589}$-[Co(L-cysu)$_3$]$^{3-}$ was converted to its bromide and chloride salts, $(+)_{436}$-$[Co(phen)_2(en)]Br_3\cdot 6H_2O$ and $(+)_{436}$-$[Co(phen)_2(en)]Cl_3\cdot 6H_2O$, by anion exchange (Dowex 21K resin, Br^- or Cl^- form). Found: C, 36.80; H, 3.68; N, 10.39%. Calcd for $C_{26}H_{36}O_6N_6Br_3Co$: C, 37.75; H, 4.39; N, 10.16%. Found: C, 44.56; H, 4.61; N, 13.03%. Calcd for $C_{26}H_{36}O_6N_6Cl_3Co$: C, 45.00; H, 5.23; N, 12.11%. The complex,

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* The ligand, cysu, should read *β*-sulfinato-L-alaninato: $H_2NCH(CO_2^-)CH_2SO_2^-$.

$[Co(phen)(en)_2]^{3+}$, was prepared and resolved using ammonium $(+)_{589}$-3-bromo-8-camphorsulfonate as previously reported.[17] The optical isomer was isolated as the iodide, bromide, and chloride salts, $(-)_{436}$-$[Co(phen)(en)_2]I_3 \cdot H_2O$, $(-)_{436}$-$[Co(phen)(en)_2]Br_3 \cdot 5H_2O$, and $(-)_{436}$-$[Co(phen)(en)_2]Cl_3 \cdot 6H_2O$. Found: C, 25.76; H, 3.20; N, 10.88%. Calcd for $C_{16}H_{26}ON_6I_3Co$: C, 25.35; H, 3.46; N, 11.09%. Found: C, 27.41; H, 4.50; N, 12.88%. Calcd for $C_{16}H_{34}O_5N_6Br_3Co$: C, 27.89; H, 4.97; N, 12.20%. Found: C, 33.39; H, 4.80; N, 15.37%. Calcd for $C_{16}H_{36}O_6N_6Cl_3Co$: C, 33.49; H, 6.32; N, 14.64%. All the complexes were powdered by grinding with a mortar and pestle to pass a 200-mesh sieve. The preparation of anhydrous samples of the complexes was performed by the method given earlier,[1] except that the operation was performed in the dark since exposure to sunlight affects the optical rotations, especially of $[Co(phen)_3]X_3 \cdot nH_2O$.[14]

Measurements. The racemization rates at different temperatures were measured for each complex by using the same heating apparatus as that used in our previous study.[1] Before the measurements were made, all the solid samples(0.005—0.007 g) of the anhydrous complexes were placed in NMR tubes(5 mm in diameter, 5 cm in length) and preserved in a desiccator over P_2O_5 in the dark. The sample tubes were placed in the heating apparatus where it was possible to prevent the samples from exposure to sunlight. The samples were taken out of the apparatus at timed intervals and cooled rapidly. The optical rotations of the samples were measured in triplicate on aqueous solutions in the conventional manner at 365 nm for $[Co(phen)_3]^{3+}$ and at 436 nm for $[Co(phen)_2(en)]^{3+}$ and $[Co(phen)(en)_2]^{3+}$ by using a Perkin-Elmer Model 141 Polarimeter and a Hg lamp, with a cell of 1-dm length. The concentrations of the solutions were determined spectrophotometrically using a Hitachi Perkin Elmer Model 139 UV-vis spectrophotometer. The wavelengths and molar extinction of absorption maximums employed are as follows: 274 nm and 6.95×10^4 mol^{-1} dm^3 cm^{-1} for $[Co(phen)_3]^{3+}$; 305 nm and 1.255×10^4 mol^{-1} dm^3 cm^{-1} for $[Co(phen)_2(en)]^{3+}$; 273 nm and 3.025×10^4 mol^{-1} dm^3 cm^{-1} for $[Co(phen)(en)_2]^{3+}$. Within experimental uncertainties, the specific rotations of aqueous solutions of the complexes were independent of concentration. These results have a precision of better than 5%. Thermogravimetric analysis (TGA) and differential thermal analysis(DTA) were carried out with a Sinku-Riko Model TGD-3000-RH instrument. Samples(0.01—0.02 g) of the hydrates were used. A heating rate of 5°/min and a static air atmosphere were employed in each run.

