Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. XXV. Composition and Stability of Aluminium Complexes with Methylmalonic Acid and Alanine

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Equilibria in the title systems have been studied by means of potentiometric (glass electrode) measurements in 0.6 M Na(Cl) medium at 25 °C. In the system H^+–Al^{3+}–methylmalonic acid the aluminium complexation is characterized by the formation of binary AlL_n^{3-2n} ($n = 1, 2, 3$) species. Equilibrium constants, defined according to the reaction

$$pH^+ + qAl^{3+} + rH_2L \rightleftharpoons H_pAl_q(H_2L)_r^{p+3q}$$

are $\log\beta_{-2,1,1} = -2.213\pm0.0064$, $\log\beta_{-4,1,2} = -5.73\pm0.010$ and $\log\beta_{-6,1,3} = -11.19\pm0.040$. With alanine, the aluminium complexation is negligible within the concentration ranges investigated (ligand to metal ratio ≤ 5; $-\log[H^+] \leq 4.3$). The dissociation constants for the ligands were determined in separate experiments. They were found to be $\log\beta_{-1,0,1} = -2.772\pm0.0012$ and $\log\beta_{-2,0,1} = -7.863\pm0.0018$ for methylmalonic acid. In the alanine system, the evaluation resulted in $\log\beta_{1,0,1} = 2.380\pm0.0011$ and $\log\beta_{-1,0,1} = -9.680\pm0.0052$. All errors reported are $3\sigma(\log\beta_{p,q,r})$. Data were analysed using the least-squares computer program LETAGROPVRID.

In a series of investigations in progress in this department, the ability of Si(IV) and Al(III) to form complexes in aqueous solution with naturally occurring inorganic and organic ligands is being studied. From the results obtained, the significance and importance of mixed ternary aluminium–hydroxo–ligand complexes have been clearly demonstrated.

In three recent parts of this series we have described the aluminium complexation to the organic ligands propionic acid[1] and lactic acid[2,3] (α-hydroxypropionic acid). From the results obtained, it can be concluded that the effect of the α-hydroxy substituent is quite considerable with respect to both the stoichiometry and the stability of the complexes formed. The probable cause of this phenomenon is that with an α-hydroxy group the acid can act as a bidentate ligand towards aluminium.

The aim of the present paper is to continue this line of investigation. The ligands chosen for this work were methylmalonic acid (α-carboxypropionic acid) and alanine (α-aminopropionic acid). Comparisons between ligand class, speciation and stability of the complexes formed can be made with regard to substituents on the same carbon atom.

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Experimental

Chemicals and analysis. Methylmalonic acid ($C_4H_6O_4$) (Fluka p.a.) and DL-alanine ($C_3H_7NO_2$) (Merck p.a.) were used after drying but without further purification. Stock solutions of methylmalonic acid were prepared by dissolving the acid in 0.6 M Na(Cl) medium, whereas the alanine solutions were prepared by dissolution of the solid in standardized hydrochloric acid in 0.6 M Na(Cl). The ligand concentrations were determined potentiometrically using the Gran extrapolation method;[4] for both ligands they were found to be 0.6 % lower than the values expected from weighing. Stock solutions of sodium chloride and aluminium chloride, and the dilute hydrochloric acid and sodium hydroxide solutions, were prepared and standardized as described earlier.[2]

Apparatus. The automatic system for precise EMF titrations, the thermostat and the electrodes have been described earlier.[2]

Method. The present investigation has been carried out as a series of potentiometric titrations at 25 °C in a constant ionic medium of 0.6 M Na(Cl). The titration procedures, calibrations and the assumptions made in connection with the use of the glass electrode were the same as described earlier.[2] The reproducibility and reversibility of equilibria

were tested by performing both forward titrations (increasing $-\log[H^+]$ by means of addition of OH^-) and backward titrations (decreasing $-\log[H^+]$ by means of addition of H^+).

The dissociation constants for methylmalonic acid and alanine were determined in separate titrations within the concentration ranges $0.004 \le C \le 0.038$ M $(1.9 \le -\log[H^+] \le 7.2)$ and $0.005 \le C \le 0.021$ M $(1.8 \le -\log[H^+] \le 9.3)$, respectively.

