Angewandte Communications

Structure Elucidation

DOI: 10.1002/anie.201206386

Single Nanoscale Cluster Species Revealed by ^{1}H NMR Diffusion-Ordered Spectroscopy and Small-Angle X-ray Scattering**

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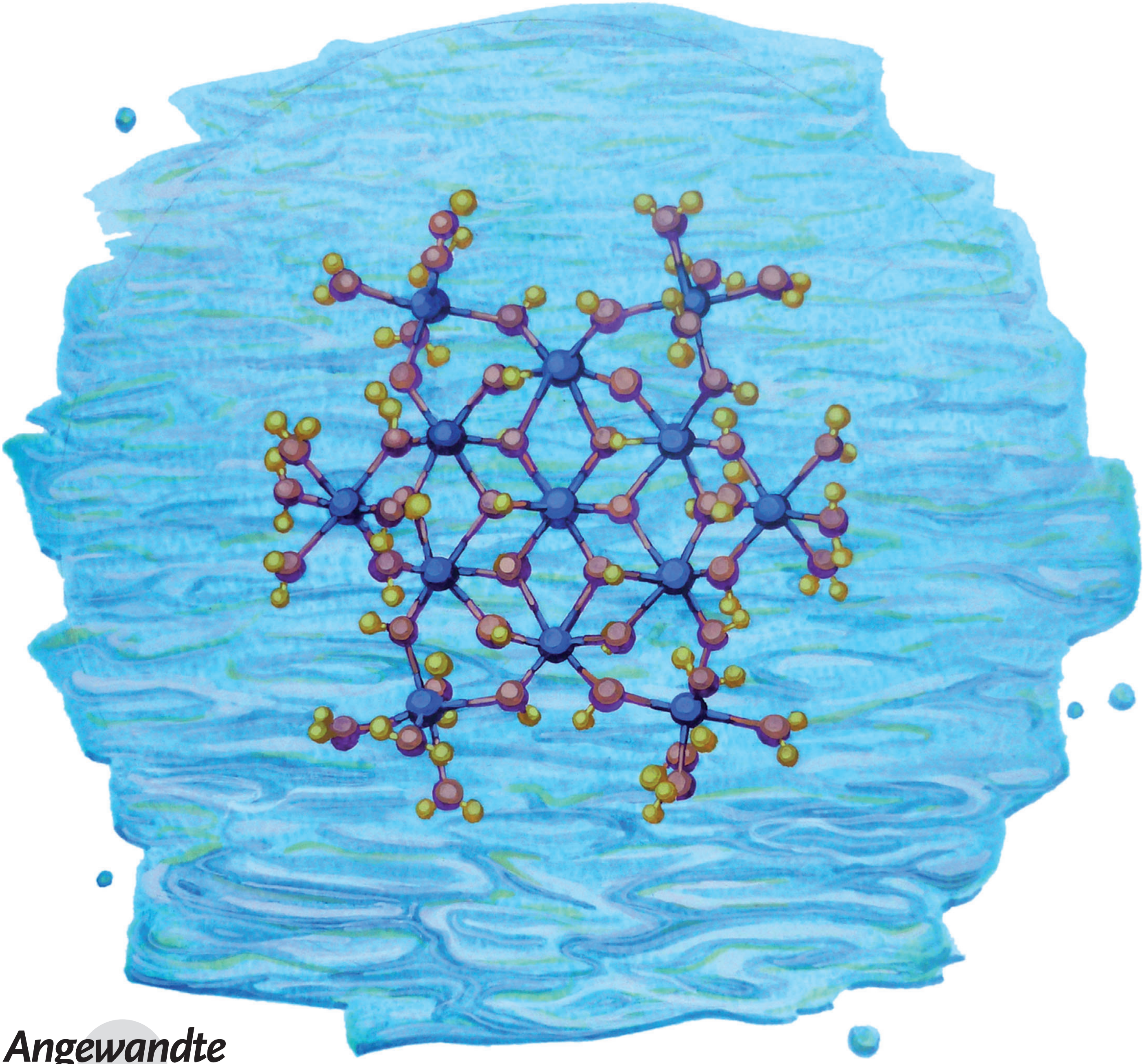

