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Mechanism of Complex Formation. Reaction between Aluminum and Salicylate Ions

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The kinetics of the reaction between Al^{3+} and salicylate ion (HA^-) have been investigated in acidic aqueous solution by the stopped-flow technique. The scheme representing the reaction paths is

$$Al^{3+} + HA^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlA^+ + H^+ \tag{i}$$

$$Al^{3+} + H_2O \overset{Q_H}{\rightleftharpoons} AlOH^{2+} + H^+ \tag{ii}$$

$$AlOH^{2+} + HA^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AlA^+ + H_2O \tag{iii}$$

where $k_1 = 9.1 \times 10^{-1}\ M^{-1}\ sec^{-1}$, $k_{-1} = 7.8 \times 10^{-1}\ M^{-1}\ sec^{-1}$, $k_2 = 1.02 \times 10^3\ M^{-1}\ sec^{-1}$, and $k_{-2} = 7.9 \times 10^{-3}\ sec^{-1}$ at 25° and ionic strength 0.1 *M* ($NaClO_4$). The activation parameters have been evaluated for paths k_1, k_{-1}, and k_{-2}. The forward paths are consistent with the SN1 mechanism formulated by Eigen and Tamm for the reactions of metal complex formation. The rate constant for the process corresponding to the conversion of the outer-sphere complex into an inner-sphere complex was estimated to be 0.17 sec^{-1}, a value in agreement with those of other Al(III) complexes and with the rate of water exchange. The reverse paths are also discussed. The dissociation quotients of salicylic acid and the equilibrium quotients of the complexation reaction i have been measured at different ionic strengths and temperatures by potentiometric titrations. The value of the equilibrium quotient of reaction i at 25° and ionic strength 0.1 *M* ($Q = 1.33$) agrees with that derived from kinetics as k_1/k_{-1} or k_2Q_H/k_{-2}.

Introduction

The mechanism of ligand penetration into metal ion coordination spheres seems to be quite clearly established for a large number of systems involving mainly complexation of alkaline earth and divalent first-row transition metal ions.[1-4] Rapidly reacting trivalent metal ion systems have been on the contrary comparatively scarcely studied and investigations have been confined in general to reactions of iron(III)[3,5-8] and rare earth ions.[3] As far as complexes of nontransition trivalent metal ions are concerned, only rate measurements of Al(III), Ga(III), and In(III) with sulfate[9-11] ion, of In(III) with murexide,[12] and of Al(III) with ferri-[13] and cobalticyanide[14] are reported in the literature.

The present study of the reaction between aluminum and salicylate ions has been undertaken in order to elucidate the kinetic behavior of aluminum(III) with respect to a ligand which differs from the above-mentioned ligands both in charge and in basicity.

Experimental Section

Aluminum perchlorate was prepared by dissolving a weighed amount of metal in an aqueous solution containing perchloric acid in stoichiometric ratio. The salt was then precipitated in a rotating evaporator and twice recrystallized from water. Other chemicals were Carlo Erba analytical grade. Conductivity water was used to prepare solutions of the reactants and was used as a reaction medium. Stock solutions of salicylic acid were standardized by potentiometric titrations with NaOH whereas the aluminum perchlorate solutions were standardized by gravimetry.[15] Fresh solutions were always used in order to prevent possible polymerization.[10] It should be noted however that studies[16,17] on aluminum salt solutions tend to exclude dimerization or polymerization.

Titrations of solutions containing the ligand alone and metal–ligand mixtures were carried out in a thermostated vessel using a Metrohm E 388 potentiometer and a combined calomel–glass electrode. The titrating agent, NaOH, was added with an "Agla" microsyringe. A stream of purified nitrogen was passed through the solution during each experiment to avoid CO_2 absorption.

Kinetic measurements were carried out with a Durrum stopped-flow apparatus by recording the decrease of transmittance due to complex formation (and the increase of transmittance for the reverse reaction) at 310 nm. Pseudo-first-order conditions were attained by working in the presence of excess of aluminum perchlorate and in solutions buffered with sodium chloroacetate–chloroacetic acid mixtures (the buffer was found to be inert toward aluminum ions). The course of the reverse reaction was studied by allowing the complex to decompose in the presence of excess perchloric acid. Sodium perchlorate was used to obtain the desired ionic strength.

