Electronic Supplementary Information (ESI)

Stabilization of Al(III) solutions by complexation with cacodylic acid: speciation and binding features

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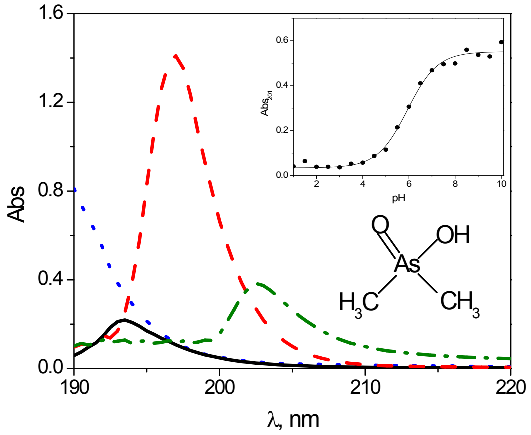


Fig. S1 Absorbance spectra of dimethylarsinic acid recorded at different pH. (•••) 1.0, (▬) 3.0, (---), 7.0, (- • -) 11.0. C_L = 1.0 × 10^{-3} M, I = 0.1 M ($NaClO_4$) and T = 25.0 °C. Inset: Absorbance variation with pH at for the HCac/Cac^- system at λ = 201 nm. For pH 3, the band with maximum at λ = 193 nm, should be related to the HCac form. Above pH 3, the spectrum shifts towards a new band centred at λ = 197 nm, ascribable to the dimethylarsinate anion (Cac-). Inside: change in absorbance upon titration in the 2-10 pH range.

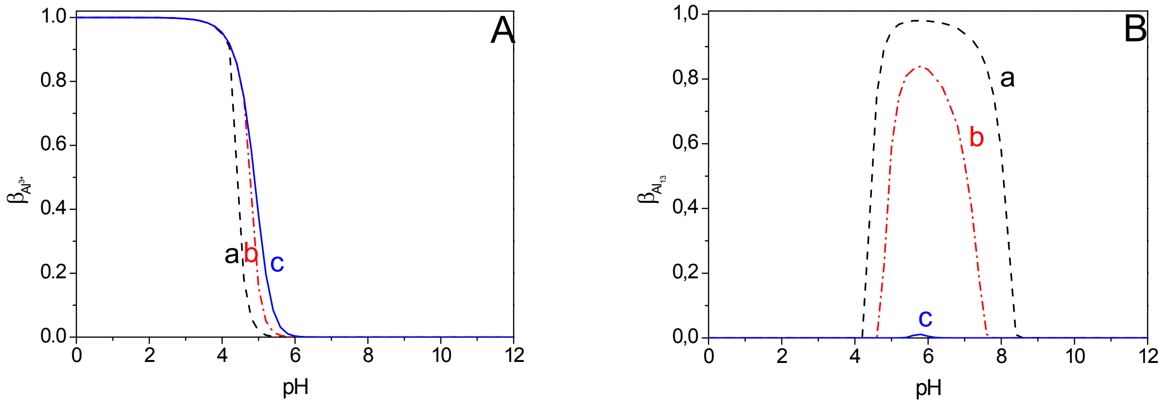
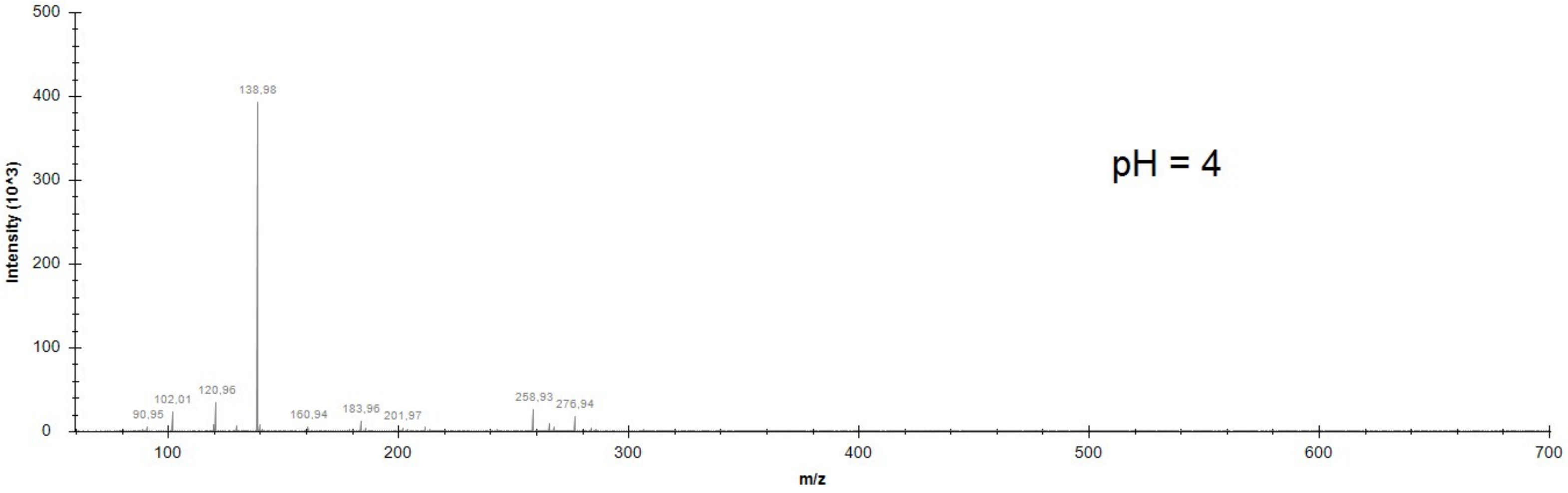