Considerable attention has been drawn to inorganic nanoscale clusters[1] because of their value and effectiveness as catalysts and catalyst precursors,[2–6] single-molecule magnets,[7,8] sensors,[1] and single-source precursors for thin films and other materials[9] as well as their important roles in geological, environmental, and life sciences.[10] In recent work, we have developed new techniques for synthesizing nanoscale clusters and transforming them into high-quality films and other designed nanostructures.[11–15] To date we have developed high-yielding, greener techniques to synthesize a variety of M_{13} precursor clusters (Ga, Al, Ga/In, and Al/In) in gram-scale quantities.[11–13] Currently, the main technique for analysis of these and related fully inorganic clusters is single-crystal X-ray diffraction. This method provides a detailed understanding of their solid-state structure; however, because of the lack of clear spectroscopic handles, little is known about solution speciation and stability of these discrete inorganic complexes at the millimolar to molar concentrations of interest to synthetic chemists, geochemists, and material scientists.

What is the dominant species in a solution of dissolved clusters? Are aggregates present? Methods such as small-angle X-ray scattering (SAXS),[16–18] wide-angle X-ray scattering (WAXS),[17] and dynamic light scattering (DLS)[18] are often used to probe solution dynamics and speciation through size analysis, but are not widely available. Electrospray ionization mass spectrometry (ESIMS) is a powerful technique for detecting cluster species and monitoring reaction intermediates; however, high-resolution instruments are not routinely available, and the technique evaluates a narrow and dilute concentration range that selects for detection of the most readily ionized species at a concentration often below that of relevance to speciation studies for materials applications.[19,20] Herein we present a powerful tandem method to provide conclusive characterization data for such aqueous inorganic nanoscale clusters in polar solvents using SAXS to probe the core inorganic structure and the universal technique of ^{1}H NMR and diffusion ordered spectroscopies (DOSY) to assess the hydrodynamic radius of the cluster.

SAXS was used to test for the presence of distinct Ga_{13} clusters in solution at 2 mM concentration in dimethyl sulfoxide (DMSO). After background subtraction and desmearing, the data were analyzed to determine size and size distribution using the scattering program IRENA.[21,22] The scattering was consistent with discrete spherical particles of a radius (5.5 ± 1.5) Å and showed no signs of significant aggregation (see Figure S1 in the Supporting Information). Gratifyingly, this result matches the value measured directly from the crystal structure from centroid to centroid of the high-Z gallium atom core ($r = 5.6$ Å).[12] This result is consistent with the presence of the Ga_{13} cluster in DMSO solution and prompted analysis of the cluster by solution phase NMR spectroscopy.

The ^{1}H NMR spectra of Ga_{13} in deuterated water and methanol are completely silent. Therefore, we were surprised to observe that the acidic protons of the hydroxo and aquo ligands of Ga_{13}, shown in Figure 1, are clearly visible in wet [D$_6$]DMSO (Figure 2 A). ^{1}H NMR has been sparingly used to analyze aqueous inorganic clusters, presumably because of fast exchange of the acidic hydroxo and aquo protons with protic solvents and solubility issues associated with the high charge of the clusters.[23–25] Consequently, DOSY has been used infrequently on such inorganic structures and only in the presence of organic supporting ligands.[26,27] To the best of our knowledge, these two techniques have not been used in

