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SUPPLEMENTARY MATERIAL

Synthesis, characterization and properties of a glycol-coordinated *ε*-Keggin-type Al_{13} chloride

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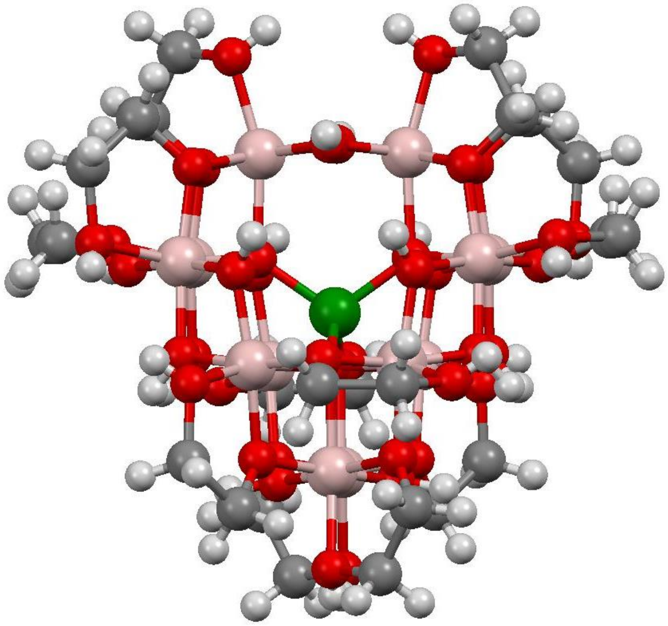

Synthesis of gl-ε-Al_{13}

Aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, 2.4 g), was dissolved in ethylene glycol (EG, 10 mL) under magnetic stirring, followed by adding ethanol (40 mL) to maintain a transparent solution. Solvothermal synthesis was carried out in a Teflon-lined stainless steel autoclave (100 mL) at 150 °C for 6 h. After being cooled down to room temperature, the mixture was centrifuged (5000 rpm) to collect the white solids, which were further washed 3 times by ethanol and dried at 60 °C. The dried white solides, *viz.*, gl-ε-Al_{13} products, were collected and weighed to calculate the yield by using Equation 1.

$$Yield\ (\%) = \frac{\frac{weight\ of\ the\ dried\ white\ solids}{mocular\ weight\ of\ gl-\varepsilon-Al_{13}} \times 13}{mole\ of\ AlCl_3\ dose} \times 100 \qquad (1)$$

Single-crystal structure determination

A colorless cube with approximate orthogonal dimensions 0.112 x 0.148 x 0.159 mm was placed and optically centered on the Bruker Venture Dual source Kappa Photon100 diffractometer system at -173 °C (100 K). Indexing of the unit cell used a random set of reflections collected from three series of 0.3° wide ω-scans, 2 seconds per frame, and 50 frames per series that were well distributed in reciprocal space. Data were collected [MoKα] with 0.3° wide scans, variable time per frame dependent upon detector 2θ angle and varying ϕ and omega angles such that nearly all unique reflections were collected at least once. The crystal to detector distance was 5.496cm, thus providing a complete sphere of data to $2\theta_{max} = 54.97°$.

All crystallographic calculations were performed on an Intel Xeon E5-1620v2 at 3.70GHz an eight core processor and 16GB of extended memory. Data collected were corrected for Lorentz and polarization effects with Saint[1] and absorption using Blessing's method and merged as incorporated with the program Sadabs[2,3]. The SHELXTL[4] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric cubic space group Fd-3m (no. 227). The structure was determined by direct methods with a majority of the non-hydrogen atoms being located directly using the program XT[5]. The structure was refined with XL[6]. The 27695 data collected were merged for least squares refinement to 874 unique data [R(int)=0.0269]. A series of single least-squares difference-Fourier cycles were required to locate and sort out the multiple disorders found to be present. All full-occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and placed in idealized locations throughout the final refinement stages.

The $Al_{13}C_{24}H_{72}O_{40}$ complex may best be described as a composite structure. The core of the molecule is well ordered while the ethylene glycol peripheral groups are disordered over two positions in any one molecule thereby creating a set of three ethylene glycol groups attached to each 3 atom Al face. Due to the high symmetry and the availability of four Al_3 faces in each molecule the resulting structure is a composite of many nearly identical orientations of the basic complex that required mathematical restraints to idealize bond distances for the individual ethylene glycol units due to large observed amount of libration. Bond distances for O-C were restrained to be 1.45(2) A, but were found to range from 1.42(1) to 1.51(2), while the distance restraint for C-C was 1.50(2) A and ranged from 1.573(9) to 1.577(9).

The partial occupancy Cl(2) (83.33%) atom also had a water molecule central oxygen O(5) (16.67%) about 1.3A away. Hydrogen atoms attached to partial occupancy atom O(5) were optimized with distance restraints (DFIX) O(5)-H(5A) = 0.84A and H(5B) was placed in a fixed position along a vector towards Cl(2) at 0.84A from O(5). A multitude of other approaches were tested but this approach was found necessary due to the short contacts that would otherwise be produced with both Hydrogen atoms refining with distance restraints and atom H(4) on the cluster. Platon[7] Squeeze was used to remove the partial occupancy solvent molecules that resided in the channels between the molecules; the calculated volume was 3455A with 473e- for the unit cell.

