Proton Exchange Rates on Hydroxide Bridges of the Mineral-Like $Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ Cluster

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Introduction:

Little is known about the molecular-scale dynamics of sheet-like hydroxide materials in spite of their importance to environmental chemistry and materials science. These sheets are often made of trivalent metals, and they have a close similarity to some metal-hydroxide clusters. For example, the mineral tsumgallite (GaO(OH)) (Figure 1B) is rare in nature but is isostructural with the very common soil minerals diaspore (AlO(OH)) and goethite (FeO(OH)).[1] Furthermore, GaO(OH) is a key intermediate in thin films formed from aqueous clusters of Ga(III). Apparently amorphous GaO(OH) is the main component of solution-processed thin films before the final annealing step dehydrates it to Ga_2O_3. Table 1 includes examples of Group 13 materials and the mineral analogues.

These clusters are important as experimental models. For many years, geochemists had no good systems to estimate the dynamics of elementary

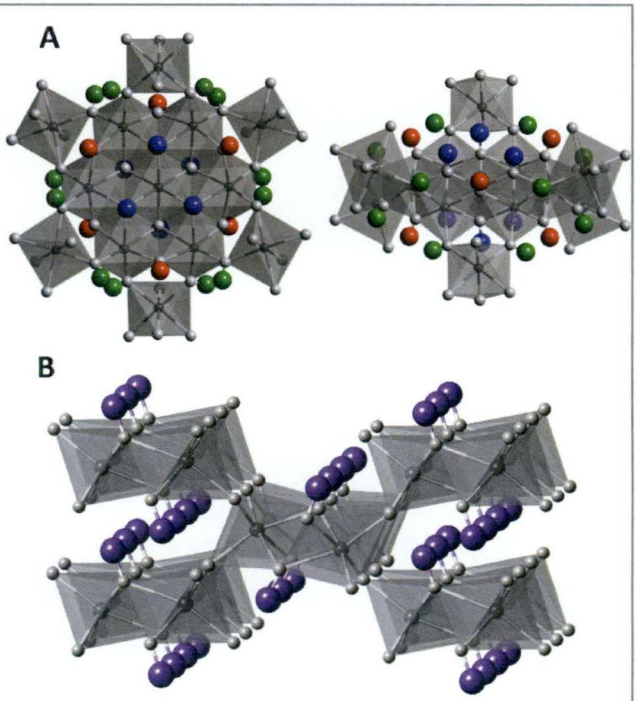

Figure 1: The structures of the Ga13 cluster (A) with capping water ligands eliminated for clarity and mineral tsumgallite, GaO(OH) (B). Sets of protons on the various hydroxide bridges are identified as colored spheres (● μ_3-OH, ● μ_2-OH_{ext}, ● μ_2-OH_{int}, and ● μ_2-$OH_{GaO(OH)}$). The μ_2-$OH_{GaO(OH)}$ protons (●) are structurally similar to the μ_2-OH_{int} (●) of the **Ga_{13}** molecule.

processes, such as proton-exchange, electron-exchange, or ligand-substitution reactions for mineral-like materials. The need for such data became more pressing as computational models advanced and the experimental verification lagged because it is so difficult to follow molecular processes in solids. Fortunately, methods of syntheses have advanced to provide stable, monospecific solutions of useful metal cluster ions. In this study we address the kinetics of proton exchange between bulk water and hydroxide bridges of the $Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (**Ga_{13}**) and $Ga_7In_6(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (**Ga_7In_6**) clusters (Figure 1A). These clusters are isostructural except that the outer six Ga(III) ions in the **Ga_{13}** are substituted for In(III) ions in the **Ga_7In_6**.

Table 1: Group 13 thin films of interest and the mineral analogues.

