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Electronic Supplementary Information, Tables S1, S2, S3 and S4

Table S1.

Resulting interatomic distances from the calculated $Al(NO_3)_3 \cdot 9H_2O$ crystal structure compared with room-temperature neutron diffraction data from Ref. 15. All experimental numbers have standard deviations of 1 in the last digit for the Al−O distances and 1 or 2 for the N−O distances.

Distances (Å) in $Al(H_2O)_6^{3+}$ octahedra			Distances (Å) in NO_3^- ions		
	Calc.	Exp.		Calc.	Exp.
Al(1)−O(1)	1.893	1.881	N(1) −O(11)	1.257	1.234
−O(2)	1.896	1.873	−O(12)	1.263	1.242
−O(3)	1.900	1.886	−O(13)	1.288	1.263
Al(2)−O(4)	1.908	1.889	N(2)−O(21)	1.268	1.246
−O(5)	1.884	1.868	−O(22)	1.268	1.238
−O(6)	1.921	1.897	−O(23)	1.270	1.249
			N(3)−O(31)	1.279	1.247
			−O(32)	1.256	1.227
			−O(33)	1.266	1.242

Table S2.
Resulting O−H distances and H−O−H angles from the calculated $Al(NO_3)_3 \cdot 9H_2O$ crystal structure compared with room-temperature neutron diffraction data from Ref. 15. The experimental numbers have standard deviations of 0.002 Å for the bond distances and 0.002° for bond angles. Δ is the difference between calculated and experimental distances.

	O-H distances (Å)			H-O-H angles (°)	
	Calc.	Exp.	Δ	Calc	Exp
O(1)−H(11)	0.999	0.975	+.024	112.4	111.7
−H(12)	1.001	0.979	+.022		
O(2)−H(21)	1.009	0.980	+.029	108.1	107.8
−H(22)	1.006	0.985	+.021		
O(3)−H(31)	0.995	0.972	+.027	112.7	112.1
−H(32)	1.014	0.985	+.029		
O(4)−H(41)	1.003	0.981	+.022	110.7	110.4
−H(42)	1.006	0.977	+.029		
O(5)−H(51)	1.014	0.981	+.033	108.6	107.5
−H(52)	1.003	0.986	+.017		
O(6)−H(61)	0.995	0.966	+.029	108.2	107.8
−H(62)	1.011	0.985	+.026		
O(7)−H(71)	1.002	0.974	+.028	106.3	105.7
−H(72)	0.993	0.969	+024		
O(8)−H(81)	1.000	0.968	+.032	107.7	106.9
−H(82)	0.989	0.963	+.026		
O(9)−H(91)	0.980	0.938	+.042	105.9	105.7
−H(92)	0.992	0.961	+.031		

Table S3.

Hydrogen bond distances and angles around the water molecules in the crystal structure of $Al(NO_3)_3 \cdot 9H_2O$. Δ is the difference between calculated and experimental[15] distances.

