Synthetic Routes to a Nanoscale Inorganic Cluster

$[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})](\text{NO}_3)_{15}$ Evaluated by Solid-State ^{71}Ga NMR

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Abstract

Solid-state ^{71}Ga NMR was used to characterize a series of $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})](\text{NO}_3)_{15}$ “ Ga_{13} ” molecular clusters synthesized by multiple methods. These molecular clusters are precursors to thin film electronics and may be employed in energy applications. The synthetic routes provide varying levels of impurities in the solid phase, and these impurities often elude traditional characterization techniques such as powder X-ray diffraction and Raman spectroscopy. Solid-state NMR can provide a window into the gallium species even in amorphous phases. This information is vital in order to prevent the impurities from causing defect sites in the corresponding thin films upon gelation and condensation (polymerization) of the Ga_{13} clusters. This work demonstrates the resolving power of solid-state NMR to evaluate structure and synthetic quality in the solid state, and the application of high-field NMR to study quadrupolar species, such as ^{71}Ga .

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1. Introduction

A persistent goal in modern electronics has been the production of high quality metal-oxide thin films, and the ability to produce these films from aqueous solution methods has received significant attention due to the scalability for depositing on large surface areas.[1, 2, 3] Hydroxo-aquo metal clusters have been envisioned as suitable candidates for precursors to metal-oxide thin films. Previous work has demonstrated the applicability of these water-based clusters to produce dense, high-quality thin films with minimal defects through solution deposition techniques such as spin-coating and spray coating.[4, 5, 6, 7]

Prior studies have shown that Group 13 clusters can be prepared on the gram-scale via multiple synthetic routes,[8, 9, 10, 11, 12, 13] and they serve as ideal candidates for metal-oxide thin films. The characterization of these clusters has been performed previously us-

ing Raman spectroscopy,[13] powder X-ray diffraction (XRD),[8, 7] single crystal XRD,[8] liquid-state nuclear magnetic resonance (NMR),[10, 11, 12] and solid-state NMR.[14, 15] However, these highly charged cationic clusters contain varying levels of impurities, such as charge-balancing counterions and waters of crystallization (hydration), which are not easily detected. An array of oligomers are known to form in the solid state under specific conditions,[16] and the lack of long-range periodicity in these clusters complicates their characterization. However, solid-state NMR is an ideal spectroscopic tool to identify the cluster and the impurities that are present in the samples.

For the purpose of our study, we focused on the $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})](\text{NO}_3)_{15}$ species, which we refer to as “ Ga_{13} .” The cluster contains 13 six-coordinate gallium species with three types of sites: the core, the middle ring, and the outer ring. The core consists of one gallium atom that is connected to the middle ring by $\mu_3\text{-OH}$ ligands. The middle ring contains six gallium atoms which are connected by two $\mu_3\text{-OH}$ bridges to the core and four $\mu_2\text{-OH}$ bridges to the outer ring. There are six outer ring sites which are coordinated by two $\mu_2\text{-OH}$ bridges and four H_2O capping ligands. A polyhedral representation (Figure 1) shows the core and middle ring lying in a plane of edge-sharing

Figure 1: Representation of the “Ga₁₃” structure, [Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)](NO₃)₁₅ as a ball-and-stick structure and as space-filling polyhedra. The core gallium, middle ring, and outer ring gallium sites are colored green, orange, and blue, respectively. The oxygen and hydrogen atoms are red and white, respectively.

octahedra, while the outer ring atoms are in corner sharing octahedral sites. The possible routes for the synthesis of the Ga₁₃ cluster includes the dibutyl nitrosamine (DBNA) addition method,[8] electrochemical reduction method,[17, 18] and zinc reduction method.[13] We recently detailed the solid-state ⁶⁹Ga and ⁷¹Ga NMR characterization of Ga₁₃. [14] The spectrum from reference [14] is reproduced (Figure 2) to provide a guide to the spectral deconvolution that follows for the clusters prepared by the different synthetic routes.

