Detection of a New Polymeric Species formed through the Hydrolysis of Gallium(III) Salt Solutions

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A previously unreported gallium species has been detected which is formed by the hydrolysis of aqueous gallium(III) solutions. N.m.r. studies have shown that this species has a tetrahedrally co-ordinated gallium nucleus whose chemical shift suggests that it is structurally analogous to the central tetrahedral aluminium occurring in the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation. The size of the polymeric gallium species was estimated by measuring the increase in the basal (d_{001}) spacing of a montmorillonite upon intercalation. The hydrated height of the gallium polymer in its orientation relative to the phyllosilicate sheets was found to be approximately 9.4 Å, which is about 5.6% larger than the size of the Al_{13} cationic unit, measured by the same method. This compares well with geometric calculations which show that a Ga_{13} cationic species would be expected to be about 5.7% larger than the analogous aluminium species. These results suggest strongly that a $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation forms during the hydrolysis of gallium(III) solutions at a pH range of approximately 3—4. The reason why this species has not been previously reported may be related to the fact that it appears to be much less stable in solution than the analogous aluminium species, as revealed by n.m.r. evidence.

Numerous studies have been undertaken which have probed the nature of the species formed when an $[Al(H_2O)_6]^{3+}$ solution is hydrolysed. Researchers have taken a particular interest in this reaction because of its importance in mineralogical and soil chemistry, and because of the possible applications of the polymeric species formed. Recent studies have involved the use of inorganic polyoxycations formed through metal hydrolysis as clay mineral pillaring agents.[1] These agents serve to prop apart the phyllosilicate sheets thus forming a two-dimensional porous network which exposes the clay mineral surface acidic sites. The pillared structures formed using aluminium polyoxycations have recently received much attention as catalytic hydrocarbon cracking reagents.[2] The study of the hydrolysis of gallium(III) salt solutions, however, has received much less attention than is the case for aluminium. As a result it is not clear as to whether or not analogous gallium polyoxycation species, which would quite likely have similar applications, are formed during gallium hydrolysis.

As an $[Al(H_2O)_6]^{3+}$ solution is hydrolysed, polyoxycation species are known to occur in solution up to a hydroxide to aluminium mole ratio (r = OH/Al) of 2.5:1. Many different polymeric cations have been proposed to exist in this range.[3–6] Johansson approached the problem of identifying the polymers formed by attempting to crystallise out any distinct species present at the various stages of hydrolysis. As a result, he isolated the sulphate salts of the dimeric[7] species $[Al_2(OH)_2(H_2O)_4]^{4+}$ and the polymeric[8] modified-Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. The latter species consists of a central tetrahedrally co-ordinated aluminium surrounded by twelve edge-linked aluminium octahedra. Subsequently, small-angle *X*-ray scattering studies of hydrolysed solutions found that a polymer having a radius of gyration of approximately 4.3 Å was present, and this is believed to be the modified-Keggin structure.[9] More recently, n.m.r. studies undertaken by Akitt and co-workers[10–14] concluded that partially hydrolysed monomeric species are present, as well as the dimeric and polymeric Al_{13} cations previously mentioned. Bottero *et al.*[15,16] attempted to quantify the distribution of these species as a function of the degree of hydrolysis by the combined use of quantitative n.m.r. spectroscopy and potentiometric titrations, and proposed that there also exists an $[Al_2(OH)_x]^{(6-x)+}$ species formed above an OH/Al ratio of approximately 2.1:1. Beyond an OH/Al ratio of 2.5:1 a gel of unknown structure forms which exists until an OH/Al ratio of 3:1 is reached, at which point $Al(OH)_3$ precipitates.[17] As hydrolysis continues, this species dissolves when an r = 4:1 ratio is reached, leaving $[Al(OH)_4]^-$ ions in solution. No other species have been detected at higher degrees of hydrolysis.

In the case of gallium, however, much less is known about the hydrolytic behaviour. On the basis of the similar ionic radii of Al^{3+} and Ga^{3+} (0.50 and 0.62 Å),[18] and of the parallel crystal structures of their oxides and oxyhydroxides,[19] it would seem reasonable to assume that the ionic species formed during gallium hydrolysis would be similar to those forming for aluminium. Thus far, however, this has not been found to be the case.