Calculations of stability and rate constants were performed with an IBM 370 computer.

Results

When aluminum ion is added to a solution of salicylic acid, a change in the spectrum of the acid is observed. This result is shown in Figure 1 where the spectra of aqueous solutions of salicylic acid alone and those in the presence of $Al(ClO_4)_3$ in the ratio 1:10 at different acidities are reported. We have also established, by means of indicators and pH measurements, that a remarkable increase of $[H^+]$ is produced as a result of the overall complexation reaction.

Equilibrium Constants. Das and Aditya[18] showed, by the method of continuous variations, that the molar ratio of Al^{3+} to salicylic acid in the complex is 1:1. The reaction which, on these grounds, represents the equilibrium between the complex and the reactants is

$$Al^{3+} + HA^- \rightleftharpoons AlA^+ + H^+ \tag{1}$$

where HA^- is the salicylate ion, and its equilibrium quotient is

$$Q = [H^+][AlA^+]/[Al^{3+}][HA^-] \tag{2}$$

In order to calculate *Q* the following equilibrium quotients and mass and charge balance equations must be considered

$$Q_A = [H^+][HA^-]/[H_2A] \tag{3}$$

$$Q_H = [H^+][AlOH^{2+}]/[Al^{3+}] \tag{4}$$

$$C_L = [H_2A] + [HA^-] + [AlA^+] \tag{5}$$

$$C_M = [Al^{3+}] + [AlOH^{2+}] + [AlA^+] \tag{6}$$

$$[Na^+] + [H^+] + [AlA^+] + 2[AlOH^{2+}] + 3[Al^{3+}] = [HA^-] + [ClO_4^-] \tag{7}$$

where $[Na^+] = [NaOH]_{added}$ and $[ClO_4^-] = 3C_M$. After

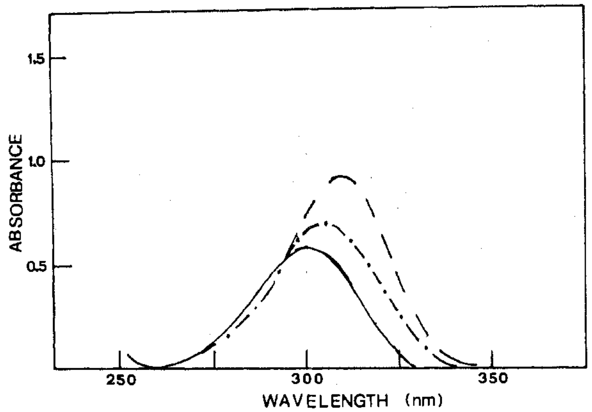


Figure 1. Ultraviolet absorption spectra of 10^{-3} *M* salicylic acid alone and spectra in the presence of 10^{-2} *M* $Al(ClO_4)_3$ at pH 1.2 (——), 10^{-3} *M* salicylic acid + 10^{-2} *M* $Al(ClO_4)_3$, at pH 2.1 (- · -), and at pH 3.0 (– –).

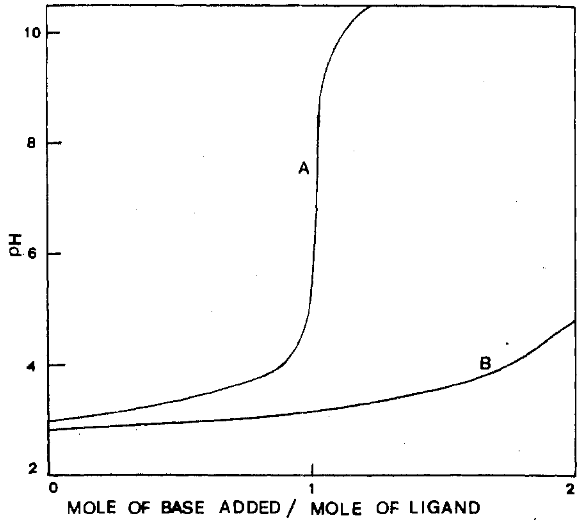


Figure 2. Titration curves of salicylic acid (A) and 1:1 metal-ligand (B) solutions at 25° and ionic strength 0.1 *M*.

