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Journal

Chemistry - A European Journal, 22(52)

ISSN

0947-6539

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Publication Date

2016-12-23

DOI

10.1002/chem.201604640

Peer reviewed

NMR Spectroscopy | Very Important Paper |

VIP Isomerization of Keggin Al₁₃ Ions Followed by Diffusion Rates

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Abstract: The solution chemistry of aluminum has long interested scientists due to its relevance to materials chemistry and geochemistry. The dynamic behavior of large aluminum–oxo–hydroxo clusters, specifically [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (Al₁₃), is the focus of this paper. ²⁷Al NMR, ¹H NMR, and ¹H DOSY techniques were used to follow the isomerization of the ε-Al₁₃ in the presence of glycine and Ca²⁺ at 90 °C. Although the conversion of ε-Al₁₃ to new clusters and/or Baker–Figgis–Keggin isomers has been studied previously, new ¹H NMR and ¹H DOSY analyses provided information about the role of glycine, the ligated intermediates, and the mechanism of isomerization. New ¹H NMR data suggest that glycine plays a critical role in the isomerization. Surprisingly, glycine does not bind to Al₃₀ clusters, which were previously proposed as an intermediate in the isomerization. Additionally, a highly symmetric tetrahedral signal (δ = 72 ppm) appeared during the isomerization process, which evidence suggests corresponds to the long-sought α-Al₁₃ isomer in solution.

Aluminum is the third most abundant element in the earth's crust and has a complex solution chemistry.^[1] The dynamic behavior of large aluminum–oxo–hydroxo clusters is interesting to both material scientists and geochemists due to the similarities in molecular structure of these large molecules to thin films and minerals.^[2] The solution chemistry of the large clusters is also interesting because some properties are distinct from the aluminum monomers, including types of reactivity, the bioavailability, and the toxicity.^[3]






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Supporting information for this article can be found under
<http://dx.doi.org/10.1002/chem.201604640>.

Table 1. Five isomers of the Baker–Figgis–Keggin cluster, ε, δ, γ, β, and α, are distinguished by the rotation of the trimeric caps from corner-shared to edge-shared octahedra. The experimental ²⁷Al NMR chemical shifts for the central tetrahedral Al³⁺ are reported.

Baker–Figgis–Keggin isomer					
	ε	δ	γ	β	α
Literature	63	64.5	76	–	71.4 ^[a]
Reference	[8, 11, 12]	[7]	[12]	–	[13]

[a] Solid-state NMR data from the aluminosilicate mineral zunyite.

There are five possible isomers of the Baker–Figgis–Keggin (Keggin) structure: α, β, γ, δ, and ε of the stoichiometry: [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (Al₁₃). Each isomer in the series differs by rotation of the exterior trimeric caps (Table 1) from edge-shared to a corner-shared geometry. The most common and well-studied aluminum cluster is the ε-isomer.^[4] In contrast, the α-isomer is the most commonly observed version among anionic transition-metal polyoxometalates. These anions are made of metals larger and more highly charged than Al^{III}, such as W^{VI}, and these require the extra space provided by the corner-sharing geometry of the α-Keggin structure.

Although ε-Al₁₃ is the most common isomer and has been observed in nature,^[5] there is rare mention of the other aluminum Keggin isomers/derivatives in the literature. The larger aluminum cations [Al₂₆O₈(OH)₅₀(H₂O)₂₀]¹²⁺ (Al₂₆), [Al₃₀O₈(OH)₅₆(H₂O)₂₆]¹⁸⁺ (Al₃₀), and [Al₃₂O₈(OH)₆₀(H₂O)₂₈]²⁰⁺ (Al₃₂) contain two δ-Al₁₃ moieties.^[6–9] The Al₃₀ has been well characterized,^[7,8,10,11] but the other large clusters have yet to be studied in detail in solution. The δ-Al₁₃ has been crystallized and studied in the solid state, in which it has a Na⁺ tightly bound to the one rotated trimeric cap.^[6,7] Most recently, the γ-Al₁₃ has been characterized by ²⁷Al NMR spectroscopy and single-crystal X-ray diffraction.^[12] The β-Al₁₃ and α-Al₁₃ have not been synthetically isolated, but a version of the α-Al₁₃ can be observed within the structure of the aluminosilicate mineral zunyite.^[13]