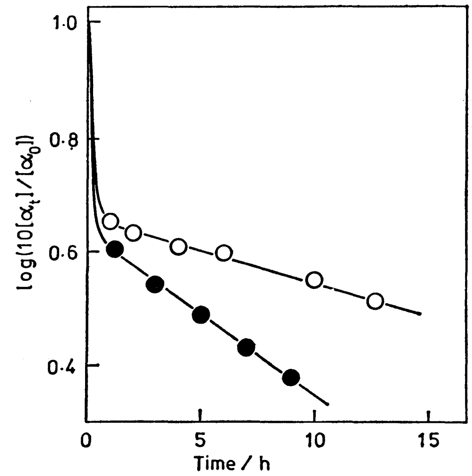

Fig. 1. Racemization of $(-)$-$[Co(phen)_3]Br_3$ at 121 °C (○) and $(-)$-$[Co(phen)_3]Cl_3$ at 119 °C (●).

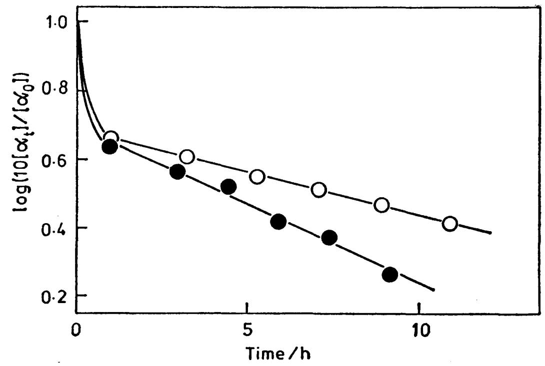

Fig. 2. Racemization of $(+)$-$[Co(phen)_2(en)]Br_3$ (○) and $(+)$-$[Co(phen)_2(en)]Cl_3$ (●) at 148 °C.

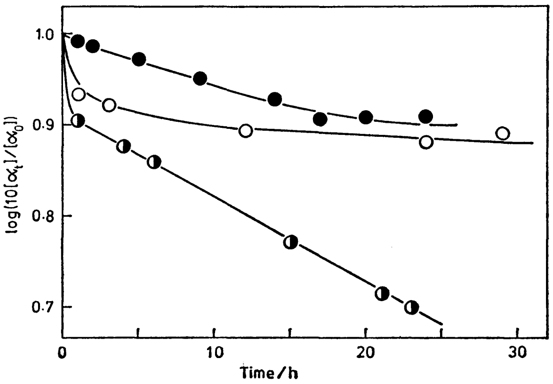

Fig. 3. Racemization of $(-)$-$[Co(phen)(en)_2]Cl_3$ at 145 °C (●), $(-)$-$[Co(phen)(en)_2]Br_3$ at 149 °C (○), and $(-)$-$[Co(phen)(en)_2]I_3$ at 145 °C (◑).

Results

Typical plots of $\log(10[\alpha_t]/[\alpha_0])$ *vs.* time for the solid-state racemization of anhydrous salts of $(-)$-$[Co(phen)_3]X_3$, $(+)$-$[Co(phen)_2(en)]X_3$, and $(-)$-$[Co(phen)(en)_2]X_3$ (X=I, Br, or Cl) are given in Figs. 1—3, respectively, where $[\alpha_t]$ is the specific rotation at time t and $[\alpha_0]$ is the specific rotation at time zero. Figures 1 and 2 show that all runs with anhydrous materials of the tris- and bis-phenanthroline complexes have the common characteristic of an initial period during which very rapid loss of optical activity occurs, followed by a first-order racemization process. On the other hand, Fig. 3 shows that the chloride and bromide salts of the mono-phenanthroline complex exhibit decreasing rates of racemization after the initial period and thus the kinetics depart from simple first-order behavior, although the iodide salt shows a first-order racemization as do the tris- and bis-phenanthroline complexes.