Fig. S2 (A) Molar fraction of Al^{3+} (β_{Al3+}) vs. pH at different analytical concentration of the metal, C_M. (B) Molar fraction of the polymeric aluminium (β_{Al12}) vs. pH at different C_M. (a) $C_M = 10^{-5}$ M, (b) $C_M = 10^{-4}$ M and (c) $C_M = 10^{-3}$ M. I = 0.1 M and T = 25.0°C.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300
200
100
0
m/z
100
200
300
400
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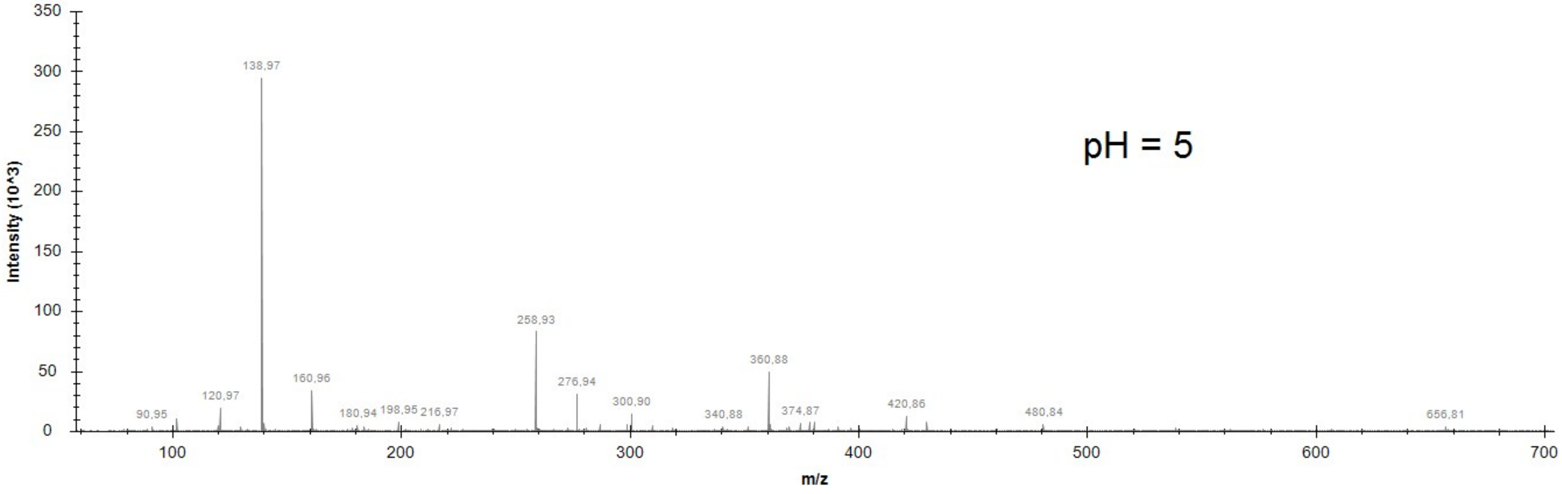
183,96
201,97
258,93
276,94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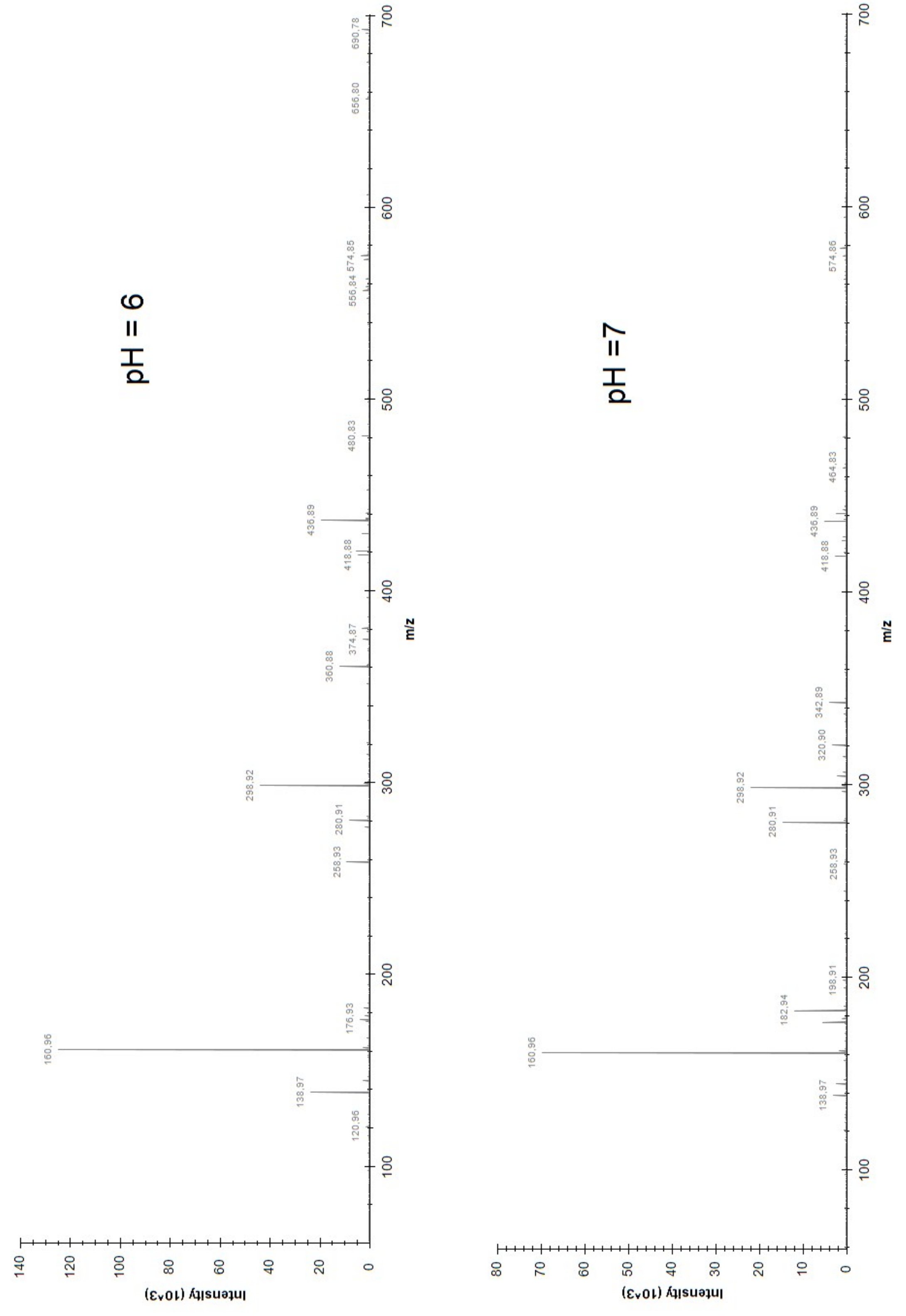