These isomers can be distinguished from one another in solution by the ²⁷Al NMR signal of the center tetrahedral Al^{III} site (Table 1). The dynamic behavior of ε-Al₁₃ was previously studied by using ²⁷Al NMR, which provided evidence for the conversion/isomerization of ε-Al₁₃ to Al₃₀ and γ-Al₁₃, respectively.^[8,11,12] Building upon Nazar's earlier work,^[14] Allouche and Taulelle observed the formation of Al₃₀ (70 ppm) and three un-

identified aluminum species ($\delta = 64.5, 76, \text{ and } 81 \text{ ppm}$) upon heating $\epsilon\text{-Al}_{13}$ (63 ppm).^[11] One of these signals has since been identified as the $\gamma\text{-Al}_{13}$ isomer (76 ppm) by Smart et al., and another was proposed to be $\delta\text{-Al}_{13}$ (64.5 ppm).^[7,12]

Smart et al. observed isomerization when $\epsilon\text{-Al}_{13}$ was heated to 90°C in the presence of glycine (Gly) and Ca^{2+} .^[12] They proposed that the $\epsilon\text{-Al}_{13}$ first becomes Al_{30} (which has two $\delta\text{-Al}_{13}$ moieties) followed by $\gamma\text{-Al}_{13}$.^[12] This transformation was evident in changes in the ^{27}Al NMR spectra. Although calculations exist to estimate the energies of trimer rotation between isomers,^[15] these energies are too large to explain the experimental observations. Such large barrier energies imply that isomerization must be assisted by the electrolyte or that the isomers form from smaller oligomers, but not cap rotation. Thus, virtually nothing about the mechanism of the actual isomerization is known with confidence.

Herein, ^1H NMR and ^1H diffusion ordered spectroscopy (DOSY) methods were paired with ^{27}Al NMR to examine the dynamic behavior of these species in further detail. The glycine molecules were monitored by using ^1H NMR and ^1H DOSY techniques to shed light on the role of this ligand in the process. By monitoring the diffusion coefficients throughout the isomerization experiment by DOSY, we can infer the relative sizes of the molecules to which glycine is bound by the Stokes–Einstein relation. It is not necessary to calculate the exact hydrodynamic radii of the molecules or viscosity of the solution when using diffusion spectroscopy as a diagnostic tool for signal assignment, because we are concerned with distinguishing large from small ions only. Potential intermediates can also be identified using this technique.

As was expected, ^{27}Al NMR experiments indicated that $\epsilon\text{-Al}_{13}$ isomerizes at elevated temperatures in the presence of 1:1:1 glycine and CaCl_2 (Figure 1). The isomerization was repeated at 0.077, 0.0385, and 0.026 M $\epsilon\text{-Al}_{13}$ (1.0, 0.5, and 0.33 M Al^{3+}), with the only visible difference being the amount of monomer present, but no other changes in the final products. The pD (pH of a D_2O solution) of the solution decreased from 5.4 to 4.4 during the experiment, and minor amounts of precipitate were formed, which were filtered away when observed. The decrease in pD is due to hydrolysis and the formation of new hydroxide/oxide bridges. This hydrolysis could be attributed to either the direct condensation of Al_{13} clusters, or to the dissociation of cluster into Al^{3+} ions, followed by the subsequent polymerization into colloids. It should be noted that slight variations in the ^1H NMR chemical shifts occur during the reaction as the pD of the solution changes.