The final structure was refined to convergence with R(F)=5.94%, wR(F^2)=17.86%, GOF=1.096 for all 874 unique reflections [R(F)=5.69%, wR(F^2)=17.56% for those 822 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted and found to be 0.00028(9); barely above three sigma.

The crystal structure is archived at the Cambridge Crystallographic Data Centre with the identifier: CCDC 1813736.

Characterizations of gl-ε-Al_{13}

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7800F microscopy. EDS analysis was operated on Oxford X-MAX.

Powder X-ray diffraction (XRD) was recorded on a PANalytical Empyrean X-ray diffractometer with Cu Kα radiation (40 kV and 40 mA).

Fourier transform infrared spectra (FT-IR) were collected using a BRUKER TENSOR27 FT-IR spectrometer equipped with DTGS detector in the frequency range of 4000 - 400 cm^{-1}. The samples were pressed into discs using KBr. For each spectrum 32 scans were performed with a resolution of 4 cm^{-1}. The background was determined using a pure KBr disc.

Raman spectra of the powder samples were collected using Senterra Raman microscope (Bruker) with 3-5 cm-1 resolution in the 100-3600 cm-1 spectral region. A laser with 532 nm wavelength and 5 mW power was used for excitation.

All the magic angle spinning (MAS) solid state NMR (SSNMR) measurements were measured at Bruker AV-I 750MHz spectrometer with 17.6 Tesla magnetic field. In this field ^{13}C, ^{27}Al and ^{1}H resonate at 188.64, 195.48 and 750.23 MHz respectively. Standard 4 mm triple resonance MAS probe was used. All the samples were packed in 4mm zirconium rotor's and were spun at magic angle (54.74) at various spinning speeds. For ^{27}Al MAS spectra, chemical shifts were referenced with respect to liquid $Al(NO_3)_3$ sample. An excitation pulse of 0.3 μs, corresponding to a π/18 pulse for $Al(NO_3)_3$ in solution was used with recycling delay of 1 s and total number of scans acquired were 64. Line broadening function of 100Hz and additional baseline correction was used for processing the data. For ^{13}C spectrum, It was obtained through CPMAS technique with TPPM decoupling. ^{1}H and ^{13}C were irradiated with 80.6 kHz and 62.5 kHz radio frequency pulses with a contact time of 2 ms were used to achieve the CPMAS condition. With a recycle delay of 1 s and 256 scans were acquired. The line broadening function of 50 Hz was applied while processing the spectra. The ^{13}C spectra were externally referenced to methyl signal of TMS. For ^{1}H MAS NMR spectra, chemical shits were referenced with TMS. An excitation pulse of 2 μs, corresponding to a 30 degree pulse was used with a recycle delay of 2 s and 32 scans were acquired. Line broadening of 10Hz and additional baseline correction was applied. All the NMR data were processed in Topspin 3.2 and MestReNova softwares.

X-ray photoelectron spectroscopy (XPS) was collected on a Thermo ESCALAB 250Xi instrument. The carbon peak at 284.6 eV was taken as reference for correction of binding energy due to sample charging. XPS spectra were well fitted using Gaussian functions by Origin software.

The analysis of Al and Cl elements were performed on Perkin Elmer AAS AAnalystTM 200 and Metrohm 883 IC Plus at Mikroanalytisches Labor Kolbe, Germany.

The solubility of gl-ε-Al_{13} in water and solvents were examined by dissolving 20 mg gl-ε-Al_{13} into 10 ml water or solvent. The mixture was gently stirred and then kept for 24 hours at room temperature to check the solubility. The stability of Al_{13} ions was checked by liquid ^{27}Al NMR.

Table S1. Crystal data and structure refinement for $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent]. (CCDC 1813736)

Identification code	$[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent].
Empirical formula	C24 H74 Al13 Cl7 O41
Formula weight	1617.72
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Fd-3m
Unit cell dimensions	a = 24.6762(11) Å = 90°.
	b = 24.6762(11) Å = 90°.
	c = 24.6762(11) Å = 90°.
Volume	15026(2) Å^3
Z	8
Density (calculated)	1.430 Mg/m^3
Absorption coefficient	0.499 mm^{-1}
F(000)	6672
Crystal size	0.159 x 0.148 x 0.112 mm^3
Crystal color and habit	Colorless Cube
Diffractometer	Bruker Photon100 CMOS
Theta range for data collection	2.334 to 27.499°.
Index ranges	-32<=h<=31, -32<=k<=32, -32<=l<=32
Reflections collected	27695
Independent reflections	874 [R(int) = 0.0269]
Observed reflections (I > 2sigma(I))	822
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9496 and 0.9148
Solution method	SHELXT (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014) Full-matrix least-squares on F^2
Data / restraints / parameters	874 / 39 / 76
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1756
R indices (all data)	R1 = 0.0594, wR2 = 0.1786
Extinction coefficient	0.00028(9)
Largest diff. peak and hole	0.518 and -0.606 e.Å^{-3}