Fig. S3 Mass Spectra of Al/Cac solution at pH = 4.0, 5.0, 6.0 and 7.0. $C_M = 2.0 \times 10^{-4}$ M, $C_L = 2.0 \times 10^{-4}$ M, T = 25.0 °C.

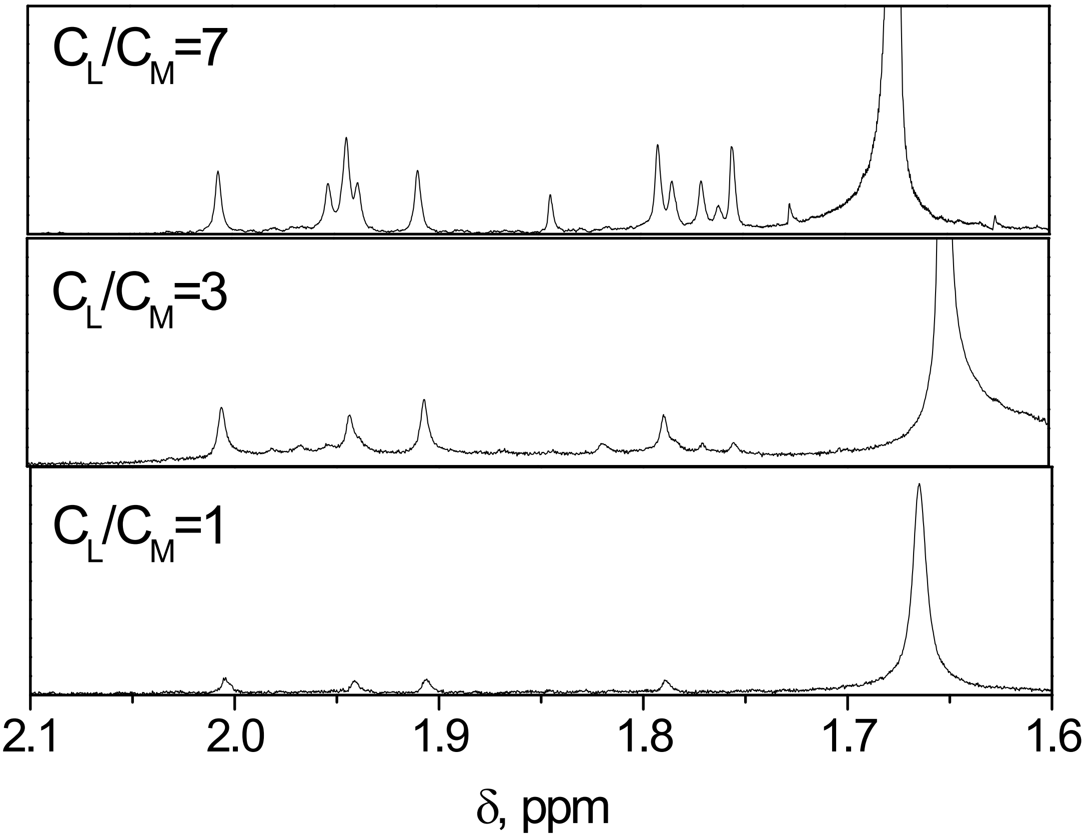


Fig. S4 NMR spectra of Al/Cac complexes at different C_L/C_M. $C_M = 1.0 \times 10^{-3}$ M, I = 0.1 M ($NaClO_4$), pH = 7.0, T = 25.0 °C.