The ^{27}Al NMR spectra showed that the signal assigned to the central atom in the $\epsilon\text{-Al}_{13}$ ($\delta = 63 \text{ ppm}$) decreased in intensity when the solution was heated (Figure 1). Simultaneously, a monomeric signal ($\text{Al}(\text{H}_2\text{O})_6^{3+}$ plus hydrolysis complexes) appeared near 0 ppm and was accompanied by four new signals that are downfield from the $\epsilon\text{-Al}_{13}$ signal (Figure 1). These new signals are assignable to the tetrahedral $\text{Al}(\text{O})_4$ in other polyoxocations and Al_{30} isomers. Based on previous work, one signal is assignable to the Al_{30} (70 ppm),^[7,8] two signals are assignable to the $\delta\text{-Al}_{13}$ and $\gamma\text{-Al}_{13}$ isomers (65 and 76 ppm), and one is an unassigned species (72 ppm).

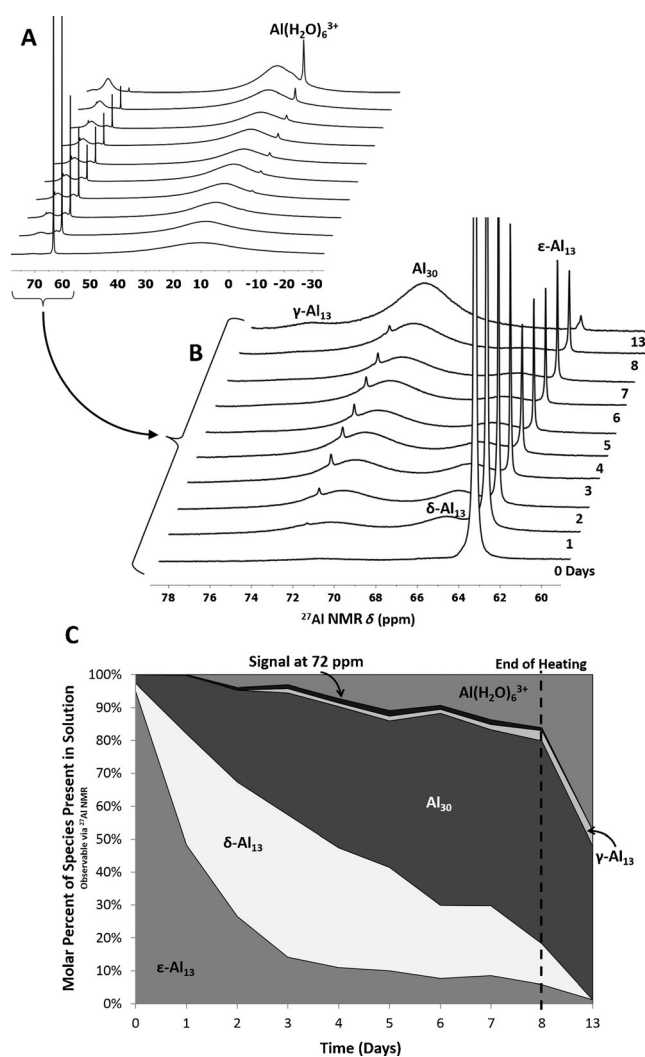


Figure 1. A) Full spectra of the ^{27}Al NMR data of a 1:1:1 $\text{Al}_{13}/\text{Gly}/\text{Ca}^{2+}$ (0.026 M) in D_2O solution. B) Tetrahedral region of the ^{27}Al NMR spectrum presented in part A. The sample was heated to 90°C for 8 days. The spectra from day 0 and 13 represent pre- and post-heating experiments. C) Relative dominance of each molecular species in solution is a function of time.