In weakly hydrolysed aqueous gallium solutions ($0 \leqslant$ OH/Ga $\leqslant 2.5$:1) studies involving pH and electrometric titrations,[20] light scattering,[21] refractive index,[22] vapour pressure,[23] and polarographic measurements[24] as a function of the degree of hydrolysis have suggested that a continuous polymerization process occurs. As such it has been proposed that hydroxide bridges serve to link the gallium octahedra into chains. Measurements of diffusion coefficients, however, have suggested the existence of a small number of discrete complexes.[25] Under normal hydrolysis conditions, attempts to crystallise out any of the polymeric species known to exist for aluminium have failed. A structure similar to that occurring in the aluminium sulphate mineral alunite, $KAl_3(OH)_6(SO_4)_2$, has been found, however.[26] Indications were also seen of another crystalline species occurring in small quantities, but unfortunately no crystal structure determination could be done. When hydrolysis progresses beyond an OH/Ga ratio of 2.5:1, a gel phase is formed, and then at a hydrolysis ratio of 3.0:1, GaO(OH) precipitates. This species has a structure analogous to that of the aluminium oxyhydroxide, diaspore α-AlO(OH).[27] As hydrolysis proceeds to an OH/Ga ratio of 4:1, the precipitate dissolves, resulting in $[Ga(OH)_4]^-$ ions in solution.

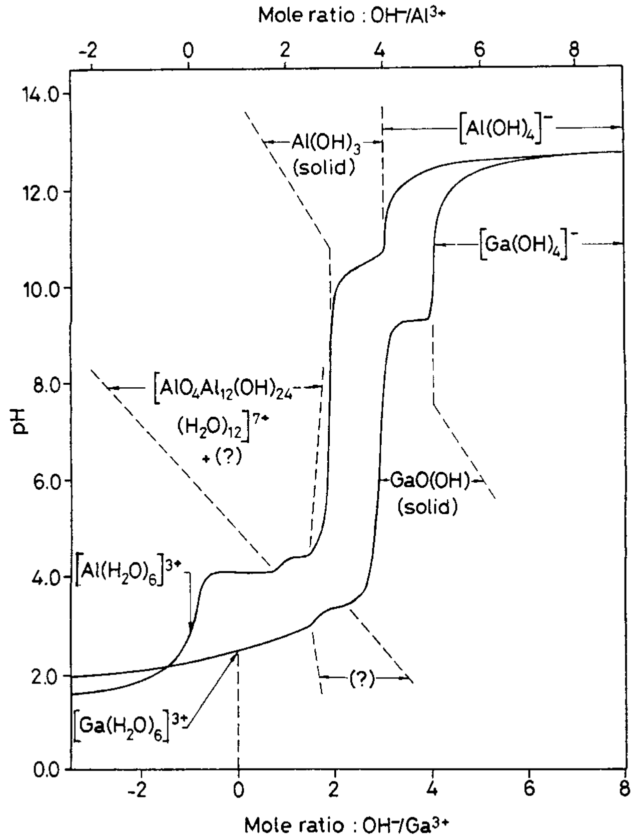

Figure 1. The pH *vs.* OH/M curves for hydrolysed 0.2 mol dm^{-3} $AlCl_3$ and 0.2 mol dm^{-3} $GaCl_3$ aqueous solutions back-titrated with 0.2 mol dm^{-3} HCl. The species which are thought to be present in the various hydrolytic regions are indicated. Note that the OH/M scales for aluminium and gallium(III) are offset from one another by one unit

From this it can be seen that although there are similarities in the hydrolytic behaviours of Al^{3+} and Ga^{3+}, differences also exist. In particular, no evidence of a Ga_{13} modified-Keggin unit similar to that known to exist for aluminium has been found. Therefore, in an attempt to determine if a gallium species analogous to that of the cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ exists, a series of experiments involving the hydrolysis of Ga^{3+} and Al^{3+} solutions was undertaken.

Experimental

Aqueous solutions of Al^{3+} and Ga^{3+} were prepared by dissolving $AlCl_3 \cdot 6H_2O$ (Aldrich, 99%) and $GaCl_3$ (Aldrich, >99.99%) in distilled/deionised water. The concentrations of the resulting solutions were determined by precipitations with 8-hydroxyquinoline.

Titration curves were prepared by measuring the pH (using a Fisher Accumet model 230 pH/ion meter) as a function of the OH/M mole ratios for 0.2 mol dm^{-3} $[Al(H_2O)_6]^{3+}$ and $[Ga(H_2O)_6]^{3+}$ solutions first hydrolysed with 0.2 mol dm^{-3} NaOH and then back-titrated with 0.2 mol dm^{-3} HCl.