The three-component titrations were performed at constant C/B ratios [where B and C stand for the total concentration of aluminium(III) and ligand, respectively]. In the methylmalonic acid system, B and C were varied within the limits $0.001 \le B \le 0.006$ M and $0.002 \le C \le 0.036$ M, with $C/B = 0.33, 0.5, 1, 2, 3, 4, 5, 10$ and 30 and $2.0 \le -\log[H^+] \le 6.3$. Corresponding data for the alanine system were: $0.002 \le B \le 0.005$ M; $0.005 \le C \le 0.012$ M; $C/B = 1, 2, 3, 4$ and 5 and $1.9 \le -\log[H^+] \le 4.3$.
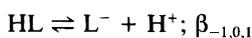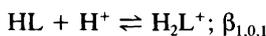
With methylmalonic acid, the upper $-\log[H^+]$ limits for data collection at $C/B > 1$ were set by the formation of a precipitate, and at $C/B \le 1$ by the observation of extremely slow equilibration, caused by the formation of the polynuclear Al-hydrolysis product $Al_{13}O_4(OH)_{24}^{7+}$. The formation of this species also set the upper $-\log[H^+]$ limit in the alanine system.

Data treatment. According to the different types of equilibria which must be considered, the present study can be divided into parts as follows:
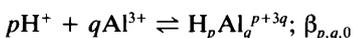
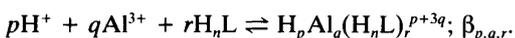(i) the binary methylmalonic acid equilibria:

$$H_2L \rightleftharpoons HL^- + H^+; \ \beta_{-1,0,1}$$

$$H_2L \rightleftharpoons L^{2-} + 2H^+; \ \beta_{-2,0,1}$$
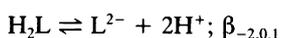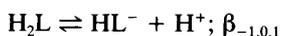
(ii) the binary alanine equilibria:

$$HL + H^+ \rightleftharpoons H_2L^+; \ \beta_{1,0,1}$$

$$HL \rightleftharpoons L^- + H^+; \ \beta_{-1,0,1}$$

(iii) the hydrolytic equilibria of Al^{3+}:

$$pH^+ + qAl^{3+} \rightleftharpoons H_pAl_q^{p+3q}; \ \beta_{p,q,0}$$

(iv) three-component equilibria of the general form:

$$pH^+ + qAl^{3+} + rH_nL \rightleftharpoons H_pAl_q(H_nL)_r^{p+3q}; \ \beta_{p,q,r}.$$

In previous parts of this series,[3,5-7] where experiments were also performed in 0.6 M Na(Cl) medium at 25 °C, we have shown that the main hydrolytic complexes formed by aluminium, with their corresponding equilibrium constants, are: $Al(OH)^{2+}$ $(\log\beta_{-1,1,0} = -5.52)$; $Al(OH)_2^+$ $(\log\beta_{-2,1,0} = -11.3)$; $Al(OH)_3$ $(\log\beta_{-3,1,0} = -17.3)$; $Al_3(OH)_4^{5+}$ $(\log\beta_{-4,3,0} = -13.57)$; $Al_{13}O_4(OH)_{24}^{7+}$ $(\log\beta_{-32,13,0} =$

-109.2, fresh, low hydroxide to aluminium ratio[5] or -105.5, aged, high hydroxide to aluminium ratio[3]) and $Al(OH)_4^-$ $(\log\beta_{-4,1,0} = -23.46)$.

The ligand dissociation constants were evaluated from separate experiments, and, in the evaluation of the three-component experimental data, the binary complex models (i, ii and iii) were considered as known. Thus, all effects above this level were treated as being caused by the formation of three-component species. The mathematical analysis of data was performed with the least-squares computer program LETAGROPVRID[8] (version ETITR).[9,10] The pqr-triplets and the corresponding equilibrium constants that provided the "best" fit to the experimental data were determined by minimizing the error square sum $U = \Sigma(H_{calc} - H_{exp})^2$. H_{calc} and H_{exp} denote the calculated and experimental values of the analytical H^+ concentration, respectively, calculated over the zero level H_2O, Al^{3+} and H_nL. The standard deviations $\sigma(H)$ and $3\sigma(\log\beta_{pqr})$, obtained in the LETAGROP calculations, were defined and calculated according to Sillén.[11,12] The computations were performed on a CD CYBER 850 computer.