We propose that this new signal at $\delta = 72 \text{ ppm}$ is assigned to the $\alpha\text{-Al}_{13}$ isomer. The signal is very sharp, indicating a highly symmetric tetrahedral site, such as would be found in either the $\epsilon\text{-Al}_{13}$ or $\alpha\text{-Al}_{13}$, and not the other isomers with partly rotated trimeric caps (Figure 2). However, the ^{27}Al NMR peak position for the $\epsilon\text{-Al}_{13}$ is known to be near 63 ppm . Assignment of the peak at $\delta = 72 \text{ ppm}$ to the $\alpha\text{-Al}_{13}$ isomer is also consistent with ^{27}Al MAS NMR data for the mineral zunyite (centered at $\delta = 71.4 \text{ ppm}$), which contains the $\alpha\text{-Al}_{13}$ isomer moiety, but with pendent silicate groups.^[13] DFT corroborations for the $\alpha\text{-Al}_{13}$ signal assignment and other isomer chemical shift assignments are presented in the Supporting Information.

The ^1H NMR and ^1H DOSY data indicated that glycine is binding to a number of aluminum species during the isomerization (Figure 3). The NMR data indicated that glycine binds through the carboxylic acid and amine moieties when ligating to monomer ions (Al^{3+} and Ca^{2+}), but only through the carboxylic acid when binding to the cluster isomers (Figure 3A and B).

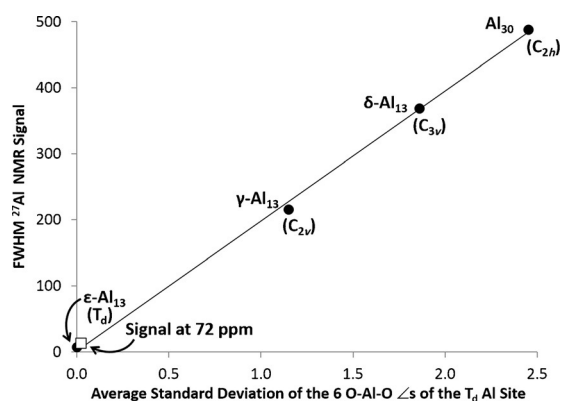


Figure 2. Distortion in the bond angles (represented by the average standard deviation) at the tetrahedral Al site determines the frequency width at half max (FWHM) of the corresponding ^{27}Al NMR signal. This relation suggests a highly symmetric tetrahedral site for the signal at $\delta = 72$ ppm, most likely the $\alpha\text{-Al}_{13}$ isomer.

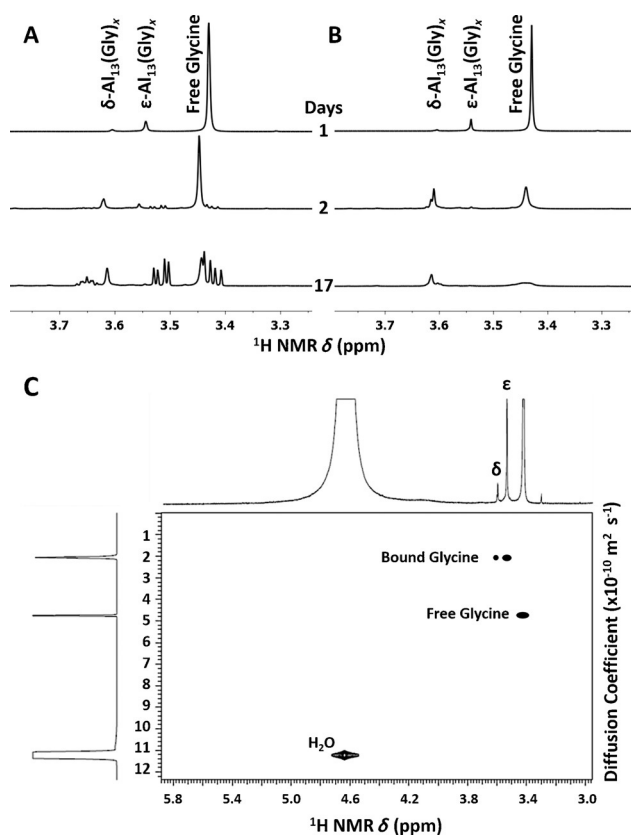


Figure 3. ^1H NMR of a 1:1:1 $\text{Al}_{13}/\text{Gly}/\text{Ca}^{2+}$ in D_2O solution at A) 0.077 M and B) 0.0385 M. C) DOSY NMR spectrum of the 0.0385 M solution after minor heating. The samples were both heated to 90°C for 8 days. The spectra from day 17 represents post-heating experiments.