For the first-order racemization, the rate constant, k, is determined by applying the equation used in our previous paper.[1] Table 1 lists the rate constants. The indicated errors are one standard deviation estimated from least-squares fits to the equation. Table 1 shows that the chloride salts racemize faster than

Table 1. Rate constants of the solid-state racemization

Complex	Temp/°C	$k/10^{-6}\ \mathrm{s}^{-1}$
$(-)$-[Co(phen)$_3$]Br$_3$	102	0.169 ± 0.027
	107	0.466 ± 0.083
	114	1.15 ± 0.10
	121	3.17 ± 0.18
$(-)$-[Co(phen)$_3$]Cl$_3$	91	0.323 ± 0.045
	100	0.909 ± 0.086
	110	3.92 ± 0.38
	119	9.43 ± 0.69
$(+)$-[Co(phen)$_2$(en)]Br$_3$	148	7.53 ± 0.48
	154	11.0 ± 0.6
	158	15.0 ± 1.5
$(+)$-[Co(phen)$_2$(en)]Cl$_3$	145	12.3 ± 0.4
	148	17.5 ± 0.6
	150	24.2 ± 1.3

Table 2. Kinetic parameters for the solid-state racemization of cobalt complexes with thermal stability

Complex	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}	T_d / °C
$(-)$-[Co(phen)$_3$]Br$_3$	181 ± 11	108 ± 27	188
$(-)$-[Co(phen)$_3$]Cl$_3$	143 ± 7	23 ± 18	170
$(+)$-[Co(phen)$_2$(en)]Br$_3$	100 ± 6	-109 ± 14	202
$(+)$-[Co(phen)$_2$(en)]Cl$_3$	195 ± 20	124 ± 47	186

the corresponding bromide salts in both series of the complexes. Although attempts were made to fit the racemization data for [Co(phen)(en)$_2$]X$_3$ to various topochemical rate laws common to solid-state reactions,[18] any fit to such kinetic expressions must be regarded as poor because of the invariably deceleratory plots throughout the course of the racemization.

Activation parameters, ΔH^* and ΔS^*, were determined by least-squares fits to Eyring plots for the first-order racemization as expressed in our previous papers,[1,12] although the first-order process may be the case of random nucleation.[18] These are presented in Table 2. The uncertainties quoted for the activation parameters are the computed standard deviations. Table 2 shows that ΔH^* for [Co(phen)$_3$]X$_3$ decreases in the order X=Br>Cl, whereas for [Co(phen)$_2$(en)]X$_3$ the sequence X=Br<Cl lies in the reverse order.

TGA runs on all the hydrated salts of the complexes in static air show that dehydration occurs soon after heating (at 30—35 °C). Then anhydrous weight levels are almost attained at 105—115 °C for [Co(phen)$_3$]X$_3$ and [Co(phen)(en)$_2$]X$_3$ and at 115—125 °C for [Co(phen)$_2$(en)]X$_3$. As the temperature is raised further, thermal decomposition of the complexes occurs in air. The temperatures (T_d) at which weight loss resulting from the decomposition begins are given in Table 2. Under the conditions employed in the racemization rate studies, TGA and DTA confirmed the absence of thermal decomposition, and the lack of color changes offered evidence that there was no change in chemical combination. In addition, when $(-)$-[Co(phen)$_3$]Br$_3$ was heated at 114 °C for 38 h in air, no reduction of the complex cation by bromide ion was shown by a conventional potentiometric titration of aqueous solutions of the sample using an Ag/Ag$^+$ electrode, although the sample lost 70% of its optical activity.

Discussion

A very rapid loss of optical activity in an initial period observed for all the cobalt complexes (Figs. 1—3) is similar to that for [M(phen)$_3$]X$_2$ and [M(bpy)$_3$]X$_2$ (M=Fe or Ni and bpy=2,2′-bipyridine).[1] Such an initial phenomenon was also reported for the solid-state racemization of other complexes, [Co(en)$_3$]X$_3\cdot n$H$_2$O[11] and K$_3$[Cr(C$_2$O$_4$)$_3$][19] and discussed in detail in previous papers.[1,8] Then it was not investigated further in this study and attention is riveted on the racemization process after the initial period as follows.