Film Structure	Mineral Analogue	Use in Materials Industry
Al_2O_3	Corundum	Solar cells[2–4]
Ga_2O_3	-	H_2 sensors,[5] thin film transistors[6]
$GaInO_3$	-	Transistors
AlO(OH)	Diaspore, Boehmite	Intermediate in Al_2O_3 film formation from $Al(OH)_3$ precursors
GaO(OH)	Tsumgallite[1]	Intermediate in Ga_2O_3 film formation from $Ga(OH)_3$ precursors
$Al(OH)_x$	Gibbsite	Soluble precursor for Al_2O_3 films
$Ga(OH)_x$	Söhngeite	Soluble precursor for Ga_2O_3 films[7]

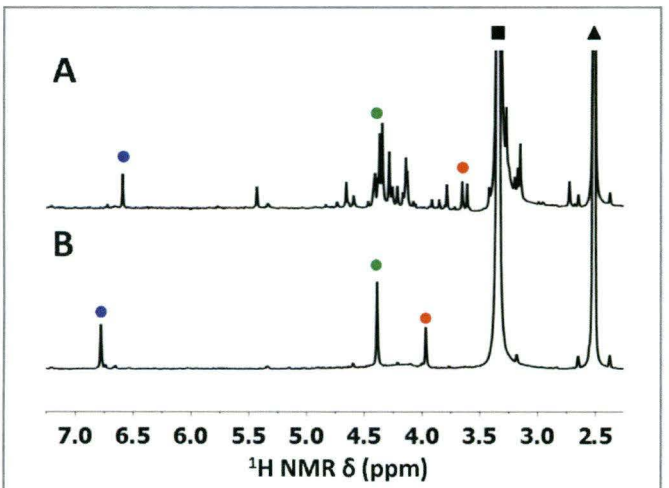

Figure 2: The 1H-NMR spectra of the Ga13 (A) and Ga7In6 (B) clusters with corresponding –OH bridge assignments (● μ3-OH, ● μ2-OHext, and ● μ2-OHint).8 Solvent signals are labeled with ▲ (DMSO) and ■ (H2O).

We recently assigned ^{1}H-NMR signals for all $[Ga_{13-x}In_x(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ ($0 \leq x \leq 6$) cluster species in wet d_6-dimethylsulfoxide (d_6-DMSO) (Figure 2).[8,9] With these peaks assigned, it is now possible to study the kinetics of proton-exchange events at specific sites within these clusters. A similar technique was previously used on the $\mathbf{Al_{13}}$ Keggin cluster;[10] however, no gallium analogues have been studied to date. To our knowledge, these are the only such data for Group 13 clusters in solution.

Structural Setting of Protons:

When they are completely ligated with water, the $\mathbf{Ga_{13}}$ and $\mathbf{Ga_7In_6}$ have D_{3d} symmetry and 3 types of hydroxide bridges (Figure 1A).[8] Each of the bridges (μ_3-OH, μ_2-OH_{ext}, and μ_2-OH_{int}) are visible in the ^{1}H-NMR spectrum, have unequivocally been assigned, and behave uniquely in solution (Figure 2). The μ_2-OH_{ext} bridges bind the exterior metal ions to the planar 7-ion Ga(III) core of the clusters. Both the μ_3-OH and μ_2-OH_{int} bridges hold together the planar 7-ion Ga(III) core. The protons on these bridges bind perpendicularly to the surface, similar to the protons on thin film surfaces and between perpendicular sheets in minerals (e.g., boehmite, gibbsite) where hydrogen bonding holds the structure together. The μ_2-OH_{int} bridges of the $\mathbf{Ga_{13}}$ cluster will provide the best model for the μ_2-$OH_{GaO(OH)}$, and the μ_3-OH of the $\mathbf{Ga_{13}}$ resemble the bridges in söhngeite.