Data, calculations and results

The H^+–methylmalonic acid system. Data used to evaluate the acidity constants for methylmalonic acid comprised 13 titrations with 493 experimental points within the concentration range $0.004 \le C \le 0.038$ M and $1.9 \le -\log[H^+] \le 7.2$. A LETAGROP calculation on these data ended at $\sigma(H) = 0.07\times10^{-3}$ M, giving $\log\beta_{-1,0,1} = -2.772\pm0.0012$ and $\log\beta_{-2,0,1} = -7.863\pm0.0018$.

The H^+–Al^{3+}–methylmalonic acid system. These data comprised 17 titrations (509 experimental points) within the
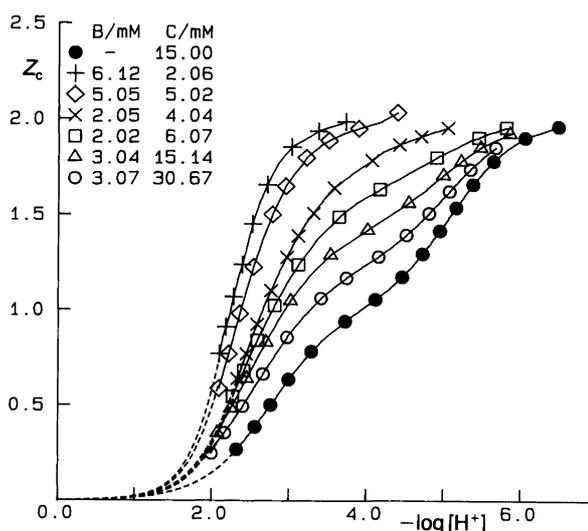

Fig. 1. Some of the experimental data in the H^+–Al^{3+}–methylmalonic acid system plotted as curves $Z_c(-\log[H^+])$. The drawn curves have been calculated with the constants proposed in Table 1. The broken curves denote an extrapolation of the present model.

Table 1. Results of the final LETAGROP calculations for the systems H^+–Al^{3+}–methylmalonic acid and H^+–Al^{3+}–alanine. The equilibrium constants ($\log \beta_{pqr}$) are defined according to the reaction $pH^+ + qAl^{3+} + rH_nL \rightleftharpoons H_pAl_q(H_nL)_r^{p+3q}$.

No. of titrations/ No. of points	p,q,r	Proposed formula	$\log (\beta_{pqr} \pm 3\sigma)$
H^+–Al^{3+}–methylmalonic acid			
13/493	−1,0,1	HL^-	−2.772±0.0012
	−2,0,1	L^{2-}	−7.863±0.0018
17/509	−2,1,1	AlL^+	−2.213±0.0064
	−4,1,2	AlL_2^-	−5.73±0.010
	−6,1,3	AlL_3^{3-}	−11.19±0.040
H^+–Al^{3+}–alanine			
6/188	1,0,1	H_2L^+	2.380±0.0011
	−1,0,1	L^-	−9.680±0.005
5/139	a	a	a

^{a}No stable Al–alanine complexes are formed at $C/B \leq 5$ and $-\log[H^+] \leq 4.3$.
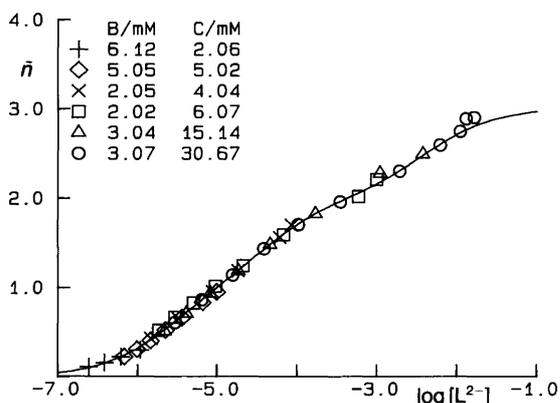