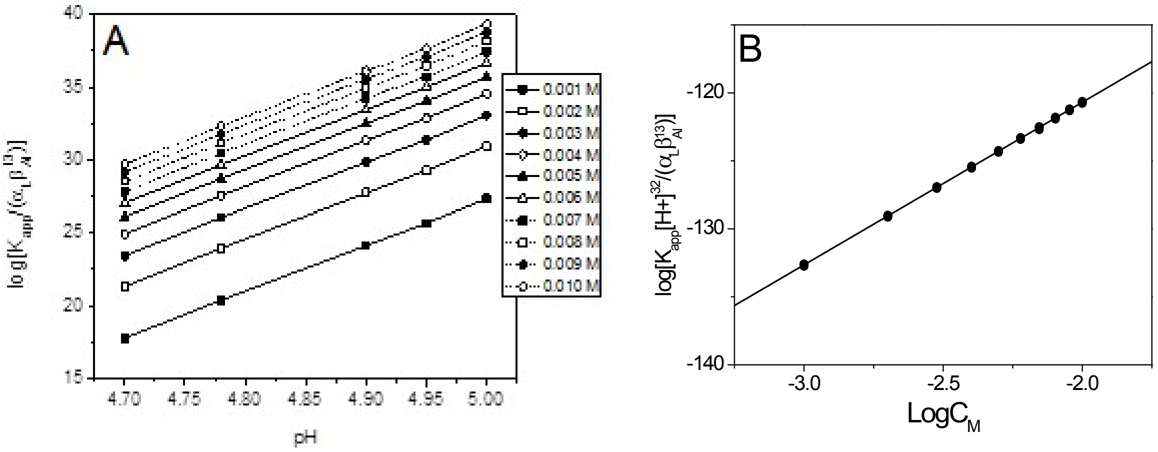


Fig. S5 (A) Data treatment of eq 8 as a function of pH at different C_M values; (B) data treatment of eq 8 as a function of LogC_M; I = 0.1 M and T = 25.0 °C.

NMR determination of K_{app} of Aluminium/Cacodylate complexes: To evaluate the apparent equilibrium constant for complex formation (K_{app}) from the NMR data of Fig. S5, quantitative analyses were conducted according to eqn. (S1), where I^n_L is the normalized peak area of free cacodylate and I^n_{ML} is the total normalized area of the bound cacodylate .

$$K_{app} = \frac{[ML]}{[M][L]} = \frac{I^{n}_{ML}C_L}{I^{n}_{L}C_L(C_M - I^{n}_{ML}C_L)} \qquad \text{(S1)}$$

Table S1 Apparent equilibrium constants for complex formation (K_{app}) obtained from the ^{1}H-NMR spectra. $C_M = C_L = 5.0 \times 10^{-3}$ M, I = 0.1 M and T = 25.0 °C.

pH	10^{-3} K_{app} (M^{-1})
4	0.2±0.1
5	4±2
6	1.5±0.5
7	0.06±0.02

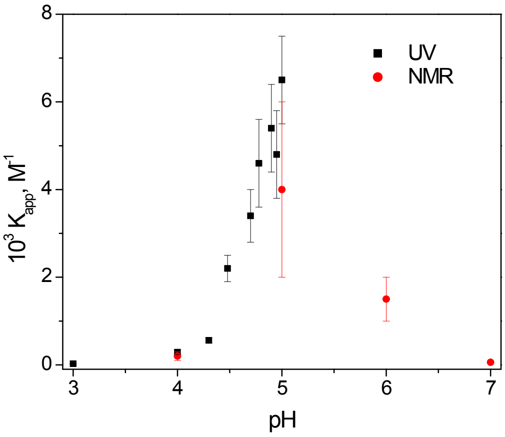
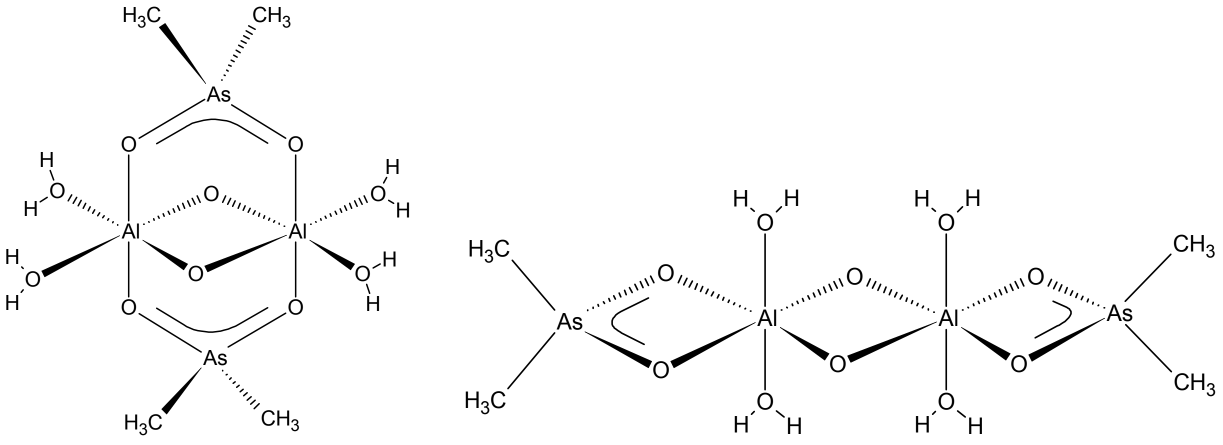


