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### Authors

Gu, Bin  
Sun, Chenglin  
Fettinger, James C  
[et al.](#)

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## Synthesis, characterization and properties of a glycol-coordinated $\epsilon$ -Keggin-type $\text{Al}_{13}$ chloride†

 Bin Gu,<sup>a</sup> Chenglin Sun,<sup>\*a</sup> James C. Fettinger,<sup>ib</sup> William H. Casey,<sup>ib</sup> Alla Dikhtiarenko,<sup>ic</sup> Jorge Gascon,<sup>ic</sup> Kamila Koichumanova,<sup>d</sup> Karthick Babu Sai Sankar Gupta,<sup>e</sup> Hero Jan Heeres<sup>if</sup> and Songbo He<sup>if</sup>

Herein we present the first example of a glycol-coordinated  $\epsilon$ -Keggin  $\text{Al}_{13}$  chloride (gl- $\epsilon$ - $\text{Al}_{13}$ ), which is the first chelated version since discovery of  $\text{Al}_{13}$  in 1960. The molecular structure consists of  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{12}(\text{OC}_2\text{H}_4\text{OH})_{12}]\text{Cl}_7\cdot\text{H}_2\text{O}$  units with chelating mono-anionic ethylene glycol units replacing one bridging and one terminal oxygen site.

The hydrolysis of aluminum salts in water produces an array of polyoxoaluminum clusters which are widely used in catalysis, water treatment, antiperspirant additives and pillaring agents for clays.<sup>1,2</sup> The Baker-Figgis-Keggin  $\text{Al}_{13}$  clusters, having the stoichiometry:  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ , are the most common multinuclear ions. The five isomers have an  $\text{Al}(\text{O})_4$  tetrahedral center surrounded by 4 trimeric aluminum-hydroxide caps ( $\text{Al}_3$ ) with aluminum coordinated in an octahedral fashion. The rotation of these  $\text{Al}_3$  caps results in  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$  isomers.<sup>3</sup> The  $\epsilon$ - $\text{Al}_{13}$  isomer, which is the most thermodynamically favored,<sup>4</sup> was first isolated by Johansson as sulfate and selenate salts.<sup>5</sup> The  $\delta$ - $\text{Al}_{13}$  isomer is less stable and was first isolated by Nazar.<sup>6,7</sup> The  $\gamma$ - $\text{Al}_{13}$  isomer was recently crystallized by Smart<sup>1</sup> and other derivatives have been reported.<sup>8</sup> In most cases, the Keggin-type clusters are crystallized as sulfate, sulfonate, or selenate salts because the interaction of  $\text{SO}_4^{2-}$  or  $\text{SeO}_4^{2-}$  with

aluminum polycations facilitates the crystallization process.<sup>3,9</sup> Although there have been many efforts,<sup>4,10–12</sup> the precise structure of  $\epsilon$ - $\text{Al}_{13}$  chloride salts is unknown since single crystals have not been isolated so far.

The conventional hydrolysis method for  $\text{Al}_{13}$  synthesis brings high concentrations of counteranions, usually  $\text{Na}^+$ , into the system, which suppresses  $\text{Al}_{13}$  chloride crystallization and purification.<sup>1,2,5,12</sup> In this work, we report a simple solvothermal method that allows the salts of the  $\epsilon$ - $\text{Al}_{13}$  isomer to crystallize in a new glycol-chelated form (gl- $\epsilon$ - $\text{Al}_{13}$ ) with the ion stoichiometry:  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{12}(\text{O}-\text{CH}_2-\text{CH}_2-\text{OH})_{12}]^{7+}$ . The overall charge is compensated by chloride ions and the ethylene glycol eliminates the bound water molecules, possibly suppressing hydrolysis. Ethylene glycol is present as a mono-anion coordinated in a bidentate fashion. The oxo replaces a  $\mu_2$ -OH in each  $\text{Al}_3$  cap and a hydroxo replaces a terminal water (Fig. 2). Single crystals can be crystallized within a few hours rather than days to weeks. To the best of our knowledge, it is the first example of an  $\epsilon$ - $\text{Al}_{13}$  isomer directly crystallized as a chloride salt or in a chelated form.