The cobalt complexes employed here are low-spin d^6 complexes in analogy with the iron complexes[20] and so the operation of the twist mechanism is considered likely. However, [Co(phen)$_3$]Cl$_3$ was found to racemize more rapidly than [Co(phen)$_3$]Br$_3$. In addition, the ΔH^* and ΔS^* values for the bromide are larger than those for the chloride. These results indicate that there is interaction of the complex cation with the anions in the transition state. The trend in ΔH^* is the same as observed for [Ni(phen)$_3$]X$_2$ and [Ni(bpy)$_3$]X$_2$[1] and then attributed to the donicity of the anions to stabilize the transition state. For the solid-state racemization of tris-chelated metal complexes, an intermolecular mechanism cannot operate owing to the absence of solvents required for dissolution of a released ligand, and for the same reason a mechanism involving one-ended dissociation of a ligand is regarded as improbable.[1,8] Thus it is reasonable to infer that the mechanism of racemization of the cobalt complex would be similar to that of the nickel complexes, that is to say, the mechanism involves expansion of a complex cation to a 7-coordinate transition state with one lattice anion, for example a capped trigonal prism.[21] Moreover, the mechanism is consistent with the decrease in ΔS^* found, as ΔH^* decreases (Table 2) as described for the nickel complexes.[1] Another support for the operation of the mechanism is furnished by thermal decomposition studies of the cobalt complexes. It was pointed out that if the racemization mechanism is operative, the ΔH^* values should be related to T_d values taken as a measure of the strength of metal-anion bonds in thermal decomposition products.[1] This is also corroborated by the present data on ΔH^* and T_d. Table 2 shows that the trend is a decrease in T_d as ΔH^* decreases, indicating that both the mechanisms of racemization and decomposition should be controlled by the donicity of the lattice anion.

It was reported that the rates of thermal decomposition of [Co(NH$_3$)$_6$]X$_3$ in the solid state increase with the anion in the order X$^-$=Cl$^-$<Br$^-$<I$^-$, which

agree with that of the electron transfer reaction of the complexes.[22] On the other hand, Kutal and Bailar pointed out in a study of the racemization of [Co(en)$_3$]X$_3$ that such an electron exchange mechanism is not operative in the solid state.[8] For the racemization of [Co(phen)$_3$]X$_3$ also, the following results suggest that a process involving reduction of the complex or an electron exchange mechanism is unlikely in the solid state. The order of anion effects on the rate for the complex is opposite to that observed for aqueous solutions ($Cl^- < Br^- < I^-$).[13,23] Moreover, despite the observation that [Co(phen)$_3$]Br$_3$ lost 70% of its optical activity at 114 °C after 38 h, no reduction of the complex in the solid state was observed.[24] In addition, it was reported that activation energies for the dehydration of the series of compounds [Co(NH$_3$)$_5$(H$_2$O)]X$_3$ in the solid state decrease with the anion in the same order, $X^- = Br^- > Cl^-$, as that observed here for the racemization of [Co(phen)$_3$]X$_3$.

When one of three phenanthroline ligands in the homochelated tris-complex, [Co(phen)$_3$]X$_3$, is replaced with an ethylenediamine ligand to yield the heterochelated tris-complex, [Co(phen)$_2$(en)]X$_3$, it is observed that ΔH^* and ΔS^* values for the bromide of the heterochelated complex are smaller than those for the corresponding chloride. Despite the observation that T_d for [Co(phen)$_2$(en)]X$_3$ decreases in the order, $X^- = Br^- > Cl^-$, which lies in the order of increasing donor strength of the halide ion as observed for the homochelated complex, the trend in ΔH^* and ΔS^* for the heterochelated complex is opposite to that for the homochelated complex (Table 2). In the racemization studies[1,7] of [Ni(phen)$_3$]X$_2$ and [Ni(bpy)$_3$]X$_2$, it was implied that there is no appreciable interaction of the aromatic ligands with the halide ions.[25] Thus, these results reflect some specific effects such as hydrogen bonding, as in [Co(en)$_3$]X$_3$.[8] If such a twisting motion of all the three chelate rings as in a Bailar twist[26] is performed in the racemization process of the complex, then the hydrogen bonds formed in the ground state are forced to be weakened or broken in the transition state. Thus, the enthalpy of activation for the process should increase with an increase in the strength of hydrogen bonds in the ground state. In conformity with this view, the sequence observed for ΔH^*, $X^- = Br^- < Cl^-$, lies in the order of increasing strength of the hydrogen bonds.[27] The ethylenediamine ligand appears to be frozen more tightly in the lattice owing to the hydrogen bonds for the chloride salt compared with the bromide salt. It is thus reasonable to expect a smaller degree of freedom of the ligand in the ground state for the chloride salt and so a larger increase in the degree of freedom of the ligand on activation. This is reflected in larger ΔS^* for the chloride salt (Table 2).