Table I. Equilibrium Quotients for Aluminum Ion Hydrolysis, pQ_H, Salicylic Acid Dissociation, pQ_A, and Aluminum-Salicylate Complex Formation, *Q*, at Different Ionic Strengths and Temperatures

I, *M*	*T*, °C	pQ_H[a]	pQ_A	*Q*
0.02	25	5.21	2.96	1.60
0.05	25	5.19	2.89	1.57
0.075	25	5.14	2.77	1.50
0.10	25	5.08	2.69	1.33
0.15	25	4.93	2.61	1.12
0.20	25	4.76	2.52	1.04
0.10	23	5.15	2.70	1.25
0.10	28	4.98	2.66	1.63
0.10	32	4.85	2.63	1.94
0.10	36	4.72	2.60	2.29
0.10	43	4.51	2.58	2.81

[a] Obtained from data of ref 22.

appropriate substitutions and rearrangements one obtains

$$[Al^{3+}] = \frac{([NaOH]_{added} + [H^+] - 2C_M) - (C_L - C_M)/(1 + [H^+]/Q_A)}{(1 + Q_H/[H^+])/(1 + [H^+]/Q_A) - Q_H/[H^+] - 2} \qquad (8)$$

$$[HA^-] = \frac{(C_L - C_M) + [Al^{3+}](1 + Q_H/[H^+])}{1 + [H^+]/Q_A} \qquad (9)$$

$$[AlA^+] = C_M - [Al^{3+}](1 + Q_H/[H^+]) \qquad (10)$$

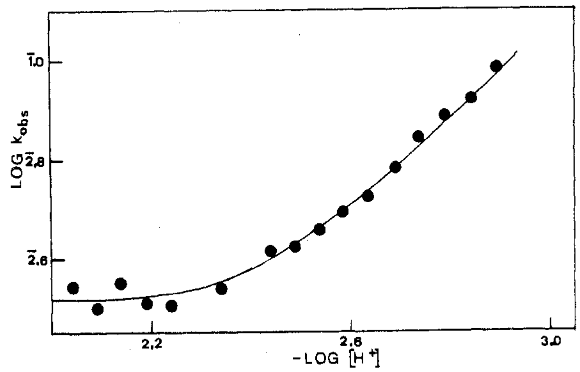


Figure 3. Plot of log k_{obsd} against $-\log [H^+]$ at $[Al^{3+}] = 10^{-2}$ *M*, 25°, and *I* = 0.1 *M*.

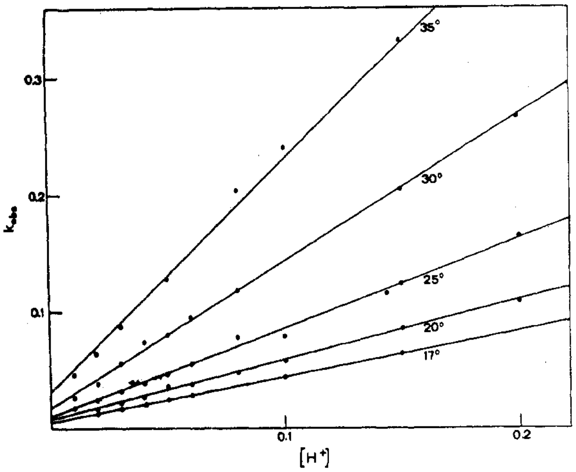


Figure 4. Plots of k_{obsd}(reverse reaction) against $[H^+]$ at different temperatures.

The preceding equations, when substituted in eq 2, yield the required *Q*. The hydrogen ion concentrations necessary to calculate Q_A and *Q* were derived from pH values along the corresponding titration curves (Figure 2) by using the Davies equation[19] with *B* = 0.2. Each value of *Q* quoted in Table I represents the average of the values calculated from 25 different points along the corresponding titration curve with a standard deviation of ca. 10%. To estimate the thermodynamic constants of equilibria 2–4 we used the equation[20,21]

$$pR - 0.51(\Sigma z^2)\frac{I^{1/2}}{1 + I^{1/2}} = pK - B'I \qquad (11)$$

where for $R = Q$ $\sum z^2 = 8$, for $R = Q_A$ $\sum z^2 = -2$, and for $R = Q_H$ $\sum z^2 = 4$. Plots of the left-hand side of eq 11 against *I* are linear and give at 25° p*K* = −0.74, *B'* = 3.5, pK_A = 3.10, *B'* = 1.4, and pK_H = 5.05, *B'* = 4.6. To make the plot for the latter case we derived the Q_H values from pH data already published[22] at ionic strengths up to 0.06 *M* and different temperatures. With the appropriate values of slope and intercepts we obtained, by use of eq 11, the Q_H values quoted in Table I.