Fig. 2. Experimental data in the H^+–Al^{3+}–methylmalonic acid system plotted as curves $\bar{n}(\log[L^{2-}])$. The full curve has been calculated with equilibrium constants given in Table 1.
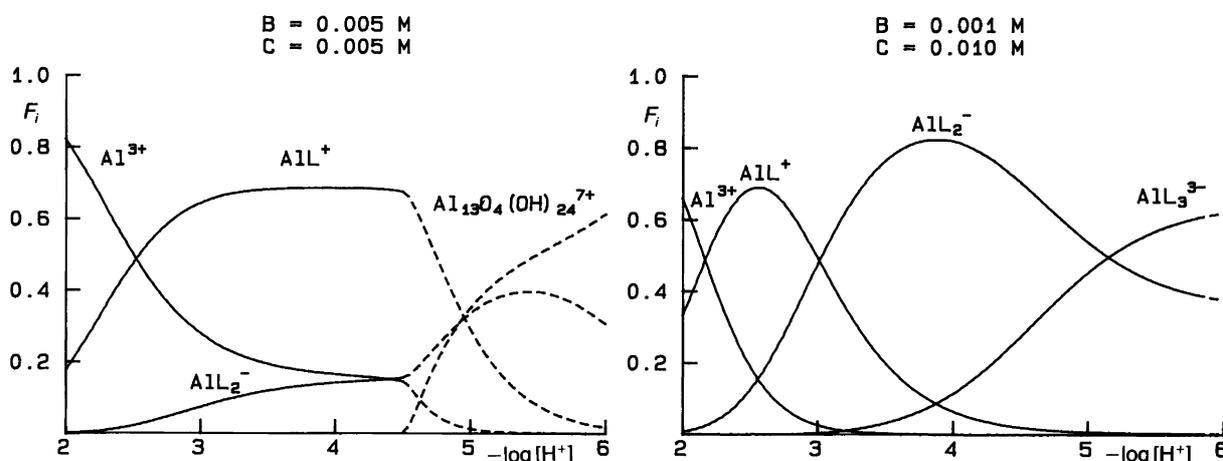
ranges $0.001 \leq B \leq 0.006$ M, $0.002 \leq C \leq 0.036$ M and $2.0 \leq -\log[H^+] \leq 6.3$, and covering the following C/B ratios: 0.33, 0.5, 1, 2, 3, 4, 5, 10 and 30. The analysis of titration data was started by constructing a $Z_c(-\log[H^+])$ plot and a Bjerrum plot $\bar{n}(\log[L^{2-}])$; these are shown in Figs. 1 and 2. From Fig. 1, which gives the average number of OH^- reacted per H_2L as a function of $-\log[H^+]$, it can be noted that, at all ratios, Z_c reaches a limiting value of 2.0. This indicates that binary AlL_n^{3-2n} complexes are the predominant products. Further, from Fig. 2, which gives the average number of L^{2-} coordinated per aluminium as a function of the free ligand concentration, it was concluded that as all curves coincide, the data can be explained by the formation of a series of AlL_n^{3-2n} species. Also, since $\bar{n}$ reaches a limiting value of 3, it was concluded that the last step in complex formation is the species AlL_3^{3-}.

The LETAGROP calculation was therefore performed directly on all data, and the formation constants for AlL^+, AlL_2^- and AlL_3^{3-} were refined simultaneously. This calculation ended at $\sigma(H) = 0.06 \times 10^{-3}$ M, and the equilibrium constants obtained were: $\log \beta_{-2,1,1} = -2.213 \pm 0.0064$, $\log \beta_{-4,1,2} = -5.73 \pm 0.010$ and $\log \beta_{-6,1,3} = -11.19 \pm 0.040$. With this set of formation constants, no remaining systematic deviations in $H_{calc} - H_{exp}$ could be observed.

In order to visualize the fractions of the different species at equilibrium as a function of $-\log[H^+]$, the computer program SOLGASWATER[13] (equipped with plotting procedures) was used to calculate some distribution diagrams. These are presented in Fig. 3.

The H^+–alanine system. For the evaluation of this binary system, six titrations (188 experimental points) were performed. The concentration range studied was $0.005 \leq C \leq 0.021$ M, with $1.8 \leq -\log[H^+] \leq 9.3$. The following equilibrium constants were obtained: $\log \beta_{1,0,1} = 2.380 \pm 0.0011$ and $\log \beta_{-1,0,1} = -9.680 \pm 0.0052$ with a resulting $\sigma(H) = 0.04 \times 10^{-3}$ M.
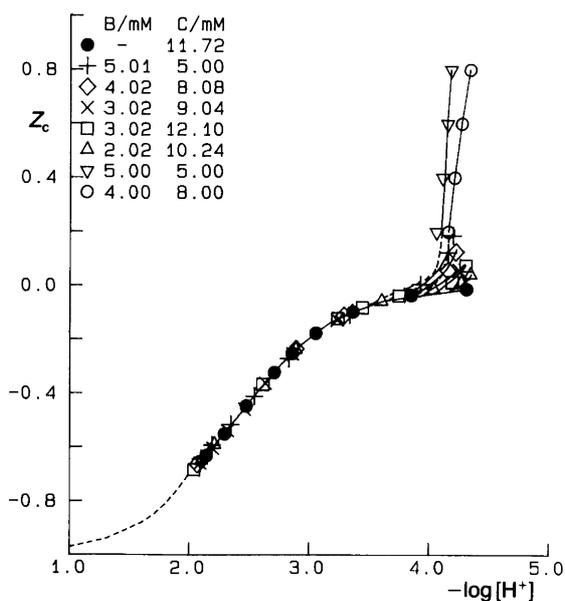