μ_3-OH Bridge Results:

The ^{1}H-NMR of the μ_3-OH bridges are the farthest downfield (6.5-6.8 ppm), and therefore the most acidic proton site on the cluster, just as one would expect.[11] In ^{1}H-NMR spectra of the $\mathbf{Ga_{13}}$, the signal associated with the proton of this bridge disappears over time, indicating a slow, yet unidentified deprotonation reaction(Figure 3).[9] This signal persists in the ^{1}H-NMR spectrum for anywhere from approximately 1 week to a few hours, depending upon the concentration of water in the d_6-DMSO

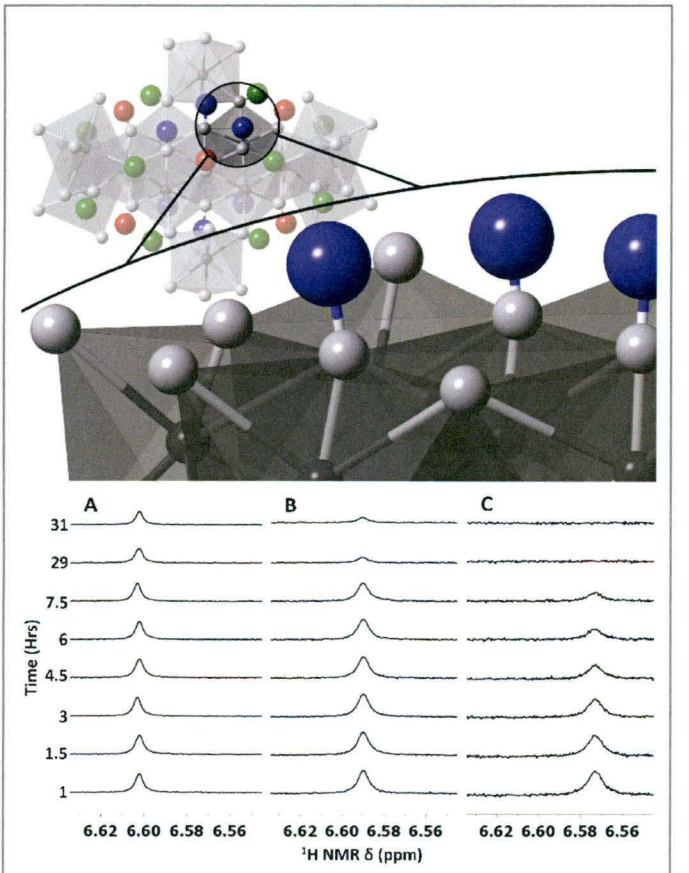

Figure 3: ^{1}H-NMR spectra for the signal assigned to the proton of the μ3-OH bridge (•) in the Ga13 at varying mole fractions of water: (A) 0.007, (B) 0.045, and (C) 0.123.

solvent. The area of the μ_3-OH peak can be directly related to concentration $\left(\frac{C(t)}{C_0}\right)$ of these sites in solution because we use an internal standard (1,3,5-trichlorobenzene). By plotting the normalized concentration of the μ_3-OH protons with respect to time (s), the resulting slope yields a reaction rate (Figure 4). Peaks with $\frac{C(t)}{C_0} \leq 0.05$ were not included because the small intensities and linewidths could not be estimated with

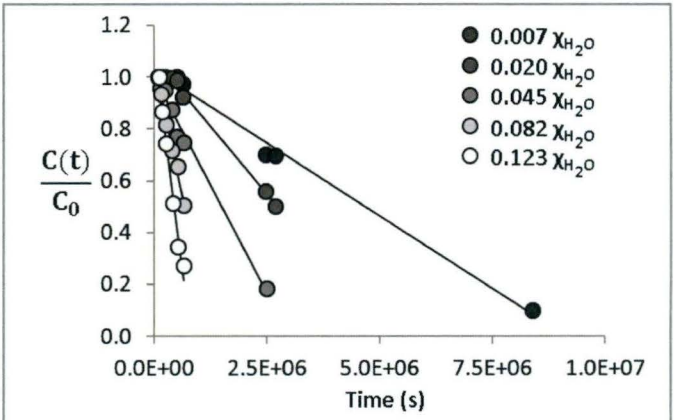

Figure 4: The normalized concentration ((C(t))/C_0) of the μ3-OH protons of the Ga13 clusters as a function of time. Note that the signals disappear more quickly at higher mole fractions of water in the solvent (χwater).