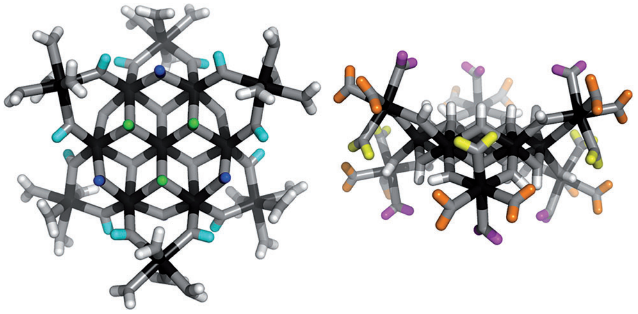

Figure 1. The molecular structure of $[Ga_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(H_2O)_{24}](NO_3)_{15}$ (Ga_{13}) determined by single-crystal X-ray diffraction. Left: Top view of Ga_{13} depicting three types of hydroxide bridges. The μ_3-OH are green and the μ-OH are blue and cyan. Right: Side view of Ga_{13} depicting the three types of capping water ligands.

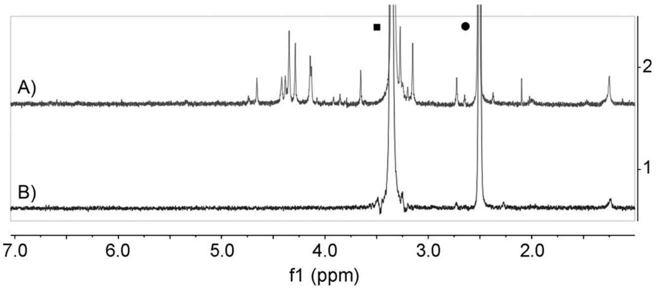

Figure 2. ^{1}H NMR spectra of gallium complexes in [D$_6$]DMSO: A) 2 mM Ga_{13} solution after five days. B) Control spectrum of a saturated $Ga(NO_3)_3$ solution showing only solvent peaks; presumably the coordinated water ligands are in fast exchange with solvent. H_2O peak (■) and DMSO peak(●).

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[**] This work was generously supported by the NSF Center for Sustainable Materials Chemistry (grant numbers CHE-0847926 and CHE-1102637), an NSF GK12 fellowship to A.F.O. (DGE-0742540), the Air Force Research Laboratory (under grant number FA8650-05-1-5041) and the M. J. Murdock Charitable Trust. The authors thank Profs. Douglas A. Keszler and Sophia E. Hayes for helpful suggestions in writing this manuscript. The University of Oregon NMR facilities are supported by NSF CHE-0923589. D.W.J. is a Scialog Fellow of Research Corporation for Science Advancement and gratefully acknowledges additional support provided to assist this project.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206386.

tandem to characterize completely inorganic nanoscale structures of relevance to materials science (inks) and aqueous hydrolysis chemistry.

The fact that Ga_{13} can be observed by ^{1}H NMR spectroscopy in solution enables investigation of the cluster by DOSY and provides insight into the hydration sphere of these nanoscale species. DOSY experiments confirmed the presence of cluster-sized species in solution. Figure 3 displays the DOSY spectra for a 2 mM [D$_6$]DMSO solution of Ga_{13}. The small differences between diffusion coefficients produced by the signals of the cluster can be attributed to water exchange,[28] peak overlap, and/or data processing.[29a] The average diffusion coefficient of all the cluster-related peaks based on quadruplicate measurements is $(0.955 \pm 0.064) \times 10^{-10}\,\mathrm{m^2 s^{-1}}$ (see representative DOSY spectrum in Figure 3).[30] By applying the Einstein–Stokes Equation (1)