Solid-state NMR is a powerful technique in the characterization of metal-oxide clusters as it is nucleus specific and can provide a wealth of information regarding structure. Here, ⁷¹Ga NMR was used to deconvolute the experimental NMR spectra of the [Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)](NO₃)₁₅ “Ga₁₃” clusters made by multiple synthetic methods. Gallium has two NMR-active isotopes, ⁶⁹Ga and ⁷¹Ga, both of which are quadrupolar and have a nuclear spin quantum number of $I = 3/2$. While ⁷¹Ga is lower in natural abundance at 40%, it has a smaller quadrupolar moment which makes it a more attractive nucleus than its ⁶⁹Ga counterpart. The nuclear quadrupolar moment (eQ) can interact with the

Figure 2: ⁷¹Ga NMR of [Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)](NO₃)₁₅ shown in black. The spectrum was recorded at 13.9 T and spinning at $\nu_R = 33.3$ kHz. * denote spinning sidebands. The simulated NMR lineshapes depicting the core, middle ring and outer ring resonances are shown in green, orange, and blue, respectively.

electric field gradient (EFG),[19] and this interaction is informative about the local environment surrounding the quadrupolar species. The quadrupolar coupling causes broadening of the NMR lineshape, and if second-order quadrupolar interactions are observed, the NMR lineshapes can be described by two parameters: axial asymmetry parameter (η_Q) and quadrupolar coupling constant (C_Q). The axial asymmetry parameter is described by the elements of the diagonalized electric field gradient tensor and can be expressed as $\eta_Q = (V_{xx} - V_{yy}) / V_{zz}$. [20] The quadrupolar coupling constant C_Q can be expressed as $C_Q = e^2 q Q / h$, where eQ is the nuclear quadrupole moment, eq is the principal field gradient element from the EFG tensor ($eq = V_{zz}$), and h is Planck’s constant. Interactions from chemical shift anisotropy and dipole-dipole coupling can be ignored as the spectra were collected under magic angle spinning (MAS) conditions.[20] The recorded spectrum is that of the quadrupolar central transition which is subject to second-order quadrupolar broadening and is unaffected by first-order quadrupolar effects. MAS does not average the second-order quadrupolar interactions to zero; therefore, these effects need to be taken into account.

Herein, we present a solid-state gallium NMR study of Ga₁₃ with powder X-ray diffraction showing that NMR is sensitive to the impurities that are present via the synthetic route chosen for cluster formation. This information will be valuable for synthetic chemists to assess purity of a particular synthetic route. Such spectra will be highly informative in the production of the corresponding thin films that are prepared from these metal hydroxo-aquo clusters as impurities can cause de-

fects in the films.

2. Materials and Methods

2.1. Synthesis of $[Ga_{13}(\mu_3-OH)_6(\mu_2-OH)_{18}(H_2O)](NO_3)_{15}$

Reagents were ACS grade with no further purification or drying procedures. $Ga(NO_3)_3 \cdot xH_2O$ was used, and the degree of hydration was determined by gravimetric analysis using a box furnace. $Ga(NO_3)_3 \cdot xH_2O$ (1.00 g) was heated at 1000 °C in air for 4 hours, Ga_2O_3 was formed and massed (234 mg) and the moles of Ga were calculated (1.25 mmol Ga_2O_3 , 2.50 mmol Ga) to give a molecular weight of 400 g/mol and an approximate molecular formula of $Ga(NO_3)_3 \cdot 8H_2O$.

Three methods of Ga_{13} synthesis were performed.

DBNA [8] Addition Method

$Ga(NO_3)_3 \cdot 8H_2O$ (0.250 g, 0.625 mmol) was dissolved in methanol (10 mL) in a 20 mL scintillation vial, and dibutyl nitrosamine, DBNA, (0.900 mL, 5.10 mmol) was added and swirled to mix the contents. The solution was allowed to slowly evaporate under ambient conditions outside of a fume hood for 14 days. Crystals were isolated by decanting the oily residue in the vial and washing with acetone (49.1% yield).

Electrochemical Reduction [17, 18] Method

$Ga(NO_3)_3 \cdot 8H_2O$ (12.0 g, 30.0 mmol) was dissolved in water (30.0 mL) to make a 1 M solution. A three-electrode electrochemical setup was utilized, with Pt working electrode, Pt counter electrode, and Ag/Ag^+ reference electrode. A potential of -1.00 V vs reference electrode was applied with vigorous stirring for ~2 hours, until 420 Coulombs of charge was passed. The solution was allowed to slowly evaporate under ambient conditions outside of a fume hood until crystals formed (~14 days). Crystals were isolated before the solution fully evaporated, and crystals were washed with acetone (43.9 % yield).