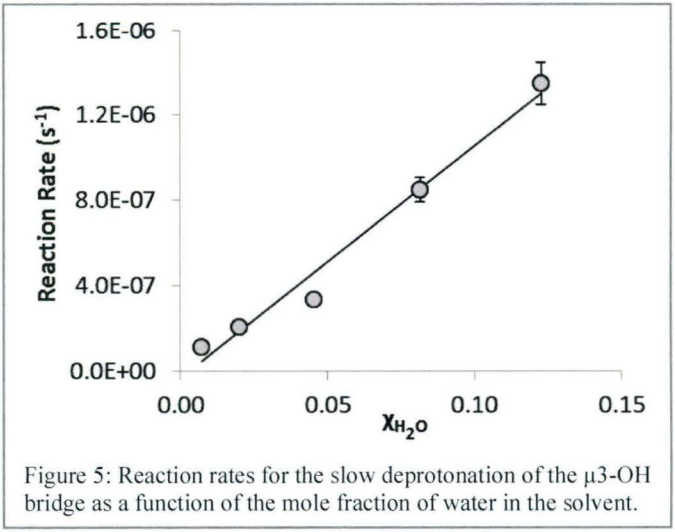

Figure 5: Reaction rates for the slow deprotonation of the μ3-OH bridge as a function of the mole fraction of water in the solvent.

precision. To determine the rate constant (k_{298}) for this slow deprotonation reaction, the rates from Figure 4 are plotted as a function of water concentration (Figure 5). The linearity of data (Figure 5) indicates that the reaction is first order with respect to water, with a rate constant $k_{298} = 1.1 \times 10^{-5} \pm 0.1 \times 10^{-5}$ s^{-1}.

In contrast to the $\mathbf{Ga_{13}}$, signals for the μ_3-OH proton in the $\mathbf{Ga_7In_6}$ cluster did not change with time in the ^{1}H-NMR spectra, indicating no apparent reaction. Because we did not see evidence for slow elimination of this proton in the $\mathbf{Ga_7In_6}$ cluster, we could conduct VT-NMR experiments to estimate the rates of exchange of the proton from NMR line broadening. However, no broadening was observed, indicating that the proton is not exchanging at the NMR time scale, which is another difference in kinetic behavior between the $\mathbf{Ga_{13}}$ and $\mathbf{Ga_7In_6}$ clusters.

μ_2-OH_{ext} Bridge Results:

Our previous work found that the outermost metal ions exchange slowly (days) in the mixed-metal clusters.[11] Because the VT-NMR indicates no rapid proton exchanges, we speculate that the protons may be exchanging with the metal ion at these outer sites. We recognize, however, that the protons may be exchanging much more rapidly than the metals, but just at rates that are much slower than the ^{1}H-NMR timescale.

μ_2-OH_{int} Bridge Results:

The μ_2-OH_{int} bridges have the only proton signals which exhibit evidence of exchange with bulk water (Figure 6) on the ^{1}H-NMR timescale. Line-shape analysis can be used to calculate exchange rates using modified forms of the Bloch Equations under the following conditions:[10] 1) The proton transfer occurs in the slow-exchange regime, where the frequency separation (Hz) between the site signal and bulk water signal is much larger than the rates of exchange. 2) The system can be approximated as undergoing only two-site exchange; practically this means that a proton on a cluster exchanges only with bulk water and not with other sites on the cluster as well. 3) There is a large excess of water relative to the exchanging site (in these experiments, there were at least 2,000 water molecules per $\mathbf{Ga_{13}}$ cluster in the driest solvent systems used). This system meets the