The enthalpy and entropy of reaction 1 have been calculated from the temperature dependence of *Q* and are $\Delta H° = 7.8 \pm 0.5$ kcal mol^{-1} and $\Delta S° = 27$ eu.

Rate Constants. The pseudo-first-order rate constants, k_{obsd}, obtained from slopes of log $(D_\infty - D)$ against time plots are independent of the initial concentration of salicylate ion provided that this does not exceed 5×10^{-4} *M*. Beyond this value a slight increase of rate is observed. Plots of k_{obsd} against $[Al^{3+}]$ at different constant acidities show that, together with paths first order in aluminum ion, also paths independent of

Al^{3+} are operative. A plot of log k_{obsd} against $-\log [H^+]$ at constant $[Al^{3+}]$ is shown in Figure 3. In the range of $-\log [H^+] = 2/2.3$ the rate constant is apparently independent of the acidity, whereas at lower hydrogen ion concentrations a path inversely proportional to $[H^+]$ becomes more and more important. At pH >3 a further increase in rate is indicative of the occurrence of an additive path inversely proportional to a power of $[H^+]$ higher than unity. In the range of the explored acidity this path is negligible. On the other hand the rate of complex decomposition was investigated by allowing mixtures of salicylate and aluminum ions at pH 4.5 (not buffered) to react with perchloric acid. The reaction is first order in complex concentration and k_{obsd} increases linearly with $[H^+]$ as shown in Figure 4, where the results at different temperatures are plotted.

The results are rationalized by the reaction scheme

$$Al^{3+} + HA^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlA^+ + H^+ \qquad (12)$$

$$Al^{3+} \overset{Q_H}{\rightleftharpoons} AlOH^{2+} + H^+ \qquad (13)$$

$$AlOH^{2+} + HA^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AlA^+ + H_2O \qquad (14)$$

where reaction 13 is known to be a fast equilibrium. According to this scheme the observed rate constant is

$$k_{obsd} = \left(k_1 + \frac{k_2'}{[H^+]}\right)\frac{[Al^{3+}]}{1 + [H^+]/Q_A} + k_{-1}[H^+] + k_{-2} \qquad (15)$$

A statistical analysis based on the least-squares treatment[23] of 41 runs was applied to eq 15. The parameters so obtained are $k_1 = (9.1 \pm 1.0) \times 10^{-1}\ M^{-1}\ sec^{-1}$, $k_{-1} = (7.8 \pm 0.2) \times 10^{-1}\ M^{-1}\ sec^{-1}$, $k_2' = k_2Q_H = (8.5 \pm 0.4) \times 10^{-3}\ sec^{-1}$, and $k_{-2} = (7.9 \pm 1.0) \times 10^{-3}\ sec^{-1}$. The observed rate constants calculated with these values in eq 15 agree with the experimental values with a percent standard deviation[23] $[(\sum(1 - k_{obsd}/k_{calcd})^2/(N - 4))^{1/2}]$ of 9.4%. In addition the values of k_{-1} and k_{-2} obtained with this treatment are in very good agreement with those derived from the plot of Figure 4 at 25° which refers to the reverse reaction. The treatment was also performed by setting $k_1/k_{-1} = Q$ and reducing to 3 the number of parameters to be evaluated. In this case we obtained $k_{-1} = (7.8 \pm 1.0) \times 10^{-1}\ M^{-1}\ sec^{-1}$, $k_2' = (8.3 \pm 0.3) \times 10^{-3}\ sec^{-1}$, $k_{-2} = (7.4 \pm 1.1) \times 10^{-3}\ sec^{-1}$, and $k_1 = k_{-1}Q = 1.04 \pm 0.1\ M^{-1}\ sec^{-1}$ with a standard deviation of 9.6%. From the values of k_{-1} and k_{-2} at different temperatures (Figure 4) we obtained $\Delta H^{\ddagger}(k_{-1}) = 16.0 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_{-1}) = -5.6$ eu, $\Delta H^{\ddagger}(k_{-2}) = 14.3 \pm 1.5$ kcal mol^{-1}, and $\Delta S^{\ddagger}(k_{-2}) = -20$ eu. Moreover, with $k_1 = k_{-1}Q$, from the known temperature dependence of Q it was calculated that $\Delta H^{\ddagger}(k_1) = 24.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger}(k_1) = 24$ eu.