Zn Reduction [13] Method

$Ga(NO_3)_3 \cdot 8H_2O$ (2.00 g, 5.00 mmol) was dissolved in water (5.00 mL) to make a 1.00 M solution. 100 mesh Zn powder (165 mg, 2.50 mmol) was added all at once under rapid stirring with a magnetic stir bar. The solution was allowed to mix overnight to dissolve all the Zn powder. The clear solution was filtered through a 0.100 μm filter into a crystallization dish, and allowed to slowly evaporate under ambient conditions outside of a fume hood until crystals formed (~14 days). Crystals were isolated before the solution fully evaporated, and crystals were washed with acetone (58.8% yield).

Figure 3: ^{71}Ga NMR of Ga_{13} at 13.9 T prepared by the a) DBNA addition, b) zinc reduction, and c) electrochemical reduction methods. The experimental spectra (black) were recorded at a spinning speed of $\nu_R = 33.3$ kHz. * denote spinning sidebands. (Ga_{13} simulated) The lineshapes for the core, middle ring, and outer ring of a Ga_{13} cluster are shown in green, orange, and blue, respectively.[14]

2.2. Solid-state ^{71}Ga MAS NMR

NMR spectra were recorded at two magnetic fields of 13.9 T (resonance frequency of 1H at 589.85 MHz and ^{71}Ga at 179.89 MHz) and 19.96 T (1H at 849.73 MHz and ^{71}Ga at 259.14 MHz). All spectra were obtained under magic angle spinning (MAS) conditions, $\nu_R = 33.3$ kHz (on the 13.9 T apparatus) and 38 kHz (19.96 T) with a central transition $\pi/2 - \tau - \pi$ rotor synchronized echo.[21] The free induction decay (FID) was then left-shifted to the top of the echo, phased, and Fourier transformed. A recycle delay of 100 ms (13.9 T) and 1 s (19.96 T) was used. A commercial 2.5 mm HX MAS probe (Bruker) and a TecMag Redstone spectrometer were used to acquire the spectra at 13.9 T. A commercial 1.6 mm HXY MAS probe and Varian Innova spectrometer were used to acquire the spectra at 19.96 T. A nonselective $\pi/2$ pulse of 3 μs (for both fields) with a radio frequency field strength of 83.3 kHz for ^{71}Ga was used. All spectra were referenced to a 1.0 M $Ga(NO_3)_3$ solution at 0 ppm.

2.3. NMR spectral fitting

^{71}Ga NMR spectra were fit using the Dmfit[22] program. Parameters from a prior study[14] and listed in Table 1 were used to begin the fitting procedure which included the isotropic chemical shift, η_Q , and C_Q for the core, middle ring, and outer ring sites. The intensities for the individual fits were then allowed to “float” to match the experimental data. The experimental spectra and fitted spectra were subtracted to yield the residuals as shown in Figures 5 and 6.

Table 1: Experimental ^{71}Ga NMR parameters (Ref. [14]) for Ga_{13} which are used to produce the lineshapes in Figures 2, 5, and 6.

	Core	Middle Ring	Outer Ring
δ_{iso} , ppm	60.7	45.6	-0.6
η_Q	0.0	0.8	0.9
C_Q , MHz	5.0	13.9	6.7

2.4. Powder X-ray diffraction (XRD) characterization

The powder diffraction data were collected between $2\theta = 5^\circ$ and 40° , with a step size of 0.01° on a Rigaku Smartlab in Bragg-Brentano geometry (Cu K- α radiation) equipped with a D/tex Ultra 250. Powder patterns were analyzed for impurities by comparing the simulated Ga_{13} powder pattern from the published single crystal data.[8] Remaining peaks were identified by comparing to reference patterns.

2.5. Raman Spectroscopy

Raman spectra were recorded using a HoloLab Series 5000 Laser Raman Microprobe (Kaiser Optical). A 532 nm laser beam was delivered to the sample using a frequency-doubled Nd:YAG laser through an 80 $\times$ objective, N.A. = 0.85 (Olympus). The spectral region of 100-4000 cm^{-1} was recorded with a spectral resolution of $\sim 3 \text{ cm}^{-1}$ with a reproducibility in peak position of 0.1 cm^{-1} . This configuration delivered a maximum of 10 mW of laser power onto the sample. The spectra were recorded with Kaiser Optical’s HoloGRAMS software using an acquisition time per analysis spot of $32 \times 4 \text{ s}$. Shown in the supplemental materials (Figure S1).