Hydrolysed gallium solutions were prepared by adding 0.2 mol dm^{-3} NaOH dropwise to stirred $[Ga(H_2O)_6]^{3+}$ solutions in the stoicheiometry required to achieve the desired OH^-/Ga^{3+} mole ratios. They were then aged for 20 min at a temperature of 50 °. Gallium-71 (122.03 MHz) n.m.r. spectra were obtained on a Bruker AM-400 spectrometer at ambient temperature using a 10-mm broad-band probe. Spectra were run of samples contained in 10-mm sample tubes with coaxial D_2O inserts for external field-frequency lock. Chemical shifts have been reported relative to the resonance of $[Ga(H_2O)_6]^{3+}$. A sample of $[Ga(OH)_4]^-$ was also prepared by hydrolysing a $[Ga(H_2O)_6]^{3+}$ solution to an OH^-/Ga^{3+} mole ratio of >4:1, and it was found to give a signal 222.2 p.p.m. downfield from that of $[Ga(H_2O)_6]^{3+}$.

As high concentrations of halide ions are known to interact with gallium in aqueous solutions,[28] n.m.r. studies were undertaken for $[Ga(OH)_4]^-$ solutions varying in Cl/Ga ratios from 0 to 10:1, and in OH/Ga ratios of from 4 to 60:1. No variation was seen in the resonance of $[Ga(OH)_4]^-$, either in terms of peak position or width. Therefore, it seems very unlikely that the chloride ions present in the solutions studied herein (Cl/Ga = 3:1) will interact with the species formed.

Pillaring studies were carried out by the addition of hydrolysed aluminium or gallium solutions (OH/M = 2.25:1) dropwise to stirred suspensions of STx-1 montmorillonite (Source Clay Minerals Repository, University of Missouri) to achieve loadings of between 10 and 30 milliequivalents of M^{3+} per gram of STx-1. The resulting suspensions were washed five times with distilled/deionised water by centrifugation. The basal (d_{001}) spacings of both hydrous (air dried) and anhydrous (dried at 150 °C) oriented thin films of the resulting intercalates were determined using a Norelco *X*-ray diffractometer with Fe-K_α radiation.

Results

Titration curves (pH *vs.* OH/M ratios) for both Al^{3+} and Ga^{3+} are shown in Figure 1. The exact appearance of these curves depends on the experimental conditions (titration rate, stirring rate, *etc.*), presumably because the formation of the complex species is controlled to some extent by factors such as diffusion and slow dissociation. At sufficiently slow titration rates, however, small plateaus can be seen at different OH/M ratios. These plateaus provide a useful guide to the regions in which different species might be expected. For example, a small plateau can be seen in the case of aluminium between an OH/Al ratio of 1.5 and 2.4:1, which is the region in which the Al_{13} polyoxycation species exists at highest concentrations. A similar plateau can also be seen in the case of the gallium curve. To investigate whether or not this parallel in their hydrolytic behaviour could be indicative of similar polymeric species being formed for hydrolysed aluminium and gallium(III) solution, n.m.r. studies were initiated.

Numerous ^{27}Al n.m.r. studies have been undertaken of hydrolysed aluminium solutions. The 100% natural abundance of ^{27}Al, which is a spin $\frac{5}{2}$ nucleus, contributes to its relatively high n.m.r. receptivity (1.17×10^3 relative to ^{13}C). Unfortunately, its high[29] quadrupole moment (0.149×10^{-28} m^2) results in such rapid quadrupolar relaxation that resonances for asymmetric aluminium species are in some cases difficult to observe. As a result, the ^{27}Al n.m.r. spectrum of a hydrolysed aluminium solution, relative to 80.0 p.p.m. for an $[Al(OH)_4]^-$ standard, shows reasonably sharp peaks for $[Al(H_2O)_6]^{3+}$ and the partially hydrolysed monomeric species (0 p.p.m.) and for the central tetrahedral aluminium in the polyoxycation species (62.5 p.p.m.). However, only at high temperatures (*ca.* 80 °C) has a peak been observed which has been suggested to arise from the 12 asymmetric aluminium octahedra in this structure.[12] This peak is extremely broad, and is centred slightly downfield of $[Al(H_2O)_6]^{3+}$, as would be expected for the deshielding environment relative to that of the monomer.