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent][1]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	8750	3750	3750	19(1)
Al(2)	7504(1)	3342(1)	3342(1)	31(1)
Cl(1)	7500	2500	5000	40(1)
Cl(2)	5818(1)	3750	3750	52(1)
O(5)	5950(11)	3429(3)	4071(3)	27(6)
O(1)	8323(1)	3323(1)	3323(1)	25(1)
O(2)	7430(1)	3423(1)	4077(1)	31(1)
O(3)	7603(1)	3380(1)	2603(1)	39(1)
O(4)	6741(1)	3193(1)	3193(1)	51(1)
C(3)	7217(5)	3174(8)	2217(5)	99(5)
C(4)	6698(4)	3168(8)	2590(4)	67(4)
C(3A)	7204(3)	3487(7)	2204(3)	89(4)
C(4A)	6729(6)	3405(10)	2621(5)	86(5)

[1] CCDC 1813736

Table S3. Bond lengths (Å) and angles (°) for $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent]. (CCDC 1813736)

Al(1)-O(1)	1.825(4)	O(1)#1-Al(1)-O(1)#2	109.5
Al(1)-O(1)#1	1.825(4)	O(1)-Al(1)-O(1)#3	109.5
Al(1)-O(1)#2	1.825(4)	O(1)#1-Al(1)-O(1)#3	109.471(1)
Al(1)-O(1)#3	1.825(4)	O(1)#2-Al(1)-O(1)#3	109.5
Al(2)-O(2)	1.8335(18)	O(2)-Al(2)-O(2)#2	77.04(13)
Al(2)-O(2)#2	1.8335(18)	O(2)-Al(2)-O(3)#4	94.07(11)
Al(2)-O(3)#4	1.8424(17)	O(2)#2-Al(2)-O(3)#4	170.74(12)
Al(2)-O(3)	1.8425(17)	O(2)-Al(2)-O(3)	170.74(12)
Al(2)-O(4)	1.955(3)	O(2)#2-Al(2)-O(3)	94.07(11)
Al(2)-O(1)	2.021(2)	O(3)#4-Al(2)-O(3)	94.67(19)
Al(2)-Al(2)#2	2.845(2)	O(2)-Al(2)-O(4)	96.34(12)
Al(2)-Al(2)#5	2.9246(18)	O(2)#2-Al(2)-O(4)	96.34(12)
Al(2)-Al(2)#4	2.9246(18)	O(3)#4-Al(2)-O(4)	87.14(10)
O(5)-H(5A)	0.840(5)	O(3)-Al(2)-O(4)	87.14(10)
O(5)-H(5B)	0.840(5)	O(2)-Al(2)-O(1)	97.26(11)
O(1)-Al(2)#5	2.021(2)	O(2)#2-Al(2)-O(1)	97.26(11)
O(1)-Al(2)#4	2.021(2)	O(3)#4-Al(2)-O(1)	81.11(9)
O(2)-Al(2)#2	1.8334(18)	O(3)-Al(2)-O(1)	81.11(9)
O(2)-H(2)	0.8400	O(4)-Al(2)-O(1)	162.59(16)
O(3)-C(3A)	1.419(13)	O(2)-Al(2)-Al(2)#2	39.11(6)
O(3)-C(3)	1.442(17)	O(2)#2-Al(2)-Al(2)#2	39.11(6)
O(3)-Al(2)#5	1.8425(17)	O(3)#4-Al(2)-Al(2)#2	131.65(9)
O(4)-C(4)#6	1.493(9)	O(3)-Al(2)-Al(2)#2	131.66(9)
O(4)-C(4)	1.493(9)	O(4)-Al(2)-Al(2)#2	105.49(11)
O(4)-C(4A)#6	1.506(9)	O(1)-Al(2)-Al(2)#2	91.91(10)
O(4)-C(4A)	1.506(9)	O(2)-Al(2)-Al(2)#5	140.39(8)
O(4)-H(4)	0.83(2)	O(2)#2-Al(2)-Al(2)#5	98.49(8)
C(3)-C(4)	1.577(9)	O(3)#4-Al(2)-Al(2)#5	86.66(8)
C(3)-H(3A)	0.9900	O(3)-Al(2)-Al(2)#5	37.47(7)
C(3)-H(3B)	0.9900	O(4)-Al(2)-Al(2)#5	123.22(9)
C(4)-C(4)#6	2.02(3)	O(1)-Al(2)-Al(2)#5	43.66(7)
C(4)-H(4A)	0.9900	Al(2)#2-Al(2)-Al(2)#5	120.0
C(4)-H(4B)	0.9900	O(2)-Al(2)-Al(2)#4	98.49(8)
C(3A)-C(4A)	1.573(9)	O(2)#2-Al(2)-Al(2)#4	140.39(8)
C(3A)-H(3C)	0.9900	O(3)#4-Al(2)-Al(2)#4	37.47(7)
C(3A)-H(3D)	0.9900	O(3)-Al(2)-Al(2)#4	86.66(8)
C(4A)-H(4C)	0.9900	O(4)-Al(2)-Al(2)#4	123.22(9)
C(4A)-H(4D)	0.9900	O(1)-Al(2)-Al(2)#4	43.66(7)
		Al(2)#2-Al(2)-Al(2)#4	120.0
O(1)-Al(1)-O(1)#2	109.471(1)	Al(2)#5-Al(2)-Al(2)#4	60.0
H(5A)-O(5)-H(5B)	107(4)	O(3)-C(3)-H(3A)	112.0
Al(1)-O(1)-Al(2)	123.35(10)	C(4)-C(3)-H(3A)	112.0
Al(1)-O(1)-Al(2)#5	123.35(10)	O(3)-C(3)-H(3B)	112.0
Al(2)-O(1)-Al(2)#5	92.67(13)	C(4)-C(3)-H(3B)	112.0