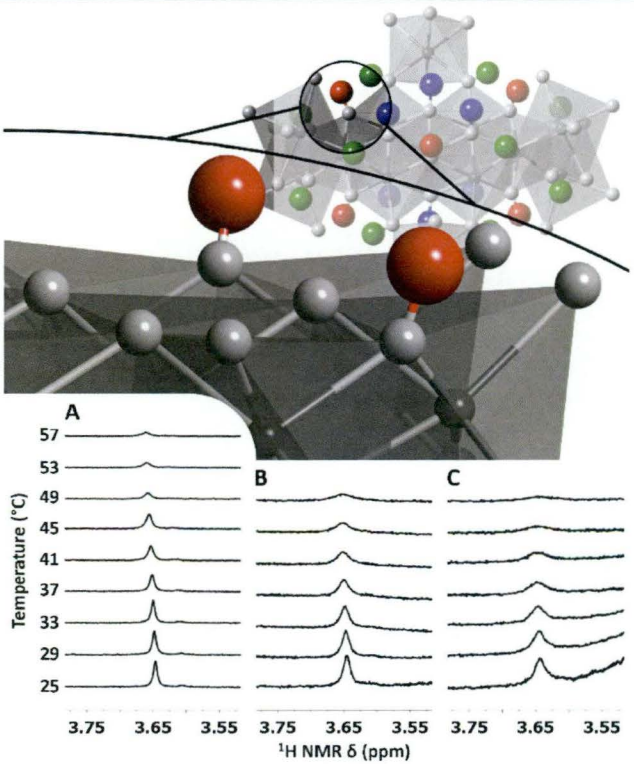

Figure 6: Variable-temperature (25-57°C) 1H-NMR spectra for the signal assigned to the proton (•) of the μ2-OHint bridge in the 7-ion Ga(III) core of Ga13 at (A) 0.001 χwater, (B) 0.007 χwater, and (C) 0.013 χwater.

three conditions; therefore, the difference of the full-width-at-half-maximum (FWHM) relative to the inherent linewidth ($FWHM_0$) of a signal can be related to the lifetime of a proton (τ) and the rate constant (k) using Equation 1:

$$\frac{1}{\tau} = k = \pi(FWHM - FWHM_0) \qquad (1)$$

The $FWHM_0$ must be measured in the absence of chemical exchange. The $FWHM_0$ for $\mathbf{Ga_{13}}$ was estimated to be 3.6 ± 0.2 Hz for all samples by

averaging the lowest-temperature measurements (25-33 °C) from samples with the least amount of water present ($\chi_{water} \leq 0.001$). At these conditions, the linewidths did not vary with temperature and had asymptotically reached a constant value (Figure 7).

To measure rates, ^{1}H-NMR spectra were collected over the temperature range 25 to 57°C with varying concentrations of water in the solvent. Although the cluster had limited solubility in d_6-DMSO(~2mM), the signal intensities were adequate. The maximum change in FWHM for $\mathbf{Ga_{13}}$ ranges from 2 to 14 Hz in this temperature range, depending on the concentration of water in the solvent (Figure 6-7).

The lifetime of a proton at room temperature (τ_{298}) for samples where χ_{water}>0.001 is ~40 ms (Figure 8). The values for τ_{298} at the driest conditions ($\chi_{water} \leq 0.001$) could only be estimated from experiments at relatively high temperatures, followed by back-calculation of the rates to room temperature conditions where there is no evidence of broadening (see below).

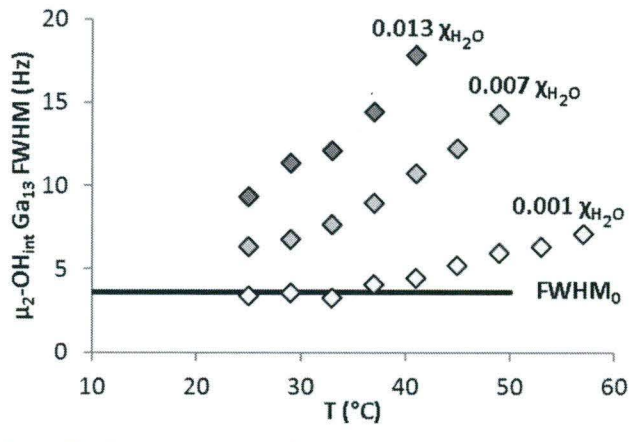

Figure 7: The 1H-NMR FWHM measurements for the μ2-OHint protons of the Ga13 cluster. The FWHM0 is approximated for all Ga13 samples as the asymptotic limit at low temperatures for the χwater ≤ 0.001 solutions, indicated by the line as 3.6 ± 0.2 Hz.