In the case of ^{71}Ga, which is a spin $\frac{3}{2}$ nucleus, the quadrupole moment (0.112×10^{-28} m^2) is slightly less than that of ^{27}Al. Although the gyromagnetic ratio is higher for ^{71}Ga than for ^{27}Al, the much lower natural abundance of this species (39.8%) results in ^{71}Ga having a lower[29] n.m.r. receptivity (3.19 ×

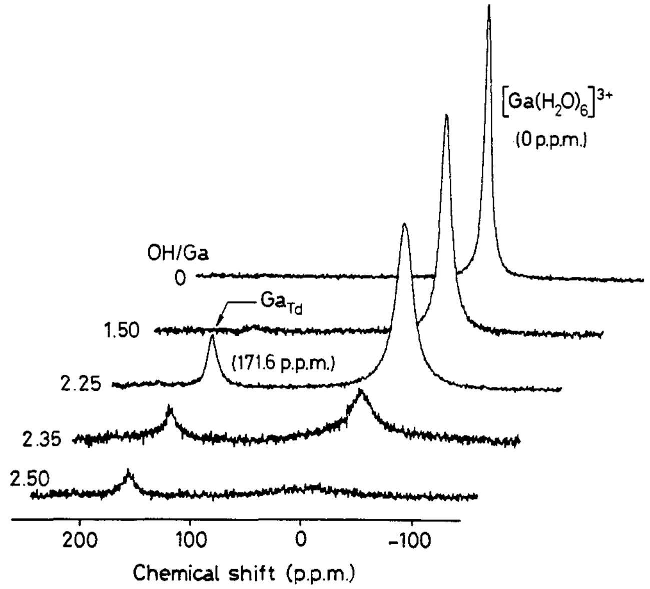

Figure 2. Gallium-71 n.m.r. spectra depicting the species present as hydrolysis progressed. The scale shown is with respect to the peak of $[Ga(H_2O)_6]^{3+}$ at 0 p.p.m. A peak representing a tetrahedrally co-ordinated gallium species was seen to appear at an OH/Ga mole ratio of 1.50:1. This peak (171.6 p.p.m.) appeared upfield of where the resonance of $[Ga(OH)_4]^-$ is known to occur (222.2 p.p.m.), and thus it represents a more shielded environment. The peak of $[Ga(H_2O)_6]^{3+}$ was observed to decrease in intensity and increase in width as hydrolysis progressed, which is indicative of the formation of partially hydrolysed monomers. An additional peak slightly downfield of this (at approximately 15 p.p.m.) became apparent at an OH/Ga ratio of 2.35:1 and appears to have completely replaced the $[Ga(H_2O)_6]^{3+}$ at a hydrolysis ratio of 2.50:1

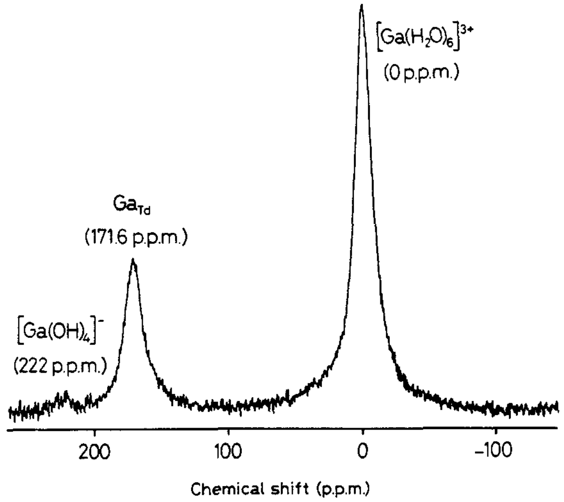

Figure 3. The ^{71}Ga n.m.r. spectrum observed for the dissolved amorphous sulphate salt of the polymeric gallium species. No $[Ga(OH)_4]^-$ was present as standard. Therefore the small peak occurring at approximately 222 p.p.m. must result from the dissolution of the polymeric species, yielding $[Ga(OH)_4]^-$ ions in solution. Integrations showed that the concentration of $[Ga(OH)_4]^-$ was approximately constant with time, while that of Ga_{Td} decreased, and that of the peak at 0 p.p.m., which represents partially hydrolysed monomers, increased

10^2 relative to ^{13}C) than ^{27}Al. Although ^{69}Ga has a higher natural abundance than ^{71}Ga (60.4%), its gyromagnetic ratio is considerably lower, resulting in its being a somewhat less receptive nucleus. In addition, it has a higher quadrupole moment than ^{71}Ga. Therefore, all gallium n.m.r. studies were undertaken for the ^{71}Ga nucleus.

