Supplementary Materials

Table S1. Literature data on Al^{3+} hydrolysis.

T/K	I/mol L^{-1}	Ionic medium	log β_{pq} [1]													
			1 1	1 2	1 3	1 4	2 2	2 4	3 4	3 6	4 3	4 2	13 32	13 35	14 34 [2]	Ref.
298.15	0		-5.00	-10.3	-16.7	-22.7	-7.7	—	-13.9	—			-98.7	—	—	3
298.15	0		-4.97	-9.3	-15.0	-23.0	-7.7	—	-13.94	—			-98.73	—	—	4
298.15	0		-5.0	-10.3	-16.2	-22.2	—	—	—	—			—	—	—	5
298.15	0		-5.17	—	—	—	-6.95	—	—	—			-100.7	—	—	5
298.15	0		-4.99	—	—	—	—	—	—	—			—	—	—	5
298.15	0		-5.02	—	—	—	—	—	—	—			—	—	—	5
298.15	0		-4.98	—	—	—	—	—	—	—			—	—	—	5
298.15	0		-5.1	—	—	—	—	—	—	—			—	—	—	5
298.15	0		-4.5	—	—	—	—	—	—	—			—	—	—	5
298.15	0		-4.60	—	—	—	—	—	—	—			—	—	—	5
288.15	0		-5.11	—	—	—	-8.03	—	—	—			—	—	—	5
293.15	0		-4.93	—	—	—	—	—	—	—			—	—	—	5
303.15	0		-4.61	—	—	—	-7.44	—	—	—			—	—	—	5
50	0		-4.6	—	—	-23.7	—	—	—	—			—	—	—	5
298.15	0.1	NaCl	-5.31	—	—	—	—	—	—	—			—	—	—	5
310.15	0.15	NaCl	—	—	—	-21.031	—	—	—	—			—	—	—	5, 6
298.15	0.60	NaCl	—	—	—	—	—	—	—	—			-105.5	—	—	5
298.15	0.60	NaCl	—	—	—	-23.46	—	—	—	—			—	—	—	5

298.15	0.60	NaCl	-5.52	—	—	—	—	—	-13.57	—			-109.2	—	—	5
298.15	3.0	NaCl	—	—	—	—	-7.53	-16.50	-13.44	—			—	—	—	5
298.15	3.0	NaCl	-5.52	—	—	—	—	—	-13.96	—			-113.35	—	—	5
298.15	0.1	KCl	-4.81	—	-14.17	—	—	—	-13.82	—			—	—	—	5
335.15	1.0	KCl	—	—	—	—	-5.90	—	-10.74	—			—	—	—	5
372.15	1.0	KCl	—	—	—	—	-4.81	—	-8.20	—			—	—	-67.9	5
303.15	3.0	KCl	—	—	—	—	-6.68	—	—	-20.90			-104.45	-117.78	—	5
298.15	0.1	LiCl	-5.62	-9.74	—	—	—	—	-13.7	—			—	—	—	5
298.15	1.0	$NaClO_4$	-5.48	-10.3	—	—	-8.0	—	-13.47	—			-104.8	—	—	5
298.15	1.0	$NaClO_4$	-4.31	—	—	—	—	—	—	—			—	—	—	5
298.15	2.0	$NaClO_4$	—	—	—	—	-7.07	—	—	—			-104.5	—	—	5
298.15	8.0	$NaClO_4$[a)]									-11.7	-25.8				5, 7
298.15	0.1	$NaNO_3$	-5.33	-10.91	—	—	—	—	-13.13	—			-107.47	—	—	5, 8
298.15	3.0	$NaNO_3$	—	—	—	—	-7.55	-16.41	-13.24	—			—	—	—	5
293.15	0.12	$BaNO_3$	-5.74	—	—	—	-8.06	—	—	—			—	—	—	5
293.15	0.6	$BaNO_3$	-5.97	—	—	—	-8.24	—	—	—			—	—	—	5