Fig. S6 Resume of the values of K_{app} obtained from the UV titrations (■) and the NMR spectra (●). I = 0.1 M and T = 25.0 °C



A B

Fig. S7 Structures for DFT analysis for the M_2L_2 dimeric system.

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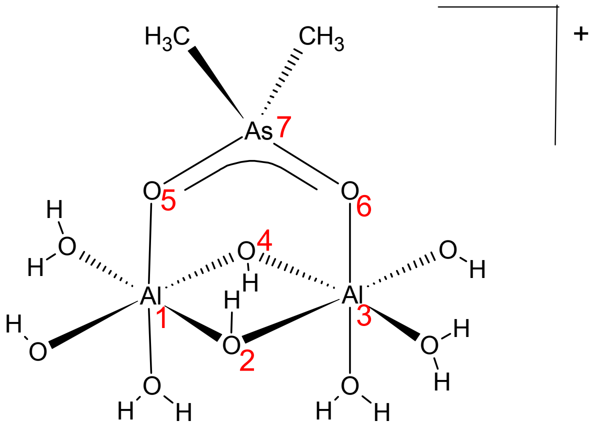
Table S2 Formula of Al/Cac complexes by the mass spectrometry data. $C_M = C_L = 2.0 \times 10^{-4}M$; T=25.0°C.

Complexes		V	m/z	10^3 Intensity			
				pH 4	pH 5	pH 6	pH 7
Monomeric	$AlCac(H_2O)_v{}^{2+}$	1	91	5	3	1	0.5
	$AlOHCac(H_2O)_v{}^{+}$	0	181	1.5	4	-	-
		1	199	2	8		
		2	217	1	6		
Dimeric	$Al_2O(OH)Cac(H_2O)_v{}^{2+}$	1	121	40	30	2	1
		2	130	17	3	-	-
	$Al_2O(OH)Cac_2(H_2O)_v{}^{+}$	0	361	-	50	13	-
		1	379		7	1	
		2	397		2	1	
	$Al_2OCac_3(H_2O)_v{}^{+}$	0	481	-	6	3	0.75
		1	499		1	0.5	-
		2	517		0.5	0.3	-
Trimeric	$Al_3O(OH)_3Cac(H_2O)_v{}^{3+}$	2	107	1	1	1	1
	$Al_3O_3(OH)Cac(H_2O)_v{}^{+}$	0	283	-	5	-	-
		1	301		7		
		2	319		2.5		
	$Al_3O_2(OH)_2Cac_2(H_2O)_v{}^{+}$	0	421	-	13	5	1
		1	439		1	1	-