3. Results and discussion

All synthetic routes investigated here are shown to lead to the formation of the Ga_{13} cluster. Figure 3 depicts the solid-state ^{71}Ga NMR spectra of the various synthetic methods to produce the Ga_{13} cluster. The three sites for the core, middle ring, and outer ring can be observed in all three methods in addition to some additional impurities. When comparing the spectra to the simulated lineshapes, the resonance of the core gallium is on the high frequency side of the spectrum, the six middle ring sites are the broadest and are barely evident at 13.9 T, and the six outer ring sites remain the sharpest and most intense resonance.

Powder XRD (Figure 4) also reveals that the three synthetic methods are capable of producing the Ga_{13} species. Here the same diffraction peaks appear in all three synthetic methods, but the ratio of intensities are different indicating that the placement of the

Figure 4: Powder X-ray diffraction for the different synthetic routes of Ga_{13} via DBNA addition (black), electrochemical reduction (blue), and Zn reduction (red) are shown in the top pane. A simulated Ga_{13} powder pattern from single crystal X-ray diffraction is shown for comparison in the bottom pane. The following symbols “•,” “▲,” “×,” and “+” denote impurities of $\text{GaO}(\text{OH})$ (Ref. [23]), $\text{Zn}(\text{OH})_2$ (Ref. [24]), $\text{Zn}(\text{OH})(\text{NO}_3)$ (Ref. [25]), $\beta\text{-GaO}(\text{OH})$ (Ref. [26]), and $\text{Ga}_5\text{O}_7(\text{OH})$ (Ref. [27]), respectively.

atoms within the unit cell are different. The DBNA addition and Zn-reduction methods contain some additional pXRD peaks that are likely due to impurities that are present in the samples. The presence of $\text{Ga}_5\text{O}_7(\text{OH})$, $\beta\text{-GaO}(\text{OH})$, and $\text{GaO}(\text{OH})$ can be noted in both the DBNA addition method and the Zn reduction method (Figure 4). The peaks at low 2θ for the DBNA addition method can be attributed to methanol being cocrystallized in the lattice. The Zn-reduction method results in additional impurities of $\text{Zn}(\text{OH})_2$ [24] and $\text{Zn}(\text{OH})(\text{NO}_3)$ [25] as seen in the pXRD (Figure 4). While pXRD is a decent tool for distinguishing long-range order, this technique does not identify amorphous impurities.

Shown in Figures 5 and 6 are the recorded spectra at 13.9 T and 19.96 T, respectively, the simulated model of the three lineshapes, and the “residual”, which is the difference between the model and experiment. The residu-

Figure 5: ^{71}Ga NMR of Ga_{13} prepared by the (a) DBNA addition, (b) electrochemical reduction, and (c) zinc reduction methods. The experimental spectra (black) were recorded at 13.9 T and spinning at $\nu_R = 33.3$ kHz. * denote spinning sidebands. The reported lineshapes for the core, middle ring, and outer ring of a Ga_{13} cluster are shown in green, orange, and blue, respectively. The simulated spectra (red) is the sum of the reported lineshapes, and the residual lineshape is depicted at the bottom of each spectrum in navy blue. “x” denote impurities in the NMR spectra. “•” and “#” denotes distortions to the outer and middle ring sites, respectively.

als are particularly helpful in this regard, because impurities may be more easily located in the spectrum. The data in Figures 5 and 6 are plotted to help make comparisons for each of the synthetic routes. It is instructive to compare the ^{71}Ga NMR spectra for these samples at two different magnetic fields, 13.9 T and 19.96 T to the quadrupolar lineshapes that were reported previously for the DBNA-synthesized Ga_{13} sample.

The high-field data (19.96 T) are useful because the narrowing of the second-order quadrupolar-broadened lineshapes is sufficient to permit sharp features to emerge, as either impurities or distortions to the lineshape, arising from local disorder of anions in the lattice (marked by filled-circle “•,” open circle “o,” and “x” symbols on Figures 5 and 6). The low-field data (13.9 T) are similarly useful, because the broadening of the middle ring gallium sites make it easier to view those residuals separately from the narrow core and outer ring resonances. These middle ring residuals are marked with a “#” symbol.

Shown in Figure 5a is a spectrum from a repeat DBNA synthesis. The residuals show a similar impurity (x) as in the first study (Ref. 14), and small deviations from the modeled lineshape. Dibutyl nitrosamine addition (DBNA) affords the highest reproducibility in terms of product yield and crystallinity. It is also the only synthetic route where transmetalation reactions have been used to access the entire series of $\text{Ga}_x\text{In}_{(13-x)}$ ($7 \leq x \leq 13$) clusters.[18, 28, 15] The main drawback is the use

of organic materials like DBNA, which is carcinogenic, and methanol, which is both flammable and teratogenic.