[1] refer to the reaction: $pAl^{3+} + qH_2O \leftrightarrows Al_p(OH)_q^{(3p-q)} + qH^+$; [2] Other species: $M_5(OH)_4$, $M_5(OH)_3$, $M_6(OH)_5$, $M_6(OH)_4$, $M_6(OH)_3$, $M_7(OH)_5$, with log β = -35.4, -17.0, -45.1, -31.2, -17.0, respectively; [3] Martell, A. E.; Smith, R. M.; Motekaitis, R. J. *Critically Selected Stability Constants of Metal Complexes. Gaithersburg*. National Institute of Standard and Technology, NIST: 2004; [4] Baes, C. F.; Mesmer, R. E., *The hydrolysis of cations*. John Wiley & sons: New York, 1976; [5] Pettit, L. D.; Powell, K. J. *IUPAC Stability Constants Database*., Academic Software, IUPAC: 2001; [6] Gumienna-Kontecka, E.; Berthon, G.; Fritsky, I. O.; Wieczorek, R.; Latajka, Z.; Kozlowski, H., 2-(Hydroxyimino)propanohydroxamic acid, a new effective ligand for aluminium. *J. Chem. Soc., Dalton Trans.* **2000**, 4201-4208; [7] Sipos, P., Capewell, S.G., Hefter, G., Laurenczy, G., Lukacs, F., Roulet, R., Spectroscopic studies of the chemical speciation in concentrated alkaline aluminate solutions. *J. Chem. Soc., Dalton Trans*., **1998**, 3007-3012**;** [8] Brown, P. L.; Sylva, R. N.; Batley, G. E.; Ellis, J., The hydrolysis of metal ions. Part 8. Aluminium(III). *J. Chem. Soc., Dalton Trans.* **1985**, 1967-1970.

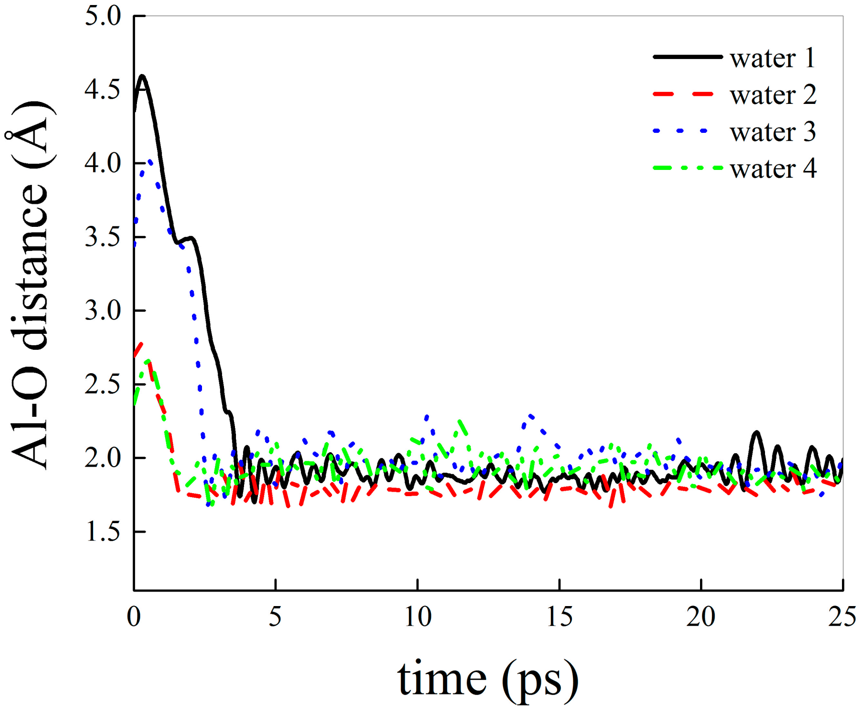

Figure S1. Instantaneous distances between the aluminium atom of the original $AlCl^{2+}$ species and the oxygen atoms of the four water molecules that hydrate the complex leading to the formation of the structure shown in Fig. 2b of the main text.