Table 2 shows that ΔH^* for the bromide of the heterochelated complex is lower than that of the bromide of the homochelated complex in spite of the additional energy required to break the hydrogen bonds on activation, and the entropy of activation is negative. These results may imply that for the racemization of the heterochelated complex such a nucleophilic attack of the halide ions as that for the homochelated complex can occur with the breaking of the hydrogen bonds. Since the ethylenediamine ligand is of lower ligand field strength than the phenanthroline ligand,[28] the replacement of one of three phenanthroline ligands by an ethylenediamine ligand causes a decrease in the enthalpy required to expand Co–N bonds in the transition state. On the other hand, the attack puts restriction on the more flexible ethylenediamine ligands due to removal of any steric hindrance, leading to a decrease in the freedom of movement of the ligand in the transition state. For the chloride salt of the heterochelated complex, however, the effect of the hydrogen bonding interaction in the ground state might be more marked than that of the nucleophilic interaction in the transition state and thus the nucleophilic effect of chloride ion is not appreciable.

Furthermore, for the heterochelated tris-complex, [Co(phen)(en)$_2$]X$_3$, a more marked retarding effect of the hydrogen bonding was found to be exerted on the racemization as seen in Fig. 3. The rate of racemization of the complex decreases with the lattice anion in the order $X^- = I^- > Br^- > Cl^-$. This sequence lies in the order of increasing strength of the hydrogen bonds of the anions and is the same as that observed for [Co(en)$_3$]X$_3$,[8] but in the order opposite to that for the homochelated complex, [Co(phen)$_3$]X$_3$. The iodide salts of the heterochelated complex exhibit a first-order linearity as well as [Co(phen)$_3$]X$_3$ and [Co(phen)$_2$(en)]X$_3$. For the chloride and bromide salts, on the other hand, deviations from simple first-order behavior were observed. Similar deviations have been reported for [Co(en)$_3$]X$_3$.[8]

In the present study, the anion effects for the series cannot be accounted for in terms of House's model as in our previous studies for the nickel complexes.[1,12] House pointed out[11] that the trigonal transition state for the intramolecular racemization process which follows the model is produced only with the expansion of the cation and that the difficulty of the expansion increases with increasing lattice energy according to the Kapustinskii equation;[29] the formation of the transition state would be most difficult in the case of the smallest anion. If the process alone gives rise to anion effects in the racemization of the solid complexes, the rate of racemization is expected to decrease with the lattice anion in the order $X^- = Br^- > Cl^-$ and the expected ΔH^* should increase in the order of anions $Br^- < Cl^-$. However, the opposite orders in the rate and ΔH^*, respectively, were observed for [Co(phen)$_3$]X$_3$. Moreover, if there is no specific interaction such as hydrogen bonding, the expected order of lattice energy effect for the homochelated complex should be the same as those for the heterochelated complexes and so no change in the order of anion effects on the rate or ΔH^* should be expected for the series. However, the order, in fact, changes as shown above. Therefore, the physical factor alone, lattice energy, is insufficient to explain these anion effects, and thus the chemical factors, donicity and hydrogen bonding ability of lattice anions, as described above, are considered to be responsible for the anion effects or the rate differences. In addition, Kutal and Bailar pointed out that the lattice anions effectively shield the complex ions from each other.[8]

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