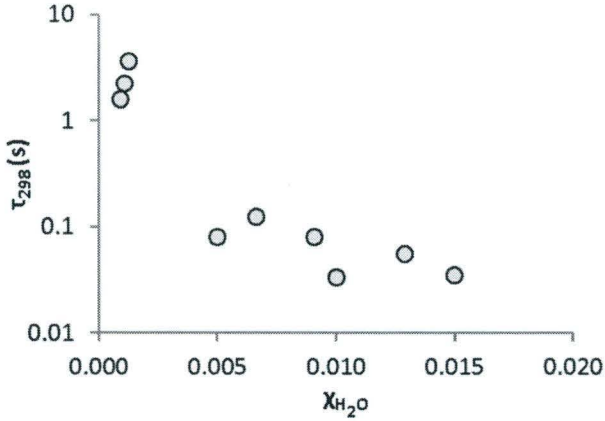

Figure 8: Lifetime of a proton at 298 K as a function of water concentration for both the Ga13 and Ga7In6 clusters.

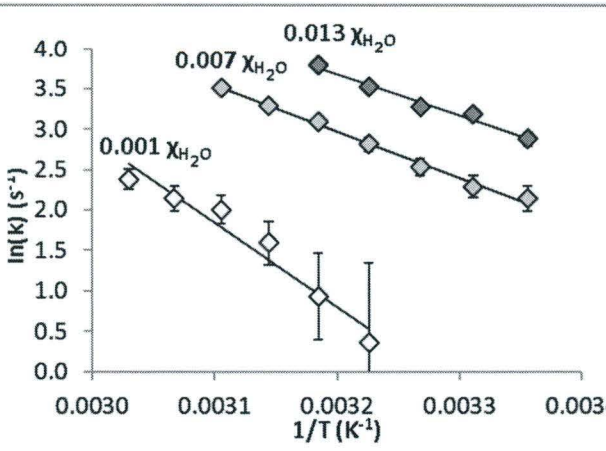

Figure 9: Arrhenius plot for exchange of the μ2-OHint protons of the Ga13 cluster.

To make the back-calculation, we used the Arrhenius Equation to determine activation parameters for the exchange reaction. The Napierian logarithm of the rate constants, ln(k), were plotted with respect to 1/T (K^{-1}) (Figure 9). The resulting data were fit to the linear equation:

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \qquad (2)$$

in order to estimate activation parameters, including the enthalpy of activation $(\Delta H^{\ddagger}_{298})$ using equation 3:

$$\Delta H^{\ddagger}_{298} = E_a - RT \qquad (3)$$

and the entropy of activation $(\Delta S^{\ddagger}_{298})$, which is calculated from the intercept and Equation 4:

$$\Delta S^{\ddagger}_{298} = R\ln(A) - R\ln\left(\frac{k_B T}{h}\right) - R \qquad (4)$$

Finally, $\Delta G_{298}{}^{\ddagger}$ can be determined using Equation 5:

$$\Delta G^{\ddagger}_{298} = \Delta H^{\ddagger}_{298} - T\Delta S^{\ddagger}_{298} \qquad (5)$$

Both $\Delta H^{\ddagger}_{298}$ and $\Delta S^{\ddagger}_{298}$ for exchange of a proton on the μ_2-OH_{int} bridges of $\mathbf{Ga_{13}}$ are affected by the addition of water (Figure 10). However, the values quickly reach a constant value as water increases in the solvent. We extrapolate the weak dependence at these concentrations to estimate rates for a purely aqueous solution. Our estimates are:

$$\Delta H^{\ddagger}_{298} = 39 \pm 4 \text{ kJ/mol}, \Delta S^{\ddagger}_{298} = -90 \pm 10 \text{ J/mol·K},$$
$$\text{and } \Delta G^{\ddagger}_{298} = 66 \pm 1 \text{ kJ/mol.}$$