The catalytic properties of the gl- $\epsilon$ - $\text{Al}_{13}$  cluster are demonstrated by employing it as a heterogeneous catalyst for the synthesis of secondary amines *via* direct *N*-alkylation/amination of primary amines (*i.e.*, aniline) and alcohols (*i.e.*, benzyl alcohol). Such a catalyst is attractive as it involves green chemistry methods<sup>13,14</sup> and could conceivably replace C–N bond formation using expensive homogeneous catalysts, such as Pd, Ru and Ir complexes.<sup>15–17</sup> The heterogeneous catalyst is also attractive because separation does not require toxic additives, *i.e.*, ligands and base,<sup>18</sup> as may be the case with homogeneous catalysts. Alumina, aluminosilicates and zeolites,<sup>19–22</sup> and the supported metal (*e.g.*, Cu, Ni, Pd, Ag, Au, Ru and Pt) catalysts<sup>23–29</sup> have been recently reported. As we show, the gl- $\epsilon$ - $\text{Al}_{13}$  exhibits excellent primary amine conversion and secondary amine selectivity.

Single crystals (yield *ca.* 90%) of the gl- $\epsilon$ - $\text{Al}_{13}$  were isolated as chloride salts through solvothermal synthesis carried out in a Teflon-lined stainless steel autoclave (100 mL) at 150 °C for 6 h. Aluminium chloride hexahydrate ( $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ , 2.4 g) was

<sup>a</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.  
 E-mail: clsun@dicp.ac.cn

<sup>b</sup> Department of Chemistry, University of California, Davis, CA 95616, USA

<sup>c</sup> King Abdullah University of Science and Technology, KAUST Catalysis Center, Advanced Catalytic Materials, Thuwal 23955, Saudi Arabia

<sup>d</sup> Faculty of Science, University of Amsterdam, 1090 GS Amsterdam, The Netherlands

<sup>e</sup> Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

<sup>f</sup> Green Chemical Reaction Engineering, University of Groningen, 9747 AG Groningen, The Netherlands. E-mail: songbo.he@rug.nl

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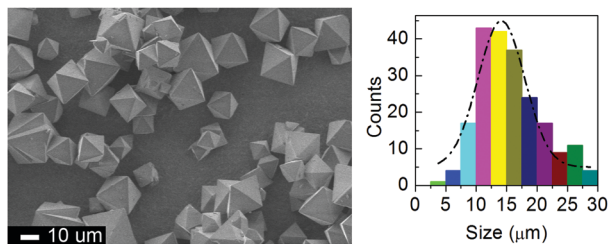


Fig. 1 SEM and particle-size distribution of single-crystal gl- $\epsilon$ -Al<sub>13</sub>.

dissolved in ethylene glycol (EG, 10 mL) under magnetic stirring, followed by adding ethanol (40 mL) to maintain a transparent solution. 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.

SEM images of gl- $\epsilon$ -Al<sub>13</sub> chloride (Fig. 1) show an octahedral morphology, with particles in the order of 3 to 30  $\mu\text{m}$  and very smooth surfaces.

The gl- $\epsilon$ -Al<sub>13</sub> structure crystallizes in the cubic space group  $F\bar{4}3m$  and has the formula of [Al<sub>13</sub>C<sub>24</sub>H<sub>72</sub>O<sub>40</sub>][Cl]<sub>7</sub>[H<sub>2</sub>O]. The structure is shown in Fig. 2A and B. Structural parameters are listed in Table S1 (ESI<sup>†</sup>). The essential structure of the  $\epsilon$ -Al<sub>13</sub> Keggin cluster, including the +7 overall charge, is preserved.<sup>30,31</sup> Correspondingly, bond-valence analysis, performed using Valist software,<sup>32</sup> indicates that the cationic Al<sub>13</sub> moiety can be described by the formula [AlO<sub>4</sub>Al<sub>12</sub>( $\mu_2$ -OH)<sub>12</sub>(OCH<sub>2</sub>CH<sub>2</sub>OH)<sub>12</sub>]<sup>7+</sup>. As expected for the Keggin isomers, the gl- $\epsilon$ -Al<sub>13</sub> contains one