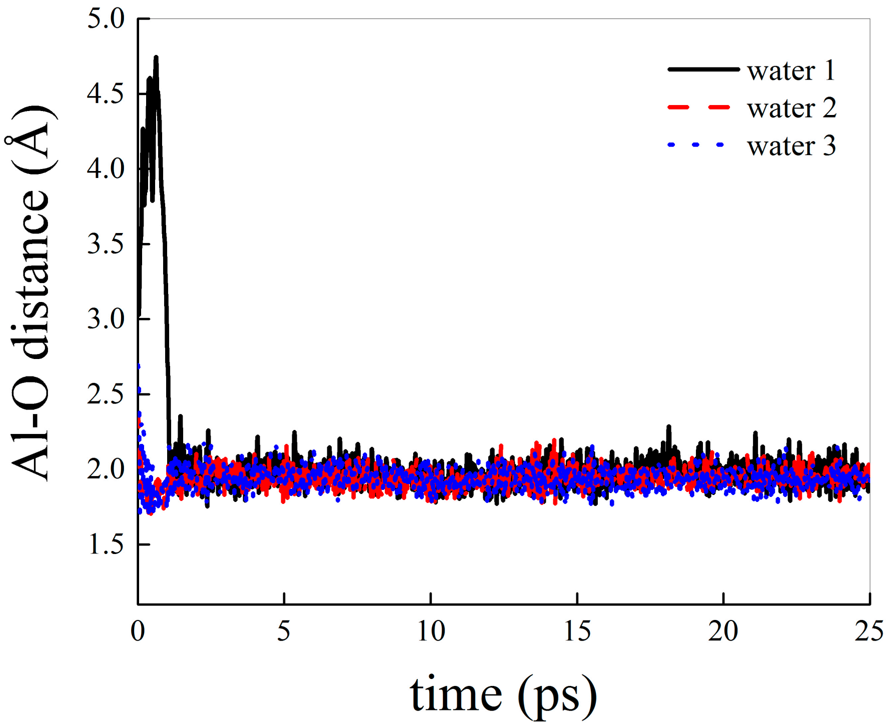

Figure S2. Instantaneous distances between the aluminium atom of the original $AlClOH^{+}$ species and the oxygen atoms of the three water molecules that hydrate the complex leading to the formation of the structure shown in Fig. 3b of the main text.

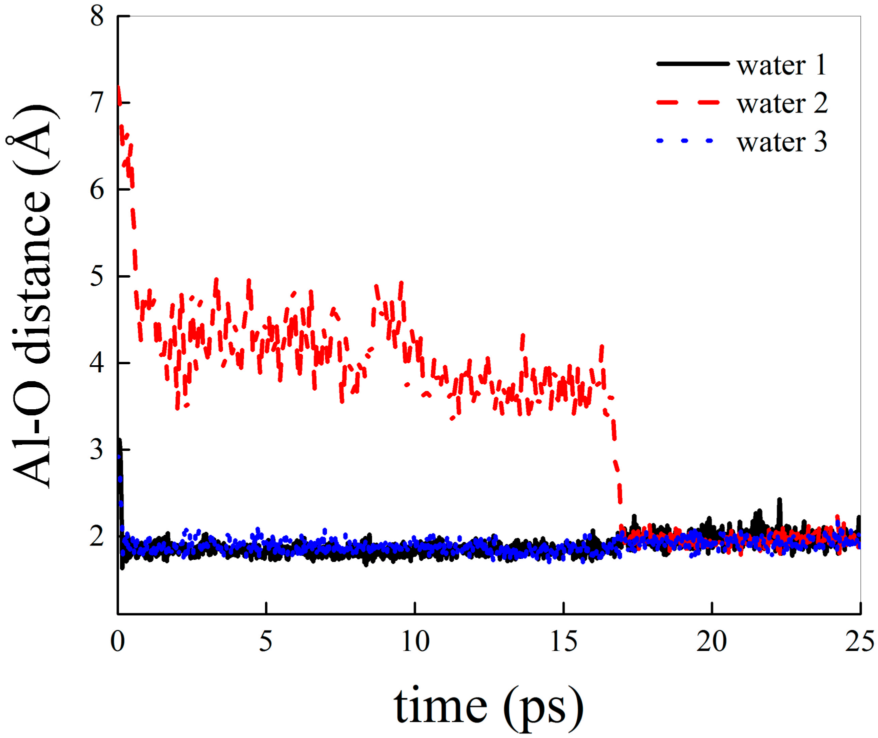

Figure S3. Instantaneous distances between the aluminium atom of the original $Al_3(OH)_4^{5+}$ species and the oxygen atoms of three of the nine water molecules that hydrate the complex leading to the formation of the complex $[Al_3(OH)_4(H_2O)_9]^{5+}$, whose structure is shown in Fig. 4b of the main text.

Table S2. *xyz* structure file containing the Cartesian components of the position of the atomic species of the molecular structure of the complex $As_3(OH)_4^{5+}$ optimized at the MP2/6-311++G(2d,2p) quantum-mechanical level under implicit solvation (see Fig. 4-a of the main text).

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11

Al      -1.956314    0.000040   -0.000519
Al       0.877481   -1.324747    0.000236
Al       0.877548    1.324715    0.000191
O        1.146175   -0.000002    1.168051
O       -0.964433   -1.448488   -0.000411
O        1.148448   -0.000049   -1.166983
O       -0.964359    1.448525   -0.000460
H       -1.402394    2.332933   -0.000746
H       -1.402513   -2.332875   -0.000730
H        1.248723   -0.000057   -2.137153
H        1.246237    0.000007    2.138231
```