When a series of aqueous gallium solutions was prepared to differing degrees of hydrolysis ($0 \leqslant OH/Ga \leqslant 2.5:1$) and aged for approximately 20 min at 50 °C, the peak (0 p.p.m.) of $[Ga(H_2O)_6]^{3+}$ was observed to broaden and decrease in intensity as hydrolysis progressed (Figure 2). This is indicative of the formation of partially hydrolysed monomeric species. No evidence was seen of a peak slightly downfield of this which would suggest the presence of a dimeric species such as $[Ga_2(OH)_2(H_2O)_4]^{4+}$ (*i.e.* similar to the dimeric species seen for aluminium). At an OH/Ga ratio of 1.50:1 a small broad peak became apparent at 171.6 p.p.m., which is in the proper region to indicate a tetrahedrally co-ordinated gallium species (Ga_{Td}) in a system such as this. This peak appeared at a position such that $\nu(Ga_{Td})/\nu[Ga(OH)_4^-]$ was 0.77. In the case of the hydrolysed aluminium solution, the ratio $\nu(Al_{Td})/\nu[Al(OH)_4^-]$ was 0.78. Since the chemical shifts of analogous aluminium and gallium(III) compounds in which the metals are co-ordinated to oxygen {*e.g.* $[M(OH_2)_6]^{3+}$, $[M(OH)_4]^-$, *etc.*} do seem to parallel one another,[30] the similarity of these ratios suggests that this broad gallium peak may represent an analogous species to the aluminium tetrahedral peak which arises from the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ species. The possibility exists, however, that this gallium n.m.r. peak may arise from some other tetrahedral species for which there is no known aluminium analogue. However, the results of clay mineral pillaring studies (see below) confirm that at this pH the hydrolysed gallium solution contains a polymeric species which is of the approximate height which would be expected for an analogous Ga_{13} polymeric cation. Therefore, the assumption that this n.m.r. peak can be identified with a $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation, or a very similar polymeric species, appears to be quite reasonable. The extremely broad nature of this tetrahedral gallium peak (*ca.* 1 800 Hz) relative to that of the tetrahedral aluminium species (*ca.* 20 Hz)[12] could be indicative of a more distorted environment in the case of the tetrahedral gallium, or of interactions between ions in solution which would contribute to an increased relaxation rate. As hydrolysis progressed, the intensity of this tetrahedral peak increased up to a hydrolysis ratio of 2.25:1, and then decreased. A very broad, weak peak centred at approximately 15 p.p.m. became apparent at a hydrolysis ratio of 2.35:1, and appeared to have completely replaced the peak at 0 p.p.m. at an OH/Ga ratio of 2.50:1. This may be indicative of the formation of a new type of polymeric species just prior to gel formation.

To determine if a resonance could be observed for any octahedral gallium nuclei in the polymer, an attempt was made to remove the peak at 0 p.p.m. by isolating the polymeric species through precipitation of its amorphous sulphate salt, and then redissolving by suspension in a $BaCl_2$ solution, following the method used for the aluminium system by Schönherr *et al.*[31] Interestingly, this technique was not found to be effective in the case of gallium. Over the time interval that this ^{71}Ga n.m.r. spectrum (Figure 3) was run (approximately 30 min) several integrals were taken and the results showed that a gradual change was taking place in the proportions of the species present.* The polymeric material was found to be dissociating, as indicated by a decrease in the intensity of the Ga_{Td} peak, and

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* Note that even in this solution of quite high chloride-ion concentration (*ca.* 0.5 mol dm^{-3}) the Ga_{Td} n.m.r. peak was not observed to shift in position or change in width with respect to the spectra obtained under much lower chloride-ion concentrations. This is an agreement with the results of varying the Cl/Ga ratio for $[Ga(OH)_4]^-$ solutions, which suggest that the chloride ions present are not interacting with the gallium species formed.