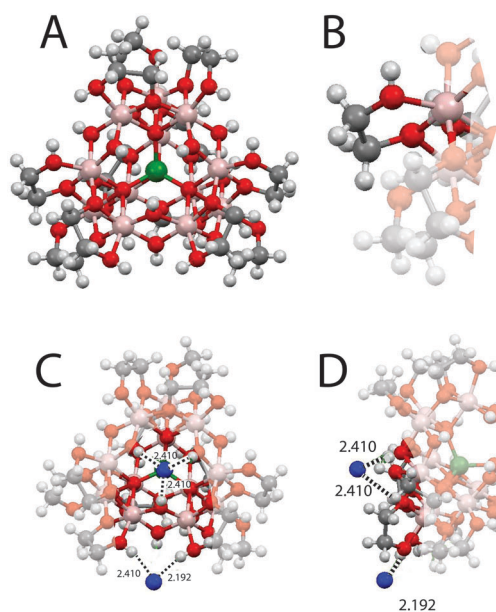


Fig. 2 (A) [AlO<sub>4</sub>Al(OH)<sub>12</sub>(OC<sub>2</sub>H<sub>4</sub>OH)<sub>12</sub>Cl]<sub>7</sub>·H<sub>2</sub>O (gl- $\epsilon$ -Al<sub>13</sub>) structure. The central Al(O)<sub>4</sub> is drawn in green, the twelve Al(O)<sub>6</sub> are drawn in light purple, oxygens are drawn in red, carbons are drawn in grey and hydrogens are drawn in white. (B) Ethylene glycols chelate to Al(O)<sub>6</sub> by having one hydroxyl functional group replace a terminal water, forming a  $\mu$ -(OH-CH<sub>2</sub>), and the other end coordinating to a bridging oxo between two Al(O)<sub>6</sub>, forming a  $\mu_3$ -(O-CH<sub>2</sub>). (C and D) The located Cl<sup>-</sup> counterions are located near a ring of  $\mu_2$ -OH and between two  $\mu_2$ -OH. The Cl(2) site is completely occupied; 5/6 of the time as Cl<sup>-</sup> and 1/6 as a water.

crystallographically unique, tetrahedrally coordinated Al(III) cation with Al-O bond length of 1.825(4) Å. It also contains twelve Al(III) cations that are each octahedrally coordinated. The inner-coordination sphere of each Al(O)<sub>6</sub> includes a  $\mu_4$ -O oxo, two  $\mu_2$ -OH, two  $\mu_3$ -O-glycols and a single  $\mu_2$ -OH-glycol. The glycols are part of a bidentate chelate that terminates at the other end in a  $\mu_2$ -OH-glycol replacing what is normally a water molecule bound to the Al<sub>13</sub>.

Two crystallographically nonequivalent Cl<sup>-</sup> anions, acting as counter anions, provide overall charge balance for the structure. Four Cl<sup>-</sup> anions (Fig. 2C and D, Cl1) are located in the cavity along the axis of the AlO<sub>4</sub> facets (Fig. 2C), in a ring of  $\mu_2$ -OH, and hydrogen-bond to the Al<sub>13</sub><sup>7+</sup> cation,<sup>10</sup> which is also indicated by the previous modeling.<sup>11</sup> Another three Cl<sup>-</sup> anions sharing positions with the crystallization water molecules (Fig. 2, Cl2) are disordered. In the crystal structure of the gl- $\epsilon$ -Keggin Al<sub>13</sub>, the distorted hexagonal channels run between the molecules along [111] direction (Fig. S2, ESI<sup>†</sup>) and possess a significant free volume where additional water, ethanol or ethylene glycol, may be located and have been removed using the program Platon-Squeeze (see ESI<sup>†</sup>).<sup>33</sup>

A comparison between the powder XRD and the simulated XRD patterns from single crystal analysis is shown in Fig. S3 (ESI<sup>†</sup>), which indicates high crystallinity and purity of the synthesized compound.

FT-IR and Raman spectra of gl- $\epsilon$ -Al<sub>13</sub> shown in Fig. 3 have a few similar vibrational bands belonging to species that are both Raman and IR active. Two broad bands at 3500 and 3100  $\text{cm}^{-1}$  are assigned to the OH stretching vibrations of the gl- $\epsilon$ -Al<sub>13</sub><sup>34</sup> and hydrogen-bonded OH groups of coordinated water, respectively. Presence of water can also be confirmed by the clear water-bending mode in FT-IR at 1636  $\text{cm}^{-1}$ . In the 3000–2800  $\text{cm}^{-1}$  region which is typical for methyl and methylene C-H stretching modes, the peaks are less clear due to underlying O-H broad band. However, 2964, 2892 and 2820  $\text{cm}^{-1}$  bands can be assigned to CH<sub>2</sub>-bands of ethoxy-groups of gl- $\epsilon$ -Al<sub>13</sub>.<sup>35</sup> These groups also give rise to CH<sub>2</sub>-bending modes at 1469, 1419, 1412, 1369 and 1350  $\text{cm}^{-1}$ , and their overtones at 2800–2600  $\text{cm}^{-1}$ . Sharp bands at 1096, 996 and 891  $\text{cm}^{-1}$  are assigned to Al-O-C bonds.

