Comparison of the Species formed Upon Base Hydrolyses of Gallium(III) and Iron(III) Aqueous Solutions: The Possibility of Existence of an $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ Polyoxocation

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The hydrolytic behaviour of iron(III) has been investigated. The infrared spectrum of the sulfate salt of a hydrolysed iron(III) solution was found to match that of a gallium sulfate that had been shown through magic angle spinning NMR spectroscopy in combination with powder X-ray diffraction studies to contain the Ga_{13} ion. This supports the view that an $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion forms. It appeared, however, that this Fe_{13} ion is extremely unstable and decomposes very rapidly in solution. The addition of small amounts of Fe^{II} ions seems to stabilize the structure somewhat, however, and allowed it to be used as a clay mineral pillaring agent. The resulting d_{001} spacing of *ca.* 19.3 Å is similar to that seen in similar studies of $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.

The $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (or 'Al_{13}') polyoxocation has recently received a great deal of attention through its use in the formation of new classes of porous solids. By this approach, layered inorganic oxides, hydroxides and hydroxide oxides (*e.g.* phyllosilicates,[1] silicic acids,[2] phosphates,[3] zirconium and titanium phosphates,[4] titanates[5] and molybdenum oxides[6]) are used to intercalate inorganic polyoxocations thereby forming structures which are porous in two dimensions. The Al_{13} ion, which is formed through the base hydrolysis of aluminium(III) salt solutions, has been the polyoxocation most commonly used in these studies. The great interest that has developed in these new layered porous solids, however, has led to a search for new metal polyoxocations that could be utilized as pillaring agents.

The Al_{13} species has a structure in which the central tetrahedrally co-ordinated aluminium atom is surrounded by twelve edge-linked octahedrally co-ordinated aluminiums[7–10] arranged in a fashion analogous to that of the Baker–Figgis ε isomer[11] of the well known Keggin structure (the Baker–Figgis α isomer) that occurs in the heteropoly oxometalates.[12,13] As early as 1933, Pauling[14] had mentioned this type of Baker–Figgis ε isomer tridecameric structure as being a building block of the spinel group of minerals. It was not until 1960 when Johansson[7–10] discovered the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation, however, that an example of this unit was known to exist. The spinel group of minerals consists of numerous $A^{II}B^{III}{}_2O_4$ compounds which have the same crystal structure as that of the mineral spinel, $MgAl_2O_4$.[15] The spinel 'sub-unit' character of the Al_{13} ion can best be envisaged by comparing adjacent 'slices' of the spinel structure parallel to the 111 planes,[16] with adjacent 'slices' of the Al_{13} ion (Fig. 1). This structural relationship between the tridecamers and the spinels suggests that it might be possible to predict which other metal ions might be expected to form tridecamers upon base hydrolysis by considering which form spinel minerals.

The majority of the 2,3 spinels (both synthetic and naturally occurring) have Al^{III}, Ga^{III}, Cr^{III}, Fe^{III}, Mn^{III} or Co^{III} as the trivalent 'parent' metal. The divalent cations are typically Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. Extensive solid solution is common between the $A^{II}B_2{}^{III}O_4$ end-members, in terms of substitution of different M^{2+} or M^{3+} species. In the γ-M_2O_3 oxides the spinel structure remains even though there has been complete substitution of M^{III} for M^{II} in the crystal lattice, thereby altering the extent of the octahedral and tetrahedral site occupancies.[17–20] All of the metal(III) ions that are commonly viewed as 'parents' of the 2,3 spinels form these quasi-stable γ-M_2O_3 oxides.[19,21–23] This illustrates that these metal atoms can pack in the conformation that aluminium has in $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.

Recently we have shown that a Ga_{13} species is formed upon base hydrolysis of gallium(III) aqueous solutions,[24] and a $GaAl_{12}$ tridecamer forms when mixed Ga^{3+} and Al^{3+} solutions are hydrolysed.[25] In all three of these cases (Al_{13}, Ga_{13} and $GaAl_{12}$) a gel forms when the $OH^-:M^{3+}$ ratio exceeds about 2.46:1, which is the stoichiometric ratio (32:13) required for the formation of the tridecameric unit [equation (1)]. For the Al_{13} and $GaAl_{12}$ cases it has been shown that this gel forms through the coalescence of the tridecameric units and therefore has, at least initially, a 'pseudo-spinel' structure.[26] Gel formation also occurs for hydrolysed iron(III) solutions, and the fact that it occurs at about the same $OH^-:M^{3+}$ ratio makes one wonder whether iron might also form a similar polyoxocation. Iron(III) seems to be a likely candidate to form a tridecameric ion for two other reasons. First, it is known to form the $[Fe(OH)_4]^-$ ion in aqueous solution at high pH; since the tridecameric unit contains a tetrahedrally co-ordinated metal ion this willingness to adopt a tetrahedral configuration may be important. Secondly, many members of the iron series of spinel minerals can be formed through base hydrolysis of iron cation solutions.

$$13[Al(H_2O)_6]^{3+} + 32OH^- \rightleftharpoons [AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+} + 70H_2O \quad (1)$$