This bonding geometry is clear from the eight signals, organized as two sets of doublets-of-doublets, which only appear on occasion, on either side of the NMR signal assignable to the free glycine. These signals represent locked AB doublets, and diffuse at a single rate that is slightly slower than free glycine and indicative of ligated monomers ($5.3 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

The new signals diffuse at an even slower rate (Figure 3C). Control experiments, which only consisted of $\epsilon\text{-Al}_{13}$ and glycine in D_2O (Figure S11-2 in the Supporting Information), confirmed that the additional signals diffuse at a rate similar to glycine bound to $\epsilon\text{-Al}_{13}$ ($\epsilon\text{-Al}_{13}(\text{Gly})_x$): $2.01 \pm 0.02 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$). The fact that the slowest diffusing species' signals are all singlets indicates that when the glycine molecules bond to the cluster they have rotational freedom, such as would be achieved by binding through only the carboxylic acid moiety.^[16,17]

The ^1H NMR data showed that after the first day of heating, most of the glycine bound to cluster-sized species is no longer $\epsilon\text{-Al}_{13}(\text{Gly})_x$ even though the ^{27}Al NMR data indicated a much slower isomerization process and that $\epsilon\text{-Al}_{13}$ still exists in solution. These results suggest that binding to glycine affects isomerization; therefore, upon heating, the $\epsilon\text{-Al}_{13}(\text{Gly})_x$ quickly becomes $\delta\text{-Al}_{13}(\text{Gly})_x$. Surprisingly, the ^1H DOSY NMR data indicated that although there is a large amount of Al_{30} in solution, it is apparently not an essential intermediate to the glycine-isomerization process. Glycine apparently does not bind to Al_{30} in these solutions and then induce isomerization—the isomerization reaction is apparently between the Al_{13} molecules themselves. However, we cannot rule out isomerization caused by dissociation of the oligomers into monomers and then reformation into the oligomers. A control experiment, which only consisted of Al_{30} and glycine in D_2O (Figure S13 in the Supporting Information), concluded that when glycine does bind to the Al_{30} , it diffuses slower ($\text{Al}_{30}(\text{Gly})_x$): $1.10 \pm 0.04 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) than any of the Al_{13} isomers, as was expected (Figure 4).

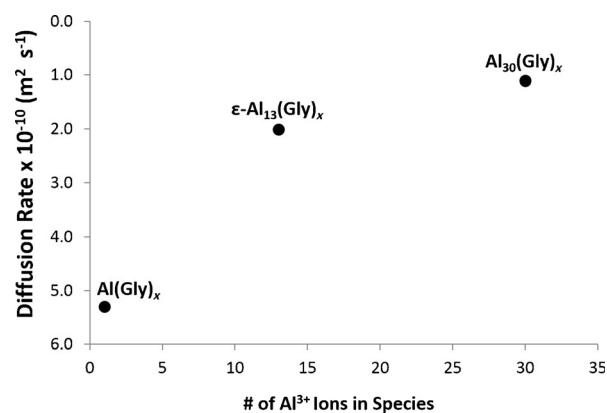


Figure 4. Relationship between the number of Al^{3+} ions in a molecule (size) and the diffusion coefficients of the bound glycine measured by ^1H DOSY technique.