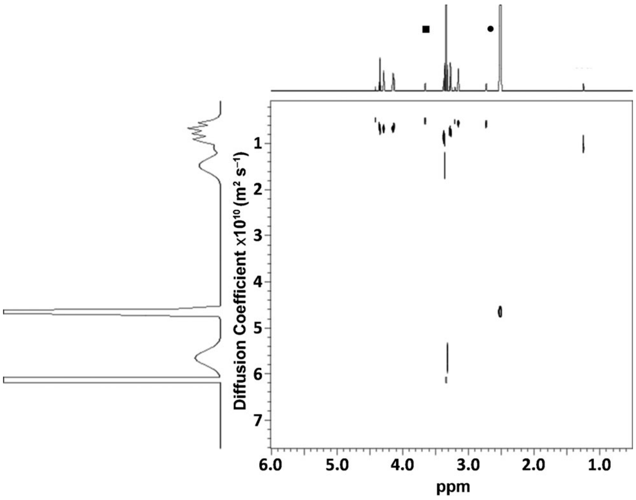

Figure 3. Representative DOSY spectrum of a hydrated Ga_{13} cluster in [D$_6$]DMSO ($D_{avg} = 0.955 \times 10^{-10} \pm 0.064 \times 10^{-10}\,\mathrm{m^2 s^{-1}}$). H_2O peak (■) and DMSO peak (●).[30]

$$D = \frac{k_B T}{6\pi\eta r} \qquad (1)$$

a radius of (11.2 ± 0.8) Å was determined.[29b] The error in hydrodynamic radius arises from averaging the multiple diffusion constants observed for the cluster that result from the numerous exchanging protons present on the cluster.[29b] Regardless, all diffusing species are consistent in size with a single highly solvated, hydrogen-bonding nanoscale cluster (A similar behavior has been observed for sucrose in wet solvents).[28] The hydrodynamic radius is obviously larger than would be expected for the Ga_{13} cluster ($r = 8.0$ Å based on the crystallographic unit cell parameters and assuming a spherical particle). However, interactions with counter ions, hydrogen bonding to solvent, and solvation spheres dramatically increase the size of the observed species drifting through solution because of Brownian motion.[31] Preliminary DLS data, which also measures the hydrodynamic radius, substantiates the presence of a cluster-sized species in DMSO under the same conditions.

The difference between the radius calculated from the DOSY results and the crystallographic unit cell data can be explained by comparison to the characteristics of sucrose, a small-molecule model containing multiple hydroxyl groups.[28] Sucrose was chosen for three reasons: 1) like the Ga_{13} cluster, it is highly solvated in DMSO solution, 2) it possesses numerous hydrogen bond donors and acceptors, and 3) it is the only related molecule we could find in the literature with both XRD and DOSY data available in DMSO solution. Sucrose has a crystallographically measured radius of 4.38 Å, and under the same conditions run for the Ga_{13} samples, a DOSY-calculated hydrodynamic radius of 6.1 Å. An even larger increase in hydrodynamic radius (11.2 Å) over crystallographic radius (5.6 Å) is observed in Ga_{13}, presumably resulting from the high charge (+15) and correspondingly higher solvation energy and weakly associated counter ions, which corroborates the SAXS data showing a single cluster species persists in solution at millimolar concentrations.

Consequently, it should be noted that immediately after dissolving crystalline Ga_{13} in [D$_6$]DMSO, the ^{1}H NMR spectrum is complicated (Figure 4). Depending on the concentration of water in the sample, the spectrum simplifies between a few hours to a few days (H_2O concentrations tested: 0.10–1.97 M, see Figures S2–S5 in the Supporting Information). Once simplified, the spectrum remains constant for at least two months, indicating long-term stability of the observed cluster species in solution (Figure 2 A). Alternately, if this initial solution is heated to 50 °C, the simplified spectrum appears immediately and again persists for months when the sample returns to room temperature (Figure 2 A). We believe the original complexity of the spectrum is due to the establishment of a slow equilibrium between coordinated aquo and DMSO ligands in the peripheral ligand shell (and corresponding hydrogen bonding to the first solvation sphere). This hypothesis is supported by DOSY evidence (Figure S6 in the Supporting Information) confirming that the size of the species in solution remains constant during this exchange process (Figure 4). Further details of this equilib-