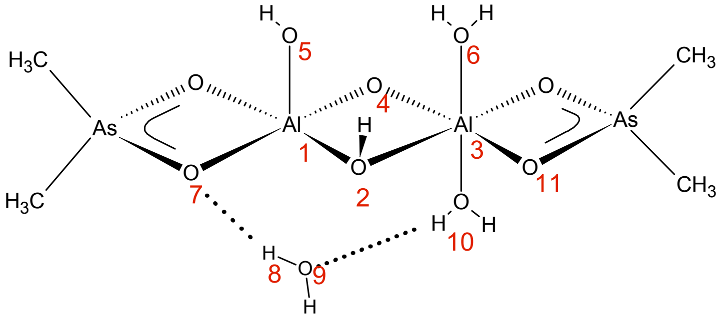
	$Al_3O(OH)_3Cac_3(H_2O)_v^+$	1	577	-	1.5	-	-
		2	595		-	0.5	0.5
		3	613		-	-	0.5
		4	631		-	0.5	-
Tetrameric	$Al_4O_2(OH)_2Cac_3(H_2O)_v^+$	1	603	-	-	-	-
		4	657		-	1.5	
		6	693		3	3	
		7	711		-	0.5	

Table S3 Selected parameters, Distances (Å) and Angles (Deg), for the 2:1 Al/Cac complex.



Distances		Angles	
Atoms	Value	Atoms	Value
Al(1)-O(2)	1.92	O(2)-Al(1)-O(4)	74.28
Al(1)-O(4)	1.93	O(2)-Al(1)-O(5)	97.82
Al(1)-O(5)	1.90	O(2)-Al(3)-O(4)	74.28
Al(1)-Al(3)	3.00	O(2)-Al(3)-O(6)	96.14
Al(3)-O(2)	1.93	Al(1)-O(2)-Al(3)	102.65
Al(3)-O(4)	1.92	Al(1)-O(4)-Al(3)	102.79
Al(3)-O(6)	1.90	O(5)-As(7)-O(6)	112.86
As(7)-O(5)	1.70		
As(7)-O(6)	1.70		

Table S4 Selected parameters, Distances (Å), Angles (Deg), and Dihedral Angles (Deg) for the 2:2 Al/Cac complex.



Distances		Angles		Dihedral angles	
Atoms	Value	Atoms	Value	Atoms	Value
Al(1)-O(2)	1.98	O(2)-Al(1)-O(4)	84.35	O(7)-Al(1)-O(2)-Al(3)	133.78
				Al(1)-O(2)-Al(3)-O(11)	164.80

Al(1)-O(4)	1.75	O(2)-Al(1)-O(5)	89.26
Al(1)-O(5)	1.82	O(2)-Al(3)-O(4)	74.28
Al(1)-Al(3)	1.95	O(2)-Al(3)-O(6)	84.69
Al(3)-O(2)	1.94	Al(1)-O(2)-Al(3)	87.87
Al(3)-O(4)	1.78	Al(1)-O(4)-Al(3)	99.98
Al(3)-O(6)	2.11	O(7)-Al(1)-O(2)	90.67
Al(3)-O(10)	2.04		
Al (1)-O(7)	1.93		
O(7)-H(8)	1.75		
O(9)-H(10)	1.65		

Derivation of Equation 8

The apparent constant K_{app} which represents the overall equilibria between the Aluminium forms and the cacodylic acid forms can be expressed by eqn. S2, where [i], is the concentration at the equilibrium of the ith form.

$$K_{app} = \frac{[AlCac^{2+}] + [Al(OH)Cac^{+}] + [Al(OH)_2Cac] + [Al(OH)_3Cac^{-}] + [Al(OH)_4Cac^{2-}] + [Al_2(OH)_2Cac^{3+}] +}{([HCac] + [Cac^{-}])([Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2{}^{+}] + [Al(OH)_3] + [Al(OH)_4{}^{-}] + [Al_2(OH)_2{}^{4+}]} \tag{S2}$$

Using the molar fraction of deprotonated cacodylate (α_L) and Al^{3+} (β_{Al})

$$\alpha_L = \frac{[Cac^{-}]}{[HCac] + [Cac^{-}]} \tag{S3}$$

$$\beta_{Al} = \frac{[Al^{3+}]}{[Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2{}^{+}] + [Al(OH)_3] + [Al(OH)_4{}^{-}] + [Al_2(OH)_2{}^{4+}] + [Al_3(OH)_4{}^{5}} \tag{S4}$$

eqn. S2 turns into eqn. S5. (Note that in eqn S3 the species H_2CaC^+ has been disregarded since the concentration of this species is negelegible in the full range of pH investigated)

$$\frac{K_{app}}{\alpha_L\beta_{Al}} = \frac{[AlCac^{2+}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al(OH)Cac^{+}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al(OH)_2Cac]}{[Al^{3+}][Cac^{-}]} + \frac{[Al(OH)_3Cac^{-}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al(OH)_4Cac^{2-}]}{[Al^{3+}][Cac^{-}]} + \\ + \frac{[Al_2(OH)_2Cac^{3+}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al_3(OH)_4Cac^{4+}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al_{13}O_4(OH)_{24}Cac^{6+}]}{[Al^{3+}][Cac^{-}]} \tag{S5}$$