This isomerization experiment was repeated with other chloride salts (NaCl, MgCl_2 , KCl, and LiCl) to establish whether Ca^{2+} was essential. The ^{27}Al NMR data indicated no difference between solutions containing CaCl_2 or other salts; however, the ^1H NMR data included two or three new ^1H NMR signals, depending on concentration, after heating (Figure S14 in the Supporting Information). These new ^1H NMR signals, in addition to the single signal observed in solutions containing Ca^{2+} , were confirmed by ^1H DOSY technique to be glycine bound to Al_{13} isomer(s). The appearance of the new signals in solutions con-

taining Na^+ , Mg^{2+} , K^+ , and Li^+ did not seem to be related to the solvated radius or charge of these cations. Clearly, bonding between glycine and Ca^{2+} is unique, but interestingly, the ^{27}Al NMR data continue to indicate that the same isomers of Al_{13} are formed in all solutions.

In summary, we found evidence that glycine enhances the isomerization process of the aqueous Al_{13} isomers, including the formation of the long-sought $\alpha\text{-Al}_{13}$ isomer. ^1H NMR and ^1H DOSY analyses indicated that glycine is ligated to intermediates and seems to be essential to the isomerization process. In the absence of bound glycine, the reaction leads to larger oligomers (e.g., Al_{30}). The ^1H NMR data revealed information that is unavailable from examination of ^{27}Al data alone; they showed, for example, that although Al_{30} forms during the process, glycine does not bind to this larger cluster.

Experimental Section

$\epsilon\text{-Al}_{13}$ was synthesized by using a standard method^[4,5] and crystallized with SO_4^{2-} counterions. Because the sulfate salt of $\epsilon\text{-Al}_{13}$ is insoluble in aqueous solutions, we extracted the free cation using a metathesis reaction with BaCl_2 .^[18] All samples were prepared in D_2O to provide a lock signal for ^1H NMR spectroscopy. Samples were heated to 90°C in an oil bath. Daily they were removed for NMR analysis. ^{27}Al NMR spectroscopy was conducted on a Bruker 500 MHz Avance NMR spectrometer built around an 11.74 T cryomagnet (130.3 MHz ^{27}Al). ^{27}Al NMR spectra were collected on a DOTY Scientific DSI-760 10 mm high-resolution probe with a low aluminum-background signal. All ^{27}Al NMR spectra were recorded with an internal standard of 50 mM $\text{NaAl}(\text{OH})_4$ inside a coaxial glass NMR insert, which was referenced to 80 ppm. ^1H NMR and DOSY data were collected with a 600 MHz Varian 5 mm probe. The DOSY experiments were performed by using the Gradient Stimulated Echo with Spin-Lock and Convection Compensation (DgsteSL_cc) pulse sequence.^[19] All Varian Software default settings were employed in the DOSY experiments with these exceptions: the diffusion delay was increased to 100 ms, the number of increments was increased to 25, the lowest gradient value was set to 1000, and the highest gradient value was set to 30000 (gradient values are unitless in the Varian Software on an arbitrary scale provided by a digital-to-analogue converter). These gradient values correspond to 2.1 and 62.1 G cm^{-1} , respectively. DOSY NMR data was processed by using VNMRJ software.

Acknowledgements

Experimental work was supported in part by NSF Phase-2 CCI, Center for Sustainable Materials Chemistry (NSF CHE-1102637).

In addition, P.H.Y.C. is the Bert and Emelyn Christensen professor of OSU, and gratefully acknowledges financial support from the Stone family. C.K.P. and P.H.Y.C. also acknowledge financial support and computing infrastructure in part provided by the NSF Phase-2 CCI, Center for Sustainable Materials Chemistry (NSF CHE-1102637). The authors thank Dr. Jeff Walton of the UCD NMR facility staff, and Dr. Andy Ohlin of Monash University for providing NMR help and the optimized structures for the isomers used in the NMR chemical shift computations, respectively.

Keywords: aluminum · glycine · isomerization · Keggin ions · NMR spectroscopy

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Received: September 30, 2016

Accepted Article published: October 26, 2016

Published online on November 23, 2016