Hydrogen bond distances (Å) and angles (˚)										
	O···O dist.			H···O dist.			O-H···O angle		O···O···O angle	
	Calc.	Exp.	Δ	Calc.	Exp.	Δ	Calc.	Exp.	Calc.	Exp.
O(1)−H(11)···O(11)	2.702	2.750	–.05	1.706	1.777	–.07	174.3	174.8	118.1	117.9
−H(12)···O(12)	2.666	2.726	–.06	1.669	1.752	–.09	173.9	173.2		
O(2)−H(21)···O(7)	2.628	2.656	–.03	1.633	1.692	–.06	168.1	166.9	101.8	100.0
−H(22)···O(23)	2.642	2.670	–.03	1.637	1.685	–.05	177.3	178.6		
O(3)−H(31)···O(33)	2.717	2.722	–.01	1.737	1.766	–.03	167.5	166.7	118.9	118.1
−H(32)···O(7)	2.621	2.693	–.07	1.608	1.711	–.11	175.2	174.6		
O(4)−H(41)···O(21)	2.685	2.723	–.04	1.682	1.742	–.06	179.1	178.0	115.2	116.1
−H(42)···O(22)	2.648	2.699	–.05	1.647	1.731	–.09	172.5	170.7		
O(5)−H(51)···O(8)	2.592	2.650	–.06	1.581	1.675	–.09	174.1	171.8	107.9	105.3
−H(52)···O(13)	2.649	2.650	–.01	1.647	1.666	–.02	176.6	175.5		
O(6)−H(61)···O(31)	2.689	2.703	–.01	1.713	1.764	–.05	165.9	162.9	100.6	99.8
−H(62)···O(8)	2.632	2.680	–.05	1.627	1.701	–.07	172.2	172.3		
O(7)−H(71)···O(9)	2.693	2.761	–.07	1.694	1.791	–.10	173.8	173.8	93.8	93.0
−H(72)···O(9')	2.778	2.851	–.07	1.805	1.901	–.10	165.4	166.1		
O(8)−H(81)···O(32)	2.687	2.782	–.10	1.690	1.814	–.12	174.6	177.1	114.7	113.3
−H(82)···O(31)	2.706	2.757	–.05	1.765	1.849	–.08	157.6	156.2		
O(9)−H(91)···O(23)	3.065	3.054	+.01	2.349	2.339	+.01	129.3	132.7	113.3 114.1	116.8 114.5
−H(91)···O(33)	2.920	2.900	+.02	2.079	2.127	–.05	142.8	138.8		
−H(92)···O(13)	2.771	2.854	–.07	1.796	1.918	–.12	167.1	164.0		

Table S4.

Charges of various types for the constituents in the complexes **A, B, C, D** and **E** (see Fig. 9) calculated at the PBE/6-311G** level with the Gaussian program and charges of the same constituents in the $Al(NO_3)_3 \cdot 9H_2O$ crystal (only Bader charges) calculated at the PBE/(PAW+plane-wave basis) with the VASP program.

	Al1	**W1**	**W1'**	**W2**	**W2'**	**W3**	**W3'**	**W7**	**NO_3**		
Complex					**Bader charges /*e***						
A	2.74	-	-	0.26	-	-	-	-		-	
B	2.60	0.07	0.07	0.07	0.07	0.07	0.07	-		-	
C	1.59	-	-	-0.03	-	-	-	0.15		0.30	
D	2.60	0.05	0.05	-0.08	0.05	0.06	0.05	0.07		-0.85	
E	2.60	-0.03	-0.03	-0.07	0.05	0.05	0.04	0.06	-0.89	-0.89	-0.89
Crystal	2.52	-0.04	-0.04	-0.04	-0.04	-0.03	-0.03	0.03	-0.79	-0.79	-0.79
Complex					**Mulliken charges / *e***						
A	2.42	-	-	0.58	-	-	-	-		-	
B	1.58	0.24	0.24	0.23	0.23	0.24	0.24	−		-	
C	1.29	-	-	0.20	-	−	−	0.19		0.33	
D	1.51	0.22	0.21	0.05	0.21	0.23	0.21	0.11		-0.75	
E	1.48	0.09	0.10	0.06	0.19	0.21	0.18	0.09	-0.81	-0.79	-0.80
Complex					**NBO charges / *e***						
A	2.77	-	-	0.23	-	-	-	-		-	
B	1.95	0.18	0.18	0.17	0.17	0.18	0.18	-		-	
C	1.54	-	-	0.00	-	-	-	0.15		0.31	
D	1.92	0.17	0.16	0.02	0.16	0.17	0.16	0.08		-0.84	
E	1.92	0.08	0.08	0.02	0.16	0.16	0.15	0.06	-0.88	-0.88	-0.88
Complex					**Chelpg charges / *e***						
A	2.72	-	-	0.28	-	-	-	-		-	
B	1.76	0.21	0.21	0.19	0.19	0.23	0.23	-		-	
C	1.23	-	-	0.17	-	-	-	0.22		0.38	
D	1.99	0.15	0.16	-0.06	0.13	0.16	0.09	0.13		-0.74	
E	2.08	0.01	0.01	-0.07	0.11	0.16	0.05	0.09	-0.81	-0.82	-0.80