Fig. 3. Distribution diagrams for the H^+–Al^{3+}–methylmalonic acid system. F_i is defined as the ratio between aluminium(III) in a species and total aluminium(III). Broken curves denote extrapolated values.

Fig. 4. Experimental data for the H^+–Al^{3+}–alanine system plotted as curves $Z_c(-\log[H^+])$. The broken curve denotes an extrapolation of the present model. Note that the titration symbols denotes initial concentrations and that the actual concentrations in the last point of the 5.01/5.00 titration are 4.11/4.10.

The H^+-Al^{3+}-alanine system. Data used for the evaluation of the ternary system comprised five titrations with 131 experimental points within the limits $0.002 \le B \le 0.005$ M; $0.005 \le C \le 0.012$ M and $1.9 \le -\log[H^+] \le 4.3$. The C/B ratios 1, 2, 3, 4 and 5 were investigated. In addition, these data were supplemented with data from eight batch solutions ($C/B = 1$ and 2; $4.0 \le -\log[H^+] \le 4.3$) which had been aged for prolonged periods. The experimental data are visualized in the form of a $Z_c(-\log[H^+])$ plot in Fig. 4; this indicates that the acid–base behaviour of the system is independent of the presence of aluminium ions at $-\log[H^+] \le 4.0$. It can therefore be concluded that, in this region, aluminium forms no (or at least extremely weak) complexes with alanine. With $-\log[H^+] > 4$ a marked increase in equilibration times was observed; for this reason measurements on the series of batch solutions were necessary. We have earlier determined the equilibrium constant for the slowly forming aluminium hydrolysis species $Al_{13}O_4$ $(OH)_{24}^{7+}$ in aged solutions.[3] When this equilibrium constant was applied to data at $-\log[H^+] > 4$, the apparent dependence on aluminium concentration noted in Fig. 4 was fully explained.

On the basis of these data it can therefore be concluded that alanine has an insignificant influence on the speciation of aluminium in slightly acidic solutions. Whether such interactions occur at higher $-\log[H^+]$ values can of course not be deduced from the present data.

Discussion

The purpose of the present study has been to investigate the composition and stability of the aluminium complexes formed with the ligands methylmalonic acid and alanine. From the results obtained it will also be possible to evaluate the effects of different substituents on the α-carbon of propionic acid.

With regard to the α-carboxypropionic acid, methylmalonic acid, the present study has shown that this ligand forms a series of AlL_n^{3-2n} complexes ($n = 1$–3) with the aluminium ion. From the high values of the stepwise constants ($\log K_n$), 5.65, 4.35 and 2.39, respectively, it can be concluded that these species contain bidentate methylmalonate dianions. The three mononuclear complexes can all form in significant amounts, and they predominate within the concentration ranges shown in Fig. 3. In the present system, there was no evidence for the formation of mixed hydroxo species.

A comparison with the oxalate[14] complexes clearly shows that the respective oxalate species AlL_n^{3-2n} are more stable ($\log K_1 = 5.97$, $\log K_2 = 4.96$ and $\log K_3 = 3.95$) than the methylmalonate species. This difference may arise from the higher stability of five-membered chelate rings (oxalate) compared to six-membered rings (methylmalonate). From this comparison it may also be concluded that the steric hindrance for the formation of AlL_3^{3-} is considerable higher for methylmalonate than for oxalate, as the difference in $\log K_3$ is much larger than the differences in $\log K_1$ and $\log K_2$.