Al(1)-O(1)-Al(2)#4	123.35(10)	H(3A)-C(3)-H(3B)	109.7
Al(2)-O(1)-Al(2)#4	92.67(13)	O(4)-C(4)-C(3)	121.6(9)
Al(2)#5-O(1)-Al(2)#4	92.68(13)	O(4)-C(4)-C(4)#6	47.5(7)
Al(2)#2-O(2)-Al(2)	101.78(13)	C(3)-C(4)-C(4)#6	114.8(10)
Al(2)#2-O(2)-H(2)	129.1	O(4)-C(4)-H(4A)	106.9
Al(2)-O(2)-H(2)	129.1	C(3)-C(4)-H(4A)	106.9
C(3A)-O(3)-Al(2)	127.23(9)	C(4)#6-C(4)-H(4A)	138.1
C(3)-O(3)-Al(2)	123.4(3)	O(4)-C(4)-H(4B)	106.9
C(3A)-O(3)-Al(2)#5	127.23(10)	C(3)-C(4)-H(4B)	106.9
C(3)-O(3)-Al(2)#5	123.4(3)	C(4)#6-C(4)-H(4B)	64.4
Al(2)-O(3)-Al(2)#5	105.06(14)	H(4A)-C(4)-H(4B)	106.7
C(4)#6-O(4)-C(4)	85.0(14)	O(3)-C(3A)-C(4A)	92.2(7)
C(4A)#6-O(4)-C(4A)	130.7(19)	O(3)-C(3A)-H(3C)	113.2
C(4)#6-O(4)-Al(2)	105.3(4)	C(4A)-C(3A)-H(3C)	113.2
C(4)-O(4)-Al(2)	105.3(4)	O(3)-C(3A)-H(3D)	113.2
C(4A)#6-O(4)-Al(2)	97.5(6)	C(4A)-C(3A)-H(3D)	113.2
C(4A)-O(4)-Al(2)	97.5(6)	H(3C)-C(3A)-H(3D)	110.6
C(4)#6-O(4)-H(4)	123(2)	O(4)-C(4A)-C(3A)	130.0(11)
C(4)-O(4)-H(4)	123(2)	O(4)-C(4A)-H(4C)	104.8
C(4A)#6-O(4)-H(4)	108.7(13)	C(3A)-C(4A)-H(4C)	104.8
C(4A)-O(4)-H(4)	108.7(13)	O(4)-C(4A)-H(4D)	104.8
Al(2)-O(4)-H(4)	112(4)	C(3A)-C(4A)-H(4D)	104.8
O(3)-C(3)-C(4)	98.9(7)	H(4C)-C(4A)-H(4D)	105.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+7/4,-y+3/4,z+0

#2 x+0,-y+3/4,-z+3/4

#3 -x+7/4,y+0,-z+3/4

#4 z+1/2,x-1/2,y

#5 y+1/2,z,x-1/2

#6 x,z,y

Table S4. Anisotropic displacement parameters ($Å^2$x10^3) for $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent][1]. The anisotropic displacement factor exponent takes the form: -2 ^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	19(1)	19(1)	19(1)	0	0	0
Al(2)	23(1)	35(1)	35(1)	-1(1)	-3(1)	-3(1)
Cl(1)	40(1)	40(1)	40(1)	12(1)	12(1)	-12(1)
Cl(2)	33(1)	61(1)	61(1)	35(1)	0	0
O(1)	25(1)	25(1)	25(1)	-3(1)	-3(1)	-3(1)
O(2)	26(1)	34(1)	34(1)	7(1)	0(1)	0(1)
O(3)	32(1)	52(2)	32(1)	-4(1)	-12(1)	-4(1)
O(4)	27(1)	63(1)	63(1)	-7(2)	-7(1)	-7(1)
C(3)	93(6)	112(9)	93(6)	-11(5)	-23(7)	-11(5)
C(4)	57(6)	79(8)	65(6)	-11(6)	-21(5)	-27(6)
C(3A)	86(5)	97(8)	86(5)	-7(4)	-57(6)	-7(4)
C(4A)	81(7)	98(9)	79(7)	-6(7)	-16(6)	0(7)

[1] CCDC 1813736

Table S5. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for [$C_{24}H_{72}Al_{13}O_{40}$][Cl]$_7$[$H_2O$] [+ solvent]. (CCDC 1813736)

	x	y	z	U(eq)
H(5A)	5870(20)	3122(10)	3946(16)	41
H(5B)	5855	3660	3840	41
H(2)	7375	3185	4315	110(30)
H(4)	6538(19)	3382(11)	3382(11)	53(16)
H(3A)	7314	2806	2088	119
H(3B)	7173	3420	1902	119
H(4A)	6469	3477	2476	81
H(4B)	6494	2834	2501	81
H(3C)	7201	3218	1906	107
H(3D)	7223	3860	2056	107
H(4C)	6554	3765	2649	103
H(4D)	6464	3171	2430	103