Discussion

The thermodynamic dissociation constant of salicylic acid at 25° (pK_A = 3.10) is lower than the value reported in the literature (3.00),[24] whereas the thermodynamic constant of reaction 1 ($K = 5.6$) is somewhat higher than that we derived from the spectrophotometric data of Das and Aditya[18] after introducing a correction for hydrolysis of Al^{3+} ion ($K = 4.8$). These differences might be due to the different experimental conditions and to the shortcoming of the equation used to extrapolate the data at $I = 0$.

As far as the kinetics is concerned it should be noted that according to eq 12–14 it must be that $k_1/k_{-1} = k_2'/k_{-2} = Q$. The rate constants evaluated by the least-squares analysis as independent parameters give the ratios $k_1/k_{-1} = 1.2$ and $k_2'/k_{-2} = 1.1$. These ratios agree between themselves and with the experimental values of the equilibrium quotient ($Q = 1.33$ by potentiometry and $Q = 1.16$ by spectrophotometry[15]) and this confirms the validity of scheme (eq 12–14).

The kinetic behavior of this system can be interpreted in terms of the dissociative mechanism proposed by Eigen[25] which involves the presence of an ion pair in fast equilibrium with the reactants, i.e.

$$(H_2O)_6Al^{3+} + HA^- \rightleftharpoons (H_2O)_5Al(H_2O),HA^{2+} \quad K_0 \qquad (16)$$

$$(H_2O)_5Al(H_2O),HA^{2+} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (H_2O)_5AlHA^{2+} + H_2O \qquad (17)$$

$$(H_2O)_5AlHA \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} (H_2O)_4AlA + H_3O^+ \quad K_3 \qquad (18)$$

Step 18 includes elimination of H_3O^+ and ring closure. Steady-state conditions for intermediates give

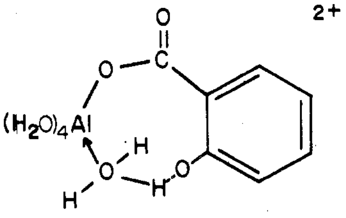
$$k_1 = \frac{K_0k_{12}k_{13}}{k_{21} + k_{13}} \qquad (19)$$

$$k_{-1} = \frac{k_{21}k_{31}}{k_{21} + k_{13}} \qquad (20)$$

The ion-pair formation constant of two ions of charge 3+ and 1−, calculated with the Fuoss equation,[26] is $K_0 = 5.3\ M$ at $I = 0.1\ M$ and 25° if the distance of closest approach is set at 5 Å. From the experimental k_1 one can therefore estimate the rate constant of ligand penetration $k_{12} = 0.17$ sec^{-1}. This value is in excellent agreement with the rate constant of water exchange of the $Al(H_2O)_6^{3+}$ ion, $k_{H_2O} = 0.13$–0.22 sec^{-1} at 25°, as measured by NMR.[27] Our value of k_{12} should be also compared with the corresponding values of 0.63 and 0.085 sec^{-1} which have been directly measured by pressure jump for $AlFe(CN)_6$[13] and $AlCo(CN)_6$[14] systems, respectively. This means (eq 19) that $k_{21} << k_{13}$. Such a result shows that the forward reaction is not controlled by steric factors as ring closure and the key process is the exit from the inner coordination sphere of the metal ion of a water molecule (step 17). This conclusion is also strongly supported by a comparison of the activation parameters of path k_1 with those of the water-exchange reaction[27] which are $\Delta H^{\ddagger}(k_{H_2O}) = 27$ kcal mol^{-1} and $\Delta S^{\ddagger}(k_{H_2O}) = 28$ eu. If one considers that for the ion-pair formation (step 16), at 25° and $I = 0.1\ M$, $\Delta H° = 0.43$ kcal mol^{-1} and $\Delta S° = 4.7$ eu, the calculated values $\Delta H^{\ddagger}(k_1)_{calcd} = 27.4$ kcal mol^{-1} and $\Delta S^{\ddagger}(k_1)_{calcd} = 32.7$ eu are in fair agreement with the experimental.