In Fig. 5 the ability of various amounts of methylmalonic acid to increase the solubility of gibbsite ($\log^* K_{s0} = 9.6$)[15] is illustrated. From this figure it can be concluded that even very low concentrations of methylmalonic acid can be expected to cause a substantial solubilization of gibbsite in near neutral solutions. Compared to previously investi-
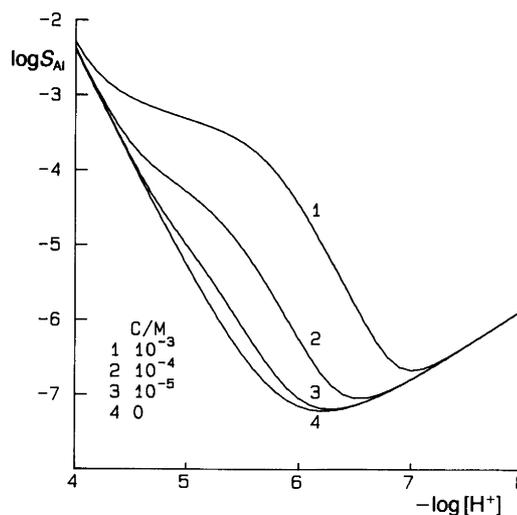

Fig. 5. Calculated solubility of gibbsite ($\log^* K_{s0} = 9.6$) expressed as a plot of $\log S_{Al}$ against $-\log[H^+]$ for different total concentrations of methylmalonic acid, C.

Table 2. A compilation of speciation and stability data for the complexes formed between aluminium(III) and α-substituted propionic acids. Log K for the species $Al_2(OH)_2L^{3+}$ is defined according to the reaction $2Al^{3+} + 2H_2O + L^- \rightleftharpoons Al_2(OH)_2L^{3+} + 2H^+$.

Ligand	pK_a	Speciation	log K_n			log K $Al_2(OH)_2L^{3+}$
			AlL	AlL$_2$	AlL$_3$	
Alanine	2.38, 9.68	c				
Propionic acid[a]	4.61	$Al_2(OH)_2L^{3+}$				−3.43
Lactic acid[b]	3.57	AlL^{2+}, AlL_2^+, AlL_3°; $Al(H_{-1}L)L^\circ$, $Al_2(OH)_2L^{3+}$, $Al_2(OH)_2(H_{-1}L)_2^\circ$, $H_{-36}Al_{13}(HL)_4^{3+}$	2.36	2.06	1.37	−3.29
Methylmalonic acid	2.77, 5.09	AlL^+, AlL_2^-, AlL_3^{3-}	5.65	4.35	2.39	

[a]Ref. 1. [b]Refs. 2 and 3. [c]No complexes at $-\log[H^+] \leq 4.3$.

gated ligands within the present series,[16] it can be stated that the complexation strength of methylmalonate is somewhat weaker than that of the oxalate ion, but considerably stronger than that of the lactate ion.[3]

With regard to α-aminopropionic acid, alanine, we have found that its interaction with the aluminium ion is negligible in weakly acidic solutions. This finding is in contrast to a recent report by Djurdjevic and Jelic,[17] in which the existence of two soluble species, $Al_2(OH)_2L_2^{2+}$ and $Al(OH)_3L^-$, was postulated. We have used the proposed stability constants from their paper to calculate a series of theoretical $Z_c(-\log[H^+])$ curves at different values of B, C and C/B. We found that the curves obtained showed a close resemblance to the effects measured by us in solutions with $-\log[H^+] \geq 4$. We are therefore of the opinion that these authors have mistakenly interpreted an effect from binary hydrolysis as being due to the formation of ternary complexes.

To compare the effects of different substituents on the α-carbon of propionic acid, Table 2 was constructed. From these data it can be concluded that the complexation strength towards aluminium decreases strongly in the order dicarboxylic acid $\gg$ hydroxycarboxylic acid $\gg$ carboxylic acid $\gg$ amino acid. The weakening effect of the $-NH_2$ substitution may be explained by the zwitterionic structure of amino acids in aqueous solutions, i.e. by the electrostatic repulsive effect of the $-NH_3^+$ group. This does not imply that the proton in R_3NH^+-containing ligands can not be displaced by coordination of aluminium. For example, very strong complexes are formed with nitrilotriacetic acid (NTA).[18] In these complexes the attractive force of the three carboxylate groups forces the nitrogen to coordinate to aluminium.

Another interesting feature concerning the speciation in the different systems is the inverse relation between the binary complexation strength and the importance of mixed hydroxo complexes. Thus, while the concentrations of the latter species are negligible in the strongly coordinating methylmalonate system, they dominate with the weakly

coordinating propionate ligand. With the lactate ion, which binds with an intermediate strength, both types of complexes can be observed.

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