Table S6. Torsion angles (°) for $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent]. (CCDC 1813736)

O(1)#1-Al(1)-O(1)-Al(2)	-120.00(14)	O(4)-Al(2)-O(3)-C(3)	-16.0(10)
O(1)#2-Al(1)-O(1)-Al(2)	0.000(1)	O(1)-Al(2)-O(3)-C(3)	151.1(10)
O(1)#3-Al(1)-O(1)-Al(2)	120.00(14)	Al(2)#2-Al(2)-O(3)-C(3)	-124.3(9)
O(1)#1-Al(1)-O(1)-Al(2)#5	0.000(1)	Al(2)#5-Al(2)-O(3)-C(3)	149.2(10)
O(1)#2-Al(1)-O(1)-Al(2)#5	120.00(14)	Al(2)#4-Al(2)-O(3)-C(3)	107.5(10)
O(1)#3-Al(1)-O(1)-Al(2)#5	-120.00(14)	O(2)#2-Al(2)-O(3)-Al(2)#5	98.64(14)
O(1)#1-Al(1)-O(1)-Al(2)#4	120.00(14)	O(3)#4-Al(2)-O(3)-Al(2)#5	-78.30(16)
O(1)#2-Al(1)-O(1)-Al(2)#4	-120.00(14)	O(4)-Al(2)-O(3)-Al(2)#5	-165.20(15)
O(1)#3-Al(1)-O(1)-Al(2)#4	0.000(1)	O(1)-Al(2)-O(3)-Al(2)#5	1.92(13)
O(2)#2-Al(2)-O(2)-Al(2)#2	-11.74(16)	Al(2)#2-Al(2)-O(3)-Al(2)#5	86.53(15)
O(3)#4-Al(2)-O(2)-Al(2)#2	165.61(11)	Al(2)#4-Al(2)-O(3)-Al(2)#5	-41.67(12)
O(4)-Al(2)-O(2)-Al(2)#2	-106.82(12)	Al(2)-O(3)-C(3)-C(4)	20.9(16)
O(1)-Al(2)-O(2)-Al(2)#2	84.07(12)	Al(2)#5-O(3)-C(3)-C(4)	164.6(8)
Al(2)#5-Al(2)-O(2)-Al(2)#2	75.93(15)	C(4)#6-O(4)-C(4)-C(3)	-96.0(15)
Al(2)#4-Al(2)-O(2)-Al(2)#2	128.16(9)	Al(2)-O(4)-C(4)-C(3)	8.6(17)
O(2)#2-Al(2)-O(3)-C(3A)	-73.8(9)	Al(2)-O(4)-C(4)-C(4)#6	104.6(5)
O(3)#4-Al(2)-O(3)-C(3A)	109.3(9)	O(3)-C(3)-C(4)-O(4)	-18(2)
O(4)-Al(2)-O(3)-C(3A)	22.4(9)	O(3)-C(3)-C(4)-C(4)#6	-71.6(11)
O(1)-Al(2)-O(3)-C(3A)	-170.5(9)	Al(2)-O(3)-C(3A)-C(4A)	-12.5(16)
Al(2)#2-Al(2)-O(3)-C(3A)	-85.9(9)	Al(2)#5-O(3)-C(3A)-C(4A)	176.7(9)
Al(2)#5-Al(2)-O(3)-C(3A)	-172.4(10)	C(4A)#6-O(4)-C(4A)-C(3A)	-84(3)
Al(2)#4-Al(2)-O(3)-C(3A)	145.9(9)	Al(2)-O(4)-C(4A)-C(3A)	22(2)
O(2)#2-Al(2)-O(3)-C(3)	-112.2(10)	O(3)-C(3A)-C(4A)-O(4)	-9(2)
O(3)#4-Al(2)-O(3)-C(3)	70.9(10)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+7/4,-y+3/4,z+0

#2 x+0,-y+3/4,-z+3/4

#3 -x+7/4,y+0,-z+3/4

#4 z+1/2,x-1/2,y

#5 y+1/2,z,x-1/2

#6 x,z,y

Table S7. Hydrogen bonds for [$C_{24}H_{72}Al_{13}O_{40}$][Cl]$_7$[$H_2O$] [+ solvent]. (CCDC 1813736)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...Cl(1)	0.84	2.41	3.225(3)	163.5
O(5)-H(5A)...O(4)	0.840(5)	2.84(4)	2.97(2)	91(3)
O(5)-H(5B)...O(5)#2	0.840(5)	1.454(6)	2.242(18)	155(3)
O(2)-H(2)...Cl(1)	0.84	2.41	3.225(3)	163.5
O(4)-H(4)...Cl(2)	0.83(2)	2.19(3)	2.995(4)	163(5)
O(4)-H(4)...O(5)	0.83(2)	2.24(3)	2.97(2)	148.1(18)
O(4)-H(4)...O(5)#2	0.83(2)	2.24(3)	2.97(2)	148.1(17)
C(3)-H(3B)...Cl(2)#7	0.99	2.8	3.392(18)	119.0
C(4A)-H(4C)...O(5)#2	0.99	2.55	3.22(2)	125.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+7/4,-y+3/4,z+0