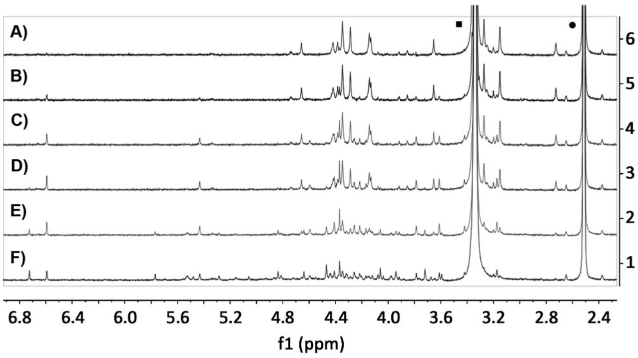

Figure 4. ^{1}H NMR spectra of 2 mM Ga_{13} in [D$_6$]DMSO over time. Adjacent to each spectrum is the radius calculated from the corresponding DOSY experiment. A) $\Delta t = 76.0$ h, $r = (11.0 \pm 1.1)$ Å, B) $\Delta t = 51.5$ h, $r = (11.0 \pm 1.0)$ Å, C) $\Delta t = 30.5$, $r = (10.6 \pm 0.7)$ Å, D) $\Delta t = 24.0$ h, $r = (10.5 \pm 0.8)$ Å, E) $\Delta t = 6.5$ h, $r = (10.5 \pm 1.3)$ Å, and F) $\Delta t = 0.5$ h, $r = (10.9 \pm 1.2)$ Å. H_2O peak (■) and DMSO peak (●).

rium will be reported in follow-up studies related to the kinetics of ligand and metal exchange reactions on these and related clusters.

In conclusion, it is possible to detect ^{1}H NMR spectral signals from the hydroxide bridges and capping water molecules of a completely inorganic nanoscale Ga_{13} cluster in aqueous [D$_6$]DMSO. This enabled the solution-phase identification of the single cluster species in the wet polar solvent DMSO by DOSY NMR in tandem with SAXS. These complementary techniques have not been previously used together to examine the solution speciation of aqueous inorganic clusters, yet they provide a powerful and convenient approach for structural investigation of clusters and particles in solution, enabling unique capabilities across a broad spectrum of polyoxometal and nanochemistries. In addition, our findings suggest that ^{1}H NMR spectroscopy is likely to be a valuable tool for elucidating the solution dynamics and reactivity of clusters, identifying compositional isomers in heterometallic clusters,[11,32] and determining the mechanisms of cluster formation and degradation. We are currently working to develop a DOSY calibration curve using other structurally characterized clusters to relate the hydrodynamic radius in a predictable manner to the solution structure. Given the emergent interest of these clusters in materials science as inks and precursors for electronic devices, developing solution-phase techniques to characterize these precursor solutions is vital to enabling new applications.

Experimental Section

Chemicals were purchased from Sigma–Aldrich and TCI America and were used as received without further purification. The $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ cluster was synthesized according to a literature procedure.[12] All ^{1}H NMR experiments were performed on Varian 300, 500, and 600 MHz spectrometers. Data was collected using Varian Software and processed using MestReNova. All spectra were acquired at 298 K in 5 mm tubes. The DOSY experiment was performed using the gradient stimulated echo with spin-lock and convection compensation (DgsteSL_cc) pulse sequences. All Varian software standard default settings were kept for DOSY unless otherwise stated. The diffusion delay was increased to 200 ms, the number of increments was increased to 20, and the highest gradient value was lowered to 20000. The alternate gradient sign on odd scans and lock gating during gradients options were also selected. Using an Ostwald viscometer the viscosity of a saturated Ga_{13} solution was measured. The average after four trials was calculated to be $(2.032 \pm 0.006) \times 10^{-3}$ Pa s at 25 °C. This value is close to that of neat DMSO (2.00×10^{-3} Pa s at 25 °C). The NOE experiment was performed using a rotating-frame Overhauser effect spectroscopy (ROESY) pulse sequence and all standard Varian software default settings were kept. An Anton Paar SAXSess instrument was used to measure SAXS and observe solutions of the clusters in DMSO. Scattering was measured 10 times for 100 seconds and averaged. SAXS data was fit using the scattering program IRENA.

Received: August 8, 2012

Keywords: cluster compounds · gallium · hydrates · NMR spectroscopy · small-angle X-ray scattering

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