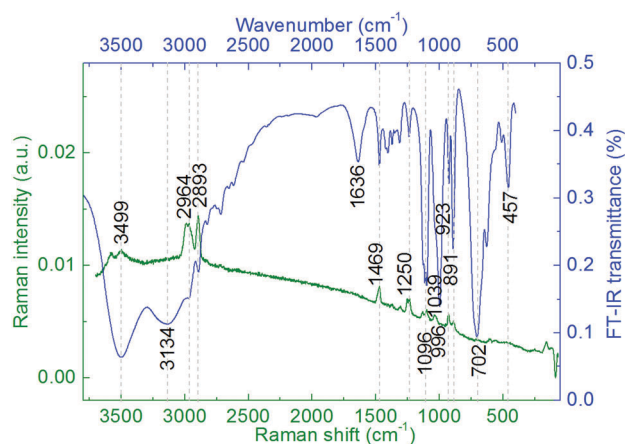


Fig. 3 FT-IR and Raman spectra of single-crystal gl- $\epsilon$ -Al<sub>13</sub>.

However, the presence of solvent C–OH and CH<sub>x</sub> bands cannot be excluded (ethanol and ethylene glycol).<sup>1,36</sup> The strong band at 702 cm<sup>-1</sup> can be attributed to Al–O–Al structural unit of gl-ε-Al<sub>13</sub> chloride and is identical to the ε-Al<sub>13</sub>.<sup>37,38</sup>

The <sup>1</sup>H MAS SSNMR spectrum of gl-ε-Al<sub>13</sub> chloride (Fig. 4A) shows two resonances at 1.3 ppm and 3.8 ppm, which are assigned to bridging –OH and –OCH<sub>2</sub>. The broad resonance peak at 4–6.5 ppm is ascribed to physically adsorbed water.<sup>39,40</sup> In the <sup>13</sup>C NMR spectrum, two adjacent resonances are observed at 60.2 ppm and 63.3 ppm (Fig. 4B), which clearly indicate the coexistence of two different chemical environments for the methylene groups. One of them is slightly more deshielded than the other, probably due to hydrogen bonding. The <sup>27</sup>Al NMR spectrum (Fig. 4C) displays a sharp peak at 61.6 ppm, which could be assigned to AlO<sub>4</sub> species, and a broad peak centered at 4.4 ppm corresponding to AlO<sub>6</sub>.<sup>41–43</sup> The broadness displays the presence of large quadrupole couplings and a possibility of presence of multiple Al environments, as expected.<sup>44</sup>

The Al/Cl atom ratio of gl-ε-Al<sub>13</sub> chloride derived from XPS analysis (Fig. S4, ESI<sup>†</sup>) is 1.95, which is in accordance with the chemical formula (1.86), elemental analysis (1.85) and the SEM-EDS analysis (1.84). Spectra fitting of Cl(2p) (Fig. S4, ESI<sup>†</sup>) reveals two intensive peaks centered at 197.7 eV and 199.3 eV, which correspond to Cl1 and Cl2. The Cl2/Cl1 ratio is 0.79, which consists well with the above theoretical value 0.75.

This gl-ε-Al<sub>13</sub> chloride was used as catalyst for the *N*-alkylation of aniline with benzyl alcohol (Table 1). Aniline, benzyl alcohol and gl-ε-Al<sub>13</sub> were successively added to 5.0 mL *o*-xylene in a 15 mL quartz tube followed by purging with nitrogen to remove oxygen. The reactor tube was sealed and transferred into a preheated oil bath to perform *N*-alkylation at 150 °C and auto-generated pressure, followed by cooling in the cold water and centrifuging. The liquid products were analyzed on an Agilent 7890A GC equipped with FID and mass spectrometer. It can be seen from Table 1 that when catalyst loading reaches 0.6 mmol/1 mmol aniline, aniline 1 conversion surpasses 90% (Entry 1–4). 100% aniline conversion can be obtained by increasing alcohol/aniline ratio (Entry 2–1 and 2–2) with the compensation of more di-alkylation to form tertiary amine 5. Instead of hydrogen