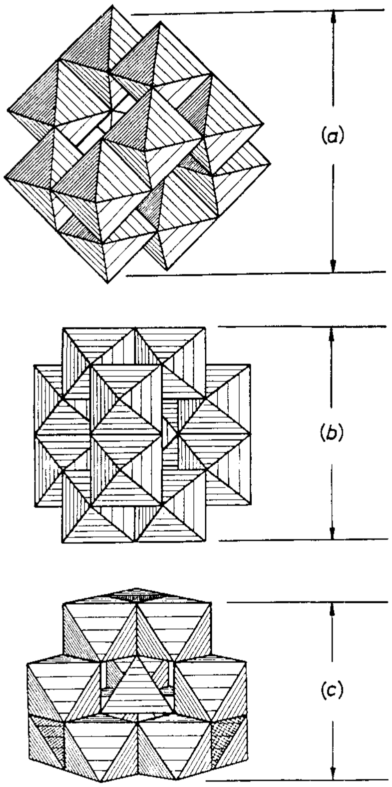

Figure 4. Graphical representations of the three likely orientations which the polymeric modified-Keggin ions could attain with respect to the phyllosilicate sheets (*i.e.* the lines shown can be taken to represent the phyllosilicate sheets). The calculated heights of the hydrous and anhydrous aluminium and gallium polyoxycation intercalates in these three orientations are outlined in the Table along with the observed heights

Table. Expected and observed d_{001}(Å) values for the $Al_{13}O_{40}$– and the proposed $Ga_{13}O_{40}$–montmorillonite intercalates as a function of polymer orientation with respect to the phyllosilicate sheets

Intercalate	Expected d_{001}[a]			Observed d_{001}[b]
$Al_{13}O_{40}$	(*a*)	(*b*)	(*c*)	
Hydrous	21.05	20.00	18.80	18.7—18.9
Anhydrous	19.97	18.83	17.63	17.6—17.7
$Ga_{13}O_{40}$				
Hydrous	21.69	20.57	19.30	19.2—19.4
Anhydrous	20.61	19.39	18.12	18.1—18.2

[a] Orientations are as outlined in Figure 4. [b] The observed d_{001} values suggest that the orientation is that shown in Figure 4(*c*).

an increase in the intensity of that at 0 p.p.m. In addition, a small peak of roughly constant intensity was apparent at 222 p.p.m., which is in the proper region to be indicative of the presence of $[Ga(OH)_4]^-$. The rapidity with which this dissociation occurred suggests that the reason that suspension in $BaCl_2$ appeared to fail to isolate the polymeric material was that the time lag (*ca.* 6 h) involved in stirring the $BaCl_2$ suspension (due to the low solubility of the sulphate salt) before the n.m.r. spectra could be run was sufficient to allow much of the polymeric material to dissociate. The Al_{13} polymeric cation is known to be quite stable in solution for much longer time periods (*e.g.* weeks), although polymerisation does eventually progress to the formation of $Al(OH)_3$. In accordance with this, when solutions of Al^{3+} and Ga^{3+} were initially hydrolysed and aged, lower temperatures had to be used for the gallium solutions (50 *vs.* 80 °C for aluminium) to prevent the gallium oxyhydroxide from precipitating out. An interesting point is that if this polymeric material is to be used as a clay mineral pillaring agent, the hydrolysed gallium solutions must be used immediately upon preparation and not allowed to age.

Clay mineral pillaring studies were undertaken to obtain an estimate of the size of the gallium species which was responsible for the ^{71}Ga n.m.r. peak at 171.6 p.p.m. which appeared in the hydrolysed gallium(III) salt solutions. As evidenced by the studies of inorganic polyoxycation pillared clays, the increase in the clays basal (d_{001}) spacing upon intercalation of a polymer can be used as a rough measure of the hydrated diameter of the adsorbed polymeric species.[32] Of course in cases where the intercalated species is not perfectly spherical, the observed increases in d_{001} will depend, in some cases quite markedly, on the orientation of the polymer with respect to the phyllosilicate sheets. In addition, if more than one type of intercalant species is present, and they are of different 'heights', the resulting d_{001} peak will be quite broad. Thus, the width of the observed peak can be used as a rough indication of the 'purity' (in terms of homogeneity of height) of the intercalated species. This will not necessarily reflect the range of ionic species present in the intercalant solution, however, as the phyllosilicate sheets may have a preference for one ionic species over another.