#2 x+0,-y+3/4,-z+3/4

#3 -x+7/4,y+0,-z+3/4

#4 z+1/2,x-1/2,y

#5 y+1/2,z,x-1/2

#6 x,z,y

#7 -z+1,x-1/4,y-1/4

Table S8. Solubility of $[C_{24}H_{72}Al_{13}O_{40}][Cl]_7[H_2O]$ [+ solvent]. (CCDC 1813736)

Entry	H_2O or Solvent	Solubility
1	H_2O	soluble
2	methanol	insoluble
3	ethanol	insoluble
4	isopropanol	insoluble
5	ethylene glycol	insoluble
6	benzyl alcohol	soluble
7	tetrahydrofuran	insoluble
8	acetonitrile	insoluble
9	dimethylformamide (DMF)	insoluble
10	dimethyl sulfoxide (DMSO)	insoluble
11	methyl isopropyl ketone	insoluble
12	ethyl acetate	insoluble
13	diethyl phthalate	soluble
14	benzene	slightly soluble
15	toluene	slightly soluble
16	*o*-xylene	slightly soluble
17	*n*-octane	insoluble
18	CS_2	insoluble
19	CCl_4	insoluble

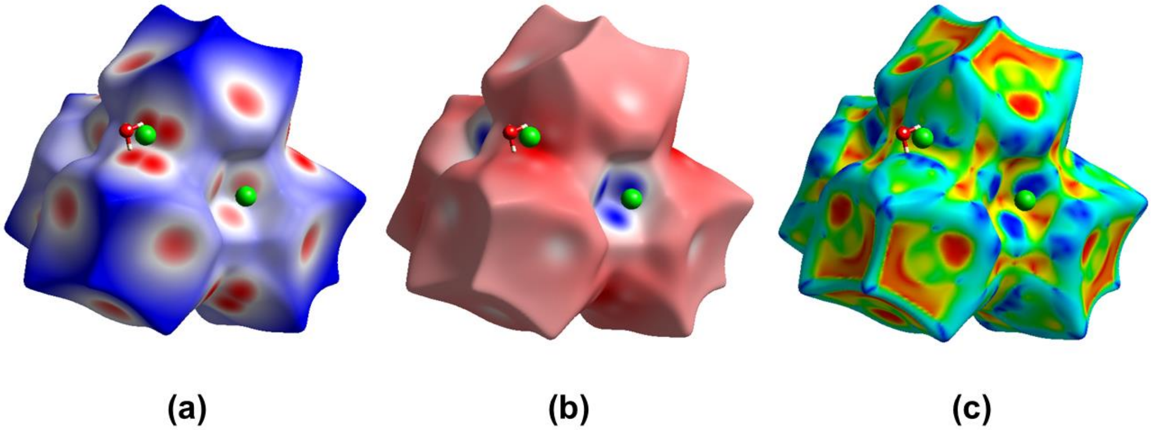

Figure S1. The Hirshfeld surface representation of single crystal gl-ε-Al_{13} chloride cation mapped with (a) d_{norm} function and showing H-bond interactions between Cl^-/H_2O and cluster molecules, (b) electrostatic potential and (c) with shape index function.[8]