The path inversely proportional to $[H^+]$ (eq 13 and 14) may also be discussed in similar terms. An ion pair involving $AlOH^{2+}$ and HA^- ions is rapidly formed and the loss of a water molecule from $Al(H_2O)_5OH,HA^+$ is rate determining. Subsequently the elimination of a second water molecule and ring closure give the product $Al(H_2O)_4A^+$. The rate constant of path 14, $k_2 = k_2'/Q_H$, is higher with respect to k_1 by a factor of 1.1×10^3 whereas from electrostatics $AlOH^{2+}$ would be expected to react with HA^- more slowly than Al^{3+}. This situation, which is common to the reactions of iron(III),[3,5-8] may arise from the labilization of the water molecules around the metal ion caused by the presence of a hydroxide group in the coordination shell.

As far as the reverse path is concerned, since $k_{21} << k_{13}$, k_{-1} must equal k_{21}/K_3. According to the principle of microscopic reversibility the rate-determining step should be the entry of a water molecule into the inner coordination sphere, while the ligand is already in the outer sphere.[8] This step is preceded by fast opening of the chelate ring, the free end of which is trapped by a proton coming from H_3O^+ or H_2O so that the possibility of closure is slowed down. In the same time a water molecule (I) and a hydroxide group for path k_{-2} (II) penetrate the vacated site.



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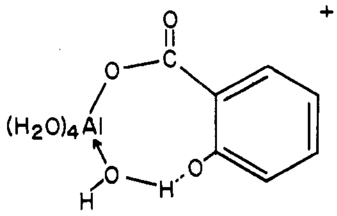

II

Our results can be compared with those of the reaction between Al^{3+} and SO_4^{2-}.[10] Assuming that the rate constant for water loss is independent of the charge of the "outer" ligand, the ratio of the experimental rate constants, k_1, of the two systems should be determined by the ratio of the respective K_0's, the ion-pair formation constants. From the value of the rate constant for penetration of SO_4^{2-} ion into the coordination sphere of the hexaaquoaluminum ion (15 M^{-1} sec^{-1} at $I = 0.6$ M) we derived at $I = 0.1$ M the value of 28.8 M^{-1} sec^{-1} by setting in the Davies equation $B = 0.3$, as done by the authors of ref 10. This divided by k_1 of the aluminum–salicylate system gives 31. The ratio of the corresponding ion–pair constants is 17. The agreement is to be considered good in view of the fact that the latter ratio is strongly dependent on the distance of closest approach of the reactants which is arbitrarily chosen, as on the other hand the choice of the Davies B is arbitrary. For our purpose it is worth mentioning that the experimentally found B of the reaction between nickel(II) and $HP_2O_7^-$ ions[28] is 0.45, a value remarkably higher than usual.

This comparison shows that the basicity of the ligand plays no role in the reactions of aluminum ion and this fact tends to discourage the hypothesis of a reaction between $AlOH^{2+}$ and the protonated form of the ligand, which is instead supported in the case of reactions of iron(III) with sulfate, fluoride, azide, and substituted phenolates. It has been demonstrated[7] that the tendency of Fe(III) to react in the form $Fe(OH)^{2+}$ increases with the ligand basicity. From this one can infer that for a given basic ligand the possibility that a metal ion reacts in the hydrolyzed form increases with its acid strength. In other words the formation of the ion pair $M(H_2O)_5OH,HL$ "via" previous hydrolysis of the hexaaquo ion or "via" internal hydrolysis[29] is made more difficult for aluminum than for iron(III) ion since $Al(H_2O)_6^{3+}$ is a much weaker acid than $Fe(OH)_6^{3+}$ ion and its contribution to the process of proton donation to the ligand is therefore weaker.

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Registry No. $Al(H_2O)_4A^+$, 55236-45-8.

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