The $\Delta S^{\ddagger}_{298}$ changes sign as water is added to the solution, indicating that water orders the system, as is expected, since hydrogen bonding from waters must activate exchange. Using the activation parameters, we can back calculate the lifetimes of protons in the driest solvent at ~2-3 s, which is, of course, beyond the NMR timescale.

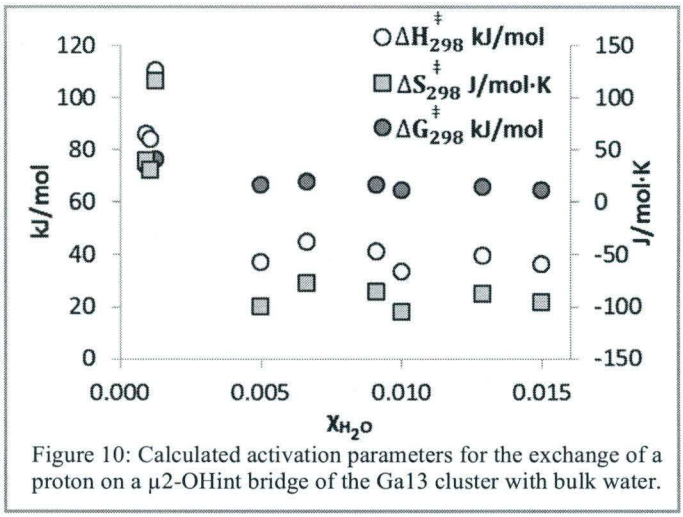

Figure 10: Calculated activation parameters for the exchange of a proton on a μ2-OHint bridge of the Ga13 cluster with bulk water.

Unfortunately, it was extremely difficult to accurately measure $FWHM_0$ of the μ_2-OH_{int} bridges in the $\mathbf{Ga_7In_6}$ cluster. The maximum observed change in FWHM was only 2-3 Hz, and these differences are too small to estimate rates accurately via Equation (1) (See Supplemental Information).

To test the accuracy of our approximations, six sets of data ($0.02 \leq \tau \leq 0.0008$ s) were generated by solving the Bloch-McConnell equations for two-site exchanges and for two cases where $|\nu_w - \nu_{Ga}| = 2000$ and 5000 Hz, and where $|\nu_w - \nu_{Ga}|$ is the difference, measured in Hertz, of the resonance of the ^{1}H-NMR signals from water and sites on the $\mathbf{Ga_{13}}$, respectively. In the simulations, the intensity of the $\mathbf{Ga_{13}}$ signal was set 0.0005 that of the proton signals to approximate our case where the concentrations of protons in exchanging sites differ by a large amount. The synthetic data were then treated as experimental results. In each case, the approximations were found to be appropriate and led to estimates of τ that are accurate to within a factor of two. This variation is within the uncertainties given by errors in the activation parameters that are exponentiated.

Conclusions:

The values for $\mathbf{Ga_{13}}$ compare well with those measured for the $\mathbf{Al_{13}}$ Keggin ion at similar conditions (Table 2) and fall into the millisecond time scales. The result is important because the clusters are not only structurally distinct but also have different Group 13 metals. The results suggest that the rates of proton exchange on these hydroxyl bridges might be determined by bonding to the oxygen and relatively unaffected by the distal metal. We recognize that these are the only such measurements, and future experiments are needed to support or reject the similarity.

Table 2: Activation parameters for exchange of protons from μ_2-OH on Group 13 clusters.