A mononuclear gallium species is seen at 0 ppm (“x” symbol), similar to that observed previously,[14] evident in both high-field and low-field data. The low-field data (13.9 T) with its broadened lineshapes show residuals arising from the middle ring gallium species, marked by a “#” symbol. Such differences would be expected for something that distorts the electric field gradient at the middle ring sites, which is likely attributable to the anions present in the solid-state packing of the Ga_{13} structure. In addition, a “•” marks a feature in the residual plot that appears prominently in both sets of spectra, and it is most likely due to a distortion of the outer ring sites, changing the shape of the resonance slightly. Again, this would not be surprising given the disorder in the anions and water molecules that occupy the interstices of the crystal. There is one additional feature evident in the high-field data (Figure 6a) on the low-frequency side of the resonance (at approximately -50 ppm), marked by an “o” symbol. Comparison amongst all three spectra suggests that it is an impurity, but its identity is impossible to assess with the limited information here. In part, it is not readily evident at low field, and hence it is only apparent in the residual plots at high field. The residual only shows large differences in the middle ring and outer ring sites, but a good match to that of the core site.

The second synthetic route uses an electrochemical

Figure 6: ^{71}Ga NMR of Ga_{13} prepared by the (a) DBNA addition, (b) electrochemical reduction, and (c) zinc reduction methods. The experimental spectra (black) were recorded at 19.96 T and spinning at $\nu_R = 38$ kHz. * denote spinning sidebands. The reported lineshapes for the core, middle ring, and outer ring of a Ga_{13} cluster are shown in green, orange, and blue, respectively. The simulated lineshape (red) is the sum of the reported lineshapes, and the residual lineshape is depicted at the bottom of each spectrum in navy blue. “x” and “o” denotes impurities in the NMR spectra. “•” denote distortions to the outer and middle ring sites, respectively.

potential to drive cluster formation, so no additional reagents are required. The electrochemical method is ideal for preparing a solution for spin-coating thin films that might be used in devices, where metal impurities are undesirable. The main difficulty is that this synthesis route requires some specialized knowledge and equipment to carry out successfully, and cannot be easily scaled up to large volumes. As seen from the solid-state NMR (Figure 5b), there are impurities present, with a large mononuclear gallium impurity resonance at 0 ppm. Like before, there appears to be distortions to the middle ring and outer ring sites. The unknown impurity at (“o”) seen at -50 ppm at 19.96 T is also present.

The last approach (Zn reduction, using zinc powder) is the best method for doing large-scale syntheses, and it is the simplest procedure to perform in the laboratory. It involves mixing relatively benign reagents in water and letting the solution evaporate to yield crystalline product.[13] One drawback is the formation of a byproduct, $\text{Zn}(\text{NO}_3)_2$, that must be removed from the reaction during the washing step. This method also suffers from lower reproducibility, where gels and powders can form, instead of crystals, during the evaporation step. Figure 5c shows little or no evidence of a mononuclear gallium species impurity, and the major residual is that marked by a “•” which appears to be a distortion to the outer ring sites. Notably, the -50 ppm resonance (“o”) is very prominent at high field (Figure 6), and a larger feature in this sample than in others. With fu-

ture modeling and computational efforts, we hope that the Zn reduction-derived samples will lead to an assignment of its chemical identity.

4. Conclusions

Solid-state ^{71}Ga NMR has confirmed the presence of the Ga_{13} cluster and has aided in the detection of impurities present in the molecular clusters prepared via multiple synthetic routes. The use of ultra-high magnetic fields allows the unmasking of impurities that are obscured at lower magnetic fields. Powder XRD also confirms that the molecular cluster is present. Solid-state NMR of less commonly-studied nuclei, such as ^{71}Ga , provides an important window into different synthetic methods, and we have demonstrated that straightforward high-field NMR techniques can have broad applicability for assessing samples.

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6. Author Contributions

All authors have given approval to the final version of the manuscript. B.A.H., Z.L.M., M.E.W., and S.E.H. all contributed to obtaining the solid-state NMR spectra, modeling, and interpretation of the data. D.A.M. and D.W.J. developed the synthesis of the materials. S.R.W. performed powder XRD on the clusters. D.W.J. is a Scialog Fellow of Research Corporation for Science Advancement.

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