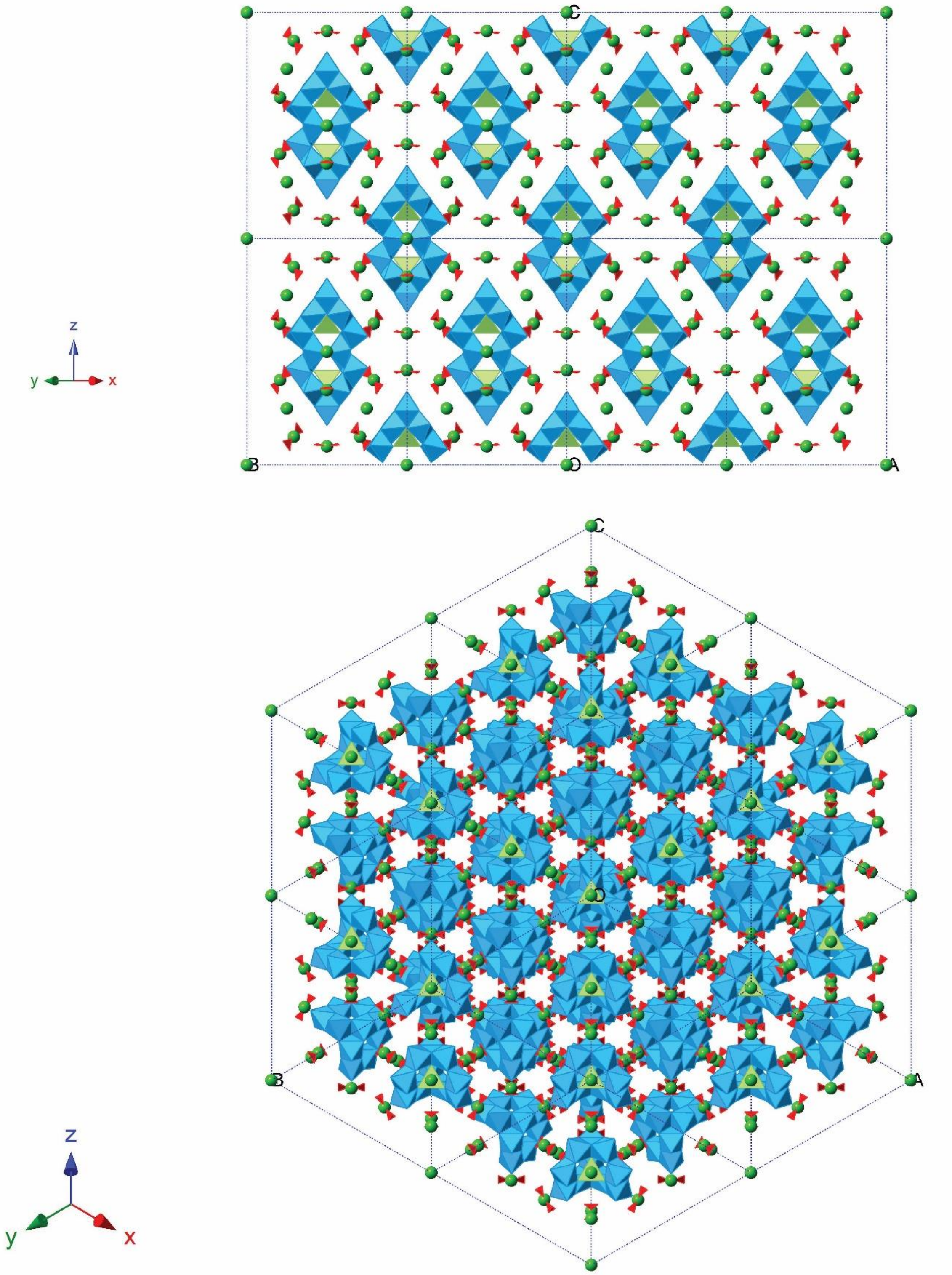

Figure S2. Crystal packing of gl-ε-Al_{13} chloride along (**top**) [110] and (**bottom**) [111] crystallographic directions. The clusters are shown in polyhedral representation with $Al(O)_6$ in blue, $Al(O)_4$ in green. The chloride ions are shown as green spheres and the small fraction of solvent waters associated with one chloride site are shown as red triangles. (CCDC 1813736)

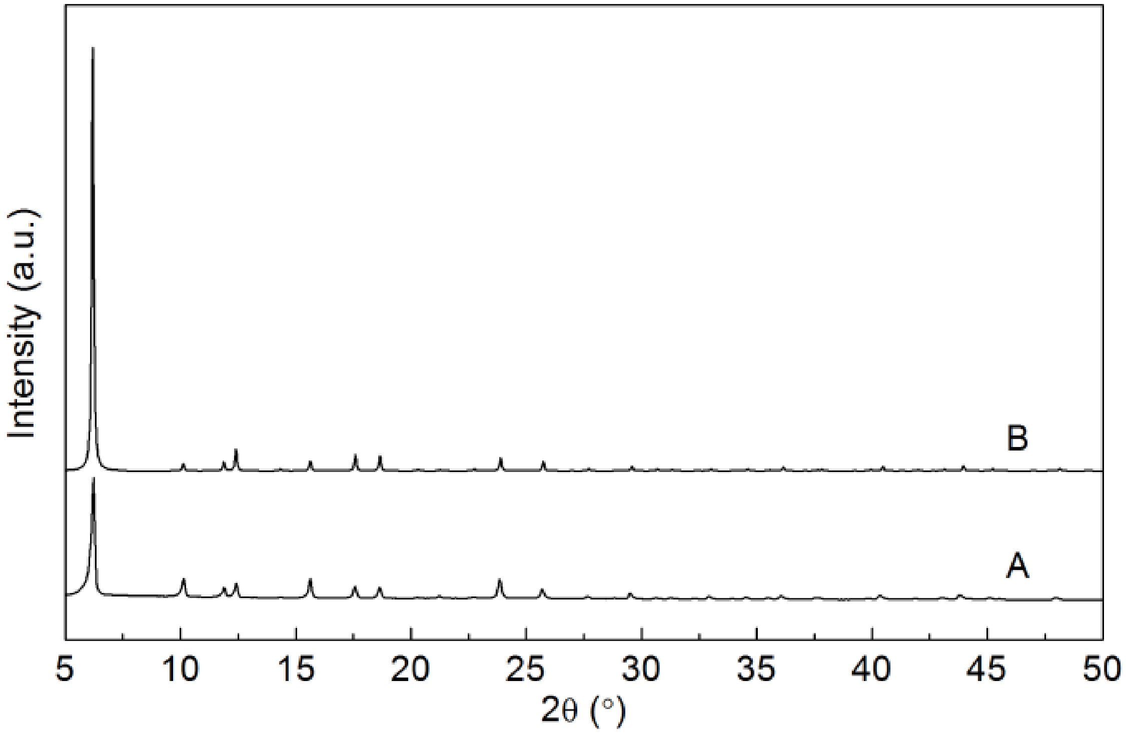

Figure S3. Comparison of experimental powder X-ray diffraction pattern (A) and the pattern simulated from single crystal analysis (B) for gl-*ε*-Al_{13}.