Cluster Bridge	τ_{298} (s)	$\Delta H^{\ddagger}_{298}$ (kJ/mol)	$\Delta S^{\ddagger}_{298}$ (J/mol·K)
Ga_{13} μ_2-OH_{int}	0.04 ± 0.01	39 ± 4	-90 ± 10
Al_{13} μ_2-OH_{fast}	0.013	20 ± 1	-140 ± 2
Al_{13} μ_2-OH_{slow}	0.201	23	-153

Besides the suggestion that rates are similar between the Ga_{13} and Al_{13} cluster, an additional unanswered question is whether the rates are affected by the cluster charges and solution pH. From studies of minerals there seems to be a strong relationship between surface charge and kinetics of reactions so that any rates vary in a broad amphoteric distribution with pH as the solid develops positive or negative surface charge. In these clusters the surface charge would be controlled by acid base reactions and possibly by ion association. In our experiments surface charge is not controllable because of the mixed-solvent systems. We can, however, change the overall charge of a cluster via suitable choice of a ligand and examine the effect on proton lifetimes. These experiments are underway.

Experimental:

The clusters used for this study were synthesized using previously published methods,[12] and the Ga:In ratio was confirmed using ^{1}H-NMR.[13] The d_6-DMSO was dried with sieves to achieve $\chi_{water} \leq 0.001$. All ^{1}H-NMR data were collected on a 500 MHz Varian Spectrometer.

References:

(1) Schluter, J.; Karl-Heinz, K.; Adiwidjaja, G.; Gebhard, G. *Neues. Jb. Miner. Monat.* **2003**, 521–527.

(2) Bai, Y.; Mora-Sero, I.; De Angelis, F.; Bisquert, J.; Wang, P. *Chem. Rev.* **2014**, *114* (19), 10095–10130.

(3) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.

(4) Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Huang, Y.; Fan, L.; Luo, G. *Chem. Rev.* **2015**, *115* (5), 2136–2173.

(5) Korotcenkov, G.; Han, S. Do; Stetter, J. R. *Chem. Rev.* **2009**, *109* (3), 1402–1433.

(6) Thomas, S. R.; Adamopoulos, G.; Lin, Y.-H.; Faber, H.; Sygellou, L.; Stratakis, E.; Anthopoulos, T. D. *App. Phys. Let.* **2014**, *105* (9).

(7) Bloor, L. G.; Carmalt, C. J.; Pugh, D. *Coord. Chem. Rev.* **2011**, *255* (11-12), 1293–1318.

(8) Oliveri, A. F.; Wills, L. A.; Hazlett, C. R.; Carnes, M. E.; Chang, I.-Y.; Ha-Yeon Cheong, P.; Johnson, D. W. *Chem. Sci.* **2015**, *6* (7), 4071–4085.

(9) Oliveri, A. F.; Carnes, M. E.; Baseman, M. M.; Richman, E. K.; Hutchison, J. E.; Johnson, D. W. *Angew. Chem. Int. Ed.* **2012**, *51* (44), 10992–10996.

(10) Houston, J. R.; Phillips, B. L.; Casey, W. H. *Geochim. Cosmochim. Ac.* **2006**, *70* (7), 1636–1643.

(11) Oliveri, A. F. Solution Characterization of Inorganic Nanoscale Cluster Species via 1H-NMR and DOSY, University of Oregon, 2015.

(12) Mensinger, Z. L.; Gatlin, J. T.; Meyers, S. T.; Zakharov, L. N.; Keszler, D. A.; Johnson, D. W. *J. Chem. Soc. Dalt. Trans.* **2008**, *120* (49), 9626–9628.

(13) Carnes, M. E.; Knutson, C. C.; Nadarajah, A.; Jackson, M. N.; Oliveri, A. F.; Norelli, K. M.; Crockett, B. M.; Bauers, S. R.; Moreno-Luna, H. A.; Taber, B. N.; Pacheco, D. J.; Olson, J. Z.; Brevick, K. R.; Sheehan, C. E.; Johnson, D. W.; Boettcher, S. W. *J. Mater. Chem. C* **2014**, *2* (40), 8492–8496.