In the case of the intercalated $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation there are three reasonable orientations which the polymeric species could be expected to assume with respect to the clay mineral sheets that would result in different basal spacings (Figure 4). By examining the crystal structure[9] of the sulphate salt of this cationic species, estimates can be made of the d_{001} basal spacing that would be expected in each case, assuming that only this cationic species was intercalated. For example, for the orientation shown in Figure 4(*b*) the height of the anhydrous polymer can be calculated as roughly 8.05 Å knowing that the average octahedral Al–O bond length for the Al–O, Al–OH, and Al–OH_2 groups in the structure is approximately 1.90 Å. However, the polymeric structure is actually distorted, due to the central tetrahedral aluminium being too small for an ideal fit. As a result, the crystal structure determination shows that the observed anhydrous height (*i.e.* ignoring O–H bond lengths) is actually 8.93 Å. For the hydrated species the height would be roughly 10.10 Å. In the case of the intercalated species, by assuming that the phyllosilicate sheets have a basal spacing of 9.9 Å, the expected d_{001} spacing of the hydrous intercalated complex would be roughly 20.0 Å.

If an analogous species were to exist for gallium a comparison of the ionic radii of $Al^{3\bullet}$ (0.50 Å) *versus* Ga^{3+} (0.62 Å) suggests that the average octahedral Ga–O bond length would be 0.12 Å longer than the analogous Al–O bond length, or roughly 2.02 Å. By calculating the expected heights of the three different orientations of the modified-Keggin structure in the same manner as for the aluminium species, it can be seen that the gallium species would be expected to be roughly 5.7% larger than the aluminium species (Table).

When samples of STx-1 montmorillonite were pillared with hydrolysed aluminium and gallium solutions prepared in the same manner a d_{001} basal spacing of 19.2—19.4 Å was observed for the hydrated gallium intercalate, and 18.7—18.9 Å for the analogous aluminium case. This corresponds to a hydrated radius of 9.3—9.5 Å for the gallium species, and 8.8—9.0 Å for the aluminium polyoxycation. Thus the gallium species was found to be roughly 5.6% larger than the aluminium species, which is close enough to the predicted size to suggest that a $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ species indeed exists. In both cases the d_{001} peaks were quite sharp (2Θ *ca.* 1°), suggesting that the pillared products were reasonably 'pure' in terms of the heights of the intercalates. As none of the other polymeric species which are suspected to exist for aluminium or gallium (*e.g.* dimers) would be of a comparable height, this is consistent with the proposal that primarily cations of a modified-Keggin type structure have been intercalated. Upon drying at 150 °C, the d_{001} basal spacing decreased to 18.1—18.2 Å for the gallium intercalate, and 17.6—17.7 Å for the aluminium case. The observed spacings suggest that the aluminium polyoxycations are oriented with respect to the phyllosilicate sheets in the manner shown in Figure 4(*c*), which is in agreement with the orientation proposed by Plee *et al.*[32] on the basis of ^{29}Si and ^{27}Al magic angle spinning n.m.r. studies of clay minerals pillared with this species.

Conclusions

A gallium polyoxycation species has been detected which is formed in the hydrolysis of aqueous gallium(III) solutions. N.m.r. studies have shown that this species has a tetrahedrally co-ordinated gallium nucleus whose chemical shift suggests it to be structurally analogous to the central tetrahedral aluminium occurring in the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation. The approximate size that was determined for this species by clay pillaring studies also suggests that it is either identical to, or very similar in nature to, the Al_{13} modified-Keggin structure. One way to determine which is the case would be to crystallise out a salt of this species and to determine the structure of a single crystal. Attempts to do so have been unsuccessful to date, perhaps because this species does not appear to be as stable as the Al_{13} polyoxycation. The time-scale of its dissociation is such that it can easily be followed by n.m.r. spectroscopy. This means that this system is ideally suited to a study of the kinetics of dissociation, which may in turn yield clues as to what happens in the gel stage when rearrangement results in the precipitation of GaO(OH). A study of this aspect of the problem is currently being made.

The ready intercalation of the gallium polyoxycation species by the STx-1 montmorillonite used in this study suggests that the polymeric species is ideally suited as a clay mineral pillaring agent. The higher electronegativity of gallium over aluminium likely would result in an increased acidity of the resulting gallium-pillared clay, and this would be important in terms of catalytic applications. The results of a study of the physico-chemical properties of gallium-*versus* aluminium-pillared clays are forthcoming.

Acknowledgements

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