The equilibrium ratio $Q_{x,y}$ for aluminium hydrolysis, defined in Ref.1 of the text are introduced in eqn. S5, to convert [Al^{3+}] into the concentrations of the desired hydrolyzed forms. So, eqn. S6 is obtained.

$$\frac{K_{app}}{\alpha_L\beta_{Al}} = \frac{[AlCac^{2+}]}{[Al^{3+}][Cac^{-}]} + \frac{[Al(OH)Cac^{+}] \quad Q_{1.1}}{[Al(OH)^{2+}][Cac^{-}][H^{+}]} + \frac{[Al(OH)_2Cac] \quad Q_{1.2}}{[Al(OH)_2{}^{+}][Cac^{-}][H^{+}]^2} + \frac{[Al(OH)_3Cac^{-}] \quad Q_{1.3}}{[Al(OH)_3][Cac^{-}][H^{+}} \\ \frac{Q_{1.4}}{[H^{+}]^4} +$$

$$+\frac{\left[Al_2(OH)_2Cac^{3+}\right]}{\left[Al_2(OH)_2{}^{4+}\right]\left[Cac^{-}\right]}\frac{Q_{2.2}C_M\beta_{Al}}{\lfloor H^{+}\rfloor^{2}}+\frac{\left[Al_3(OH)_4Cac^{4+}\right]}{\left[Al_3(OH)_4{}^{5+}\right]\left[Cac^{-}\right]}\frac{Q_{3.4}C_M{}^{2}\beta_{Al}{}^{2}}{\lfloor H^{+}\rfloor^{4}}+\frac{\left[Al_{13}O_4(OH)_{24}Cac^{6+}\right]}{\left[Al_{13}O_4(OH)_{24}{}^{7+}\right]\left[Cac^{-}\right]}\frac{Q_{13.32}C_M{}^{12}\beta_{Al}{}^{12}}{\lfloor H^{+}\rfloor^{32}} \qquad \text{(S6)}$$

The equilibrium constants of the different complexes can be expressed as $K^x=[ML]/([M][L])$. Introduction of this equation in eqn. S6 yields equation eqn. S7.

$$\frac{K_{app}}{\alpha_L\beta_{Al}}=K^{I}+K^{II}\frac{Q_{1.1}}{\lfloor H^{+}\rfloor}+K^{III}\frac{Q_{1.2}}{\lfloor H^{+}\rfloor^{2}}+K^{IV}\frac{Q_{1.3}}{\lfloor H^{+}\rfloor^{3}}+K^{V}\frac{Q_{1.4}}{\lfloor H^{+}\rfloor^{4}}+K^{VI}\frac{Q_{2.2}C_M\beta_{Al}}{\lfloor H^{+}\rfloor^{2}}+K^{VII}\frac{Q_{3.4}C_M{}^{2}\beta_{Al}{}^{2}}{\lfloor H^{+}\rfloor^{4}}+K^{VIII}\frac{Q_{13.32}C_M{}^{12}\beta_{Al}{}^{12}}{\lfloor H^{+}\rfloor^{32}} \qquad \text{(S7)}$$

However, since the predominant species are Al^{3+} and Al_{13} in the experimental conditions, the equation can be simplified, resulting the eqn. S8, which corresponds to eqn. 8 of the text

$$\frac{K_{app}}{\alpha_L\beta_{Al}}=K^{I}+K^{VIII}\frac{Q_{13.32}C_M{}^{12}\beta_{Al}{}^{12}}{\lfloor H^{+}\rfloor^{32}} \qquad \text{(S8)}$$