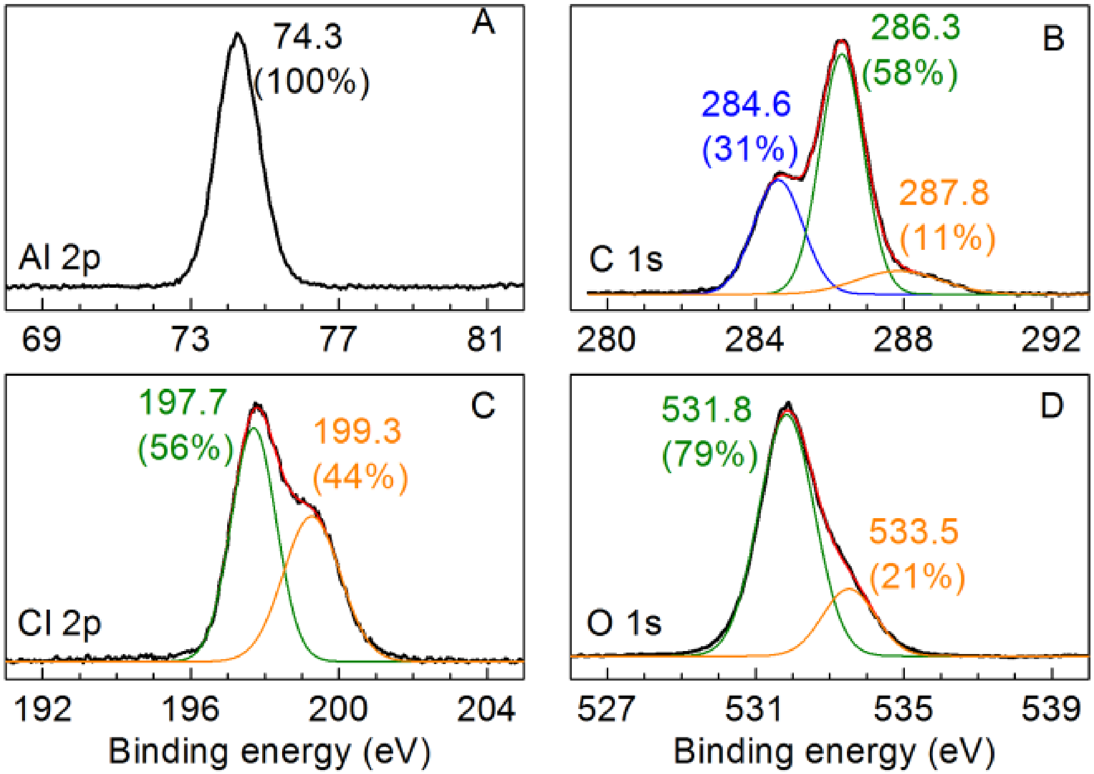

Figure S4. XPS spectra of gl-ε-Al_{13}.

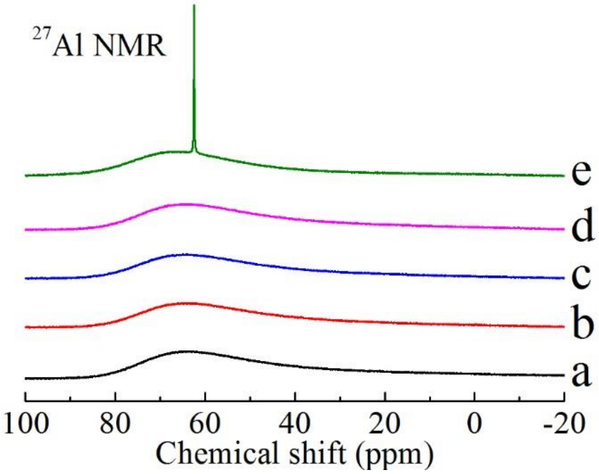

Figure S5 Liquid ^{27}Al NMR spectra of (a) blank and gl-ε-Al_{13} dissolved in (b) diethyl phthalate, (c) benzyl alcohol, (d) o-xylene and (e) H_2O.

There are no resonances for $Al(O)_4$ or $Al(O)_6$ observed for gl-ε-Al_{13} dissolved in diethyl phthalate (b), benzyl alcohol (c) and o-xylene (d). A sharp peak at δ=62.5 ppm assigned to $Al(O)_4$ is observed when gl-ε-Al_{13} is dissolved in H_2O, indicating the stability of Al_{13}^{7+} ions being dissolved in water.

References

1. Bruker (2017) APEX3 (Version 2017.3) and (2013) SAINT (Version 8.34a). Bruker AXS Inc., Madison, Wisconsin, USA.
2. An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.
3. Sheldrick, G.M., SADABS (2016) Version 2016/2, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.
4. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
5. Sheldrick, G. M., (2014) SHELXT, Universität Göttingen: Göttingen, Germany. Structure determination program. Private communication.
6. Sheldrick, G. M., (2014). SHELXL2014/7. Universität Göttingen: Göttingen, Germany.
7. A.L.Spek, Acta Cryst. 2009, D65, 148-155.
8. J. J. McKinnon, M. A. Spackman, A. S. Mitchell, *Acta Crystallographica Section B-Structural Science* **2004**, *60*, 627-668; bJ. J. McKinnon, D. Jayatilaka, M. A. Spackman, *Chemical Communications* **2007**, 3814-3816; cM. A. Spackman, J. J. McKinnon, D. Jayatilaka, *Crystengcomm* **2008**, *10*, 377-388.