Table 1 *N*-Alkylation of aniline with benzyl alcohol using single crystal gl-ε-Al<sub>13</sub> chloride salt as the catalyst

Entry	Catalyst/reactant (mmol)			Reaction time (h)	Conversion/selectivity (%)			
	ε-Al <sub>13</sub>	1	2		1	3	4	5
0–1	0	1	1	12	0	0	0	0
0–2	0	1	3	12	0	0	0	0
1–1	0.06	1	1	12	22.3	5.4	94.6	0
1–2	0.19	1	1	12	43.3	3.8	96.2	0
1–3	0.43	1	1	12	87.3	4.9	95.1	0
1–4	0.6	1	1	12	90.4	4.4	95.6	0
2–1	0.6	1	2	12	100	0.2	85.8	3.4
2–2	0.6	1	3	12	100	0.2	89.7	2.7
3–1	0.6	1	1	4	35.5	0.6	99.5	0

autotransfer (HA) or borrowing hydrogen (BH) strategy,<sup>13,14</sup> direct *N*-alkylation of primary amine with alcohol over the single crystal gl-ε-Al<sub>13</sub> chloride seems to follow well what is expected from intermolecular dehydration, which were also reported by Ready *et al.*<sup>21</sup> (0% yield of secondary amine 4 over SiO<sub>2</sub> and 98% yield of 4 over nanosized zeolite beta), Sreenivasulu *et al.*<sup>20</sup> (100% selectivity of imine 3 over nano-aluminosilicate) and Srinivasu *et al.*<sup>19</sup> (60% yield of 4 over 2-D hexagonal aluminosilicate). Extending the reaction time from 4 hours (Entry 3–1) to 12 hours (Entry 2–2) increases aniline conversion while decreases the selectivity of 4 from 99.5% to 89.7%.

These results indicate promise for the gl-ε-Al<sub>13</sub> chloride to be useful in green catalysis. However, the significance of successful synthesis of gl-ε-Al<sub>13</sub> chloride even transcends the catalytic properties. The Keggin ions are among the few cationic clusters of nanometer sizes and attempts to isolate clusters made of metals besides aluminum have met with little success. There are still few other clusters of trivalent metals, although they have been speculated about for decades.<sup>45–48</sup> Attempts at aqueous synthesis of new metal cation clusters often fail because of uncontrolled hydrolysis – the bound water molecules deprotonated leading to uncontrolled gel formation. This point was emphasized recently by Sadeghi *et al.*<sup>49</sup> who obtained a version of the Fe<sub>13</sub> as a Keggin cluster only by replacing the terminal water molecules with organic ligands. In this paper we suggest a simple means of accomplishing this replacement, which indicates a new strategy for expanding the library of hydrolytic clusters. The replacement of bound water molecules with bridging glycols may allow dissolution of the ε-Al<sub>13</sub> into a wider range of organic solvents (Table S8 and Fig. S5, ESI<sup>†</sup> however the Al<sub>13</sub> was not found to be stable in those solvents). If so, it suggests a pathway for isolating new clusters that would hydrolyze uselessly in aqueous solutions, including perhaps clusters of other trivalent metals or larger aluminum clusters (*e.g.*, Al<sub>30</sub>) that build upon the Keggin structural moieties.

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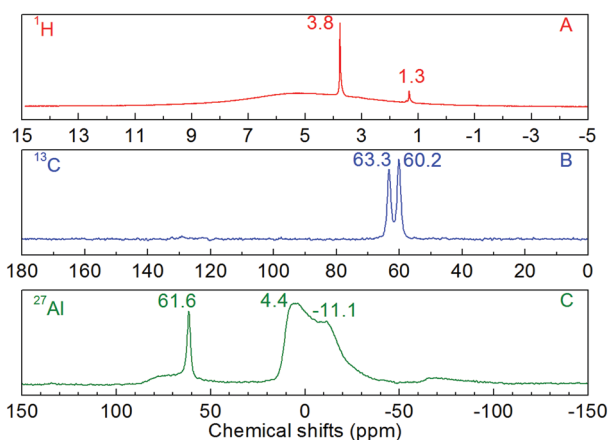


Fig. 4 MAS solid state NMR spectra of single-crystal gl-ε-Al<sub>13</sub>.

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## Conflicts of interest

There are no conflicts to declare.

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