The species formed upon the base hydrolysis of iron(III) solutions depend very much on the rate and degree of hydrolysis, the counter ions present and their concentrations, the solution temperatures and the rate of addition of base. In the case of nitrate or perchlorate solutions, polymeric species of unknown structure occur in solution up to a hydrolysis ratio of 2.5:1, following which a gel phase is formed, and then at an $OH^-:Fe^{3+}$ ratio of 3.0:1, $FeO(OH)\cdot H_2O$ precipitates out; this has predominantly the α structure (goethite) but also in some cases, a small amount of the γ structure (lepidocrosite) is formed. By comparison, the hydroxide oxide formed for the gallium system is the isostructural α-$GaO(OH)\cdot H_2O$. When hydrolysis is continued to $OH^-:Fe^{3+}$ ratios of above 4:1 only a

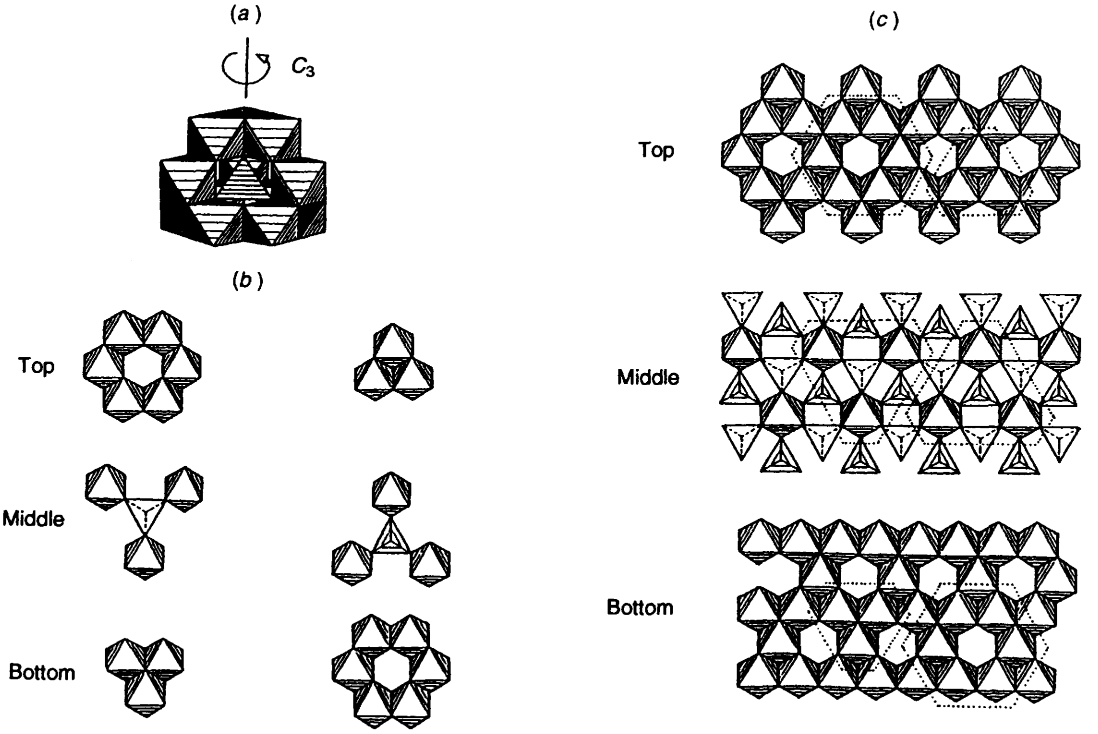

Fig. 1 A comparison of the structure of the Al_{13} unit to the spinel structure. (*a*) the Al_{13} unit; (*b*) cross-sections perpendicular to the C_3 axis of two orientations of the Al_{13} unit; one orientation is for the Al_{13} unit as shown, and the other is for the Al_{13} unit 'upside-down'; (*c*) cross-sections of the spinel structure parallel to the 111 planes; faint dotted lines outline parts which can be seen in the Al_{13} unit

small amount of $Fe(OH)_4^-$ is formed in solution, due to the very low solubility of the iron hydroxide oxides under alkaline conditions.[27,28] For solutions rapidly hydrolysed to $OH^- : Fe^{3+}$ ratios of above 3:1, the product formed is protoferrihydrite which is a poorly ordered hydroxide/hydroxide oxide.[29–32]

The presence of both sulfate ions and ammonium ions in solution results in the precipitation of the $[NH_4][Fe_3(OH)_6(SO_4)_2]$ salt (jarosite),[32] which is isostructural with the aluminium sulfate, alunite, $K[Al_3(OH)_6(SO_4)_2]$ and with the gallium sulfate, $[H_3O][Ga_3(OH)_6(SO_4)_2]$.[33] This gallium alunite phase forms under similar hydrolytic conditions to that of jarosite, whereas the aluminium phase requires hydrothermal conditions.

In the case of perchlorate solutions in which the α-$FeO(OH)\cdot H_2O$ phase is formed, and in which the counter ions are thought not to be directly involved in the polymerization process, it has long been believed that the hydrolytic process is continuous, the hydroxide oxide being built up in accordance with the 'core + links' model.[31,34] In 1975 it was calculated that the results could be interpreted in terms of the formation of partially hydrolysed monomers, dimers, trimers, as well as a very small amount of an oligomer consisting of 12.3 ± 2.4 Fe atoms.[35] No subsequent work appears to have been done to investigate this, nor has any proposal been put forth concerning a structure for a possible polymer. Upon aging of solutions having an $OH^- : Fe^{3+}$ ratio of *ca.* 2.0:1, a structure having a composition of $[\{Fe_4O_3(OH)_4\}_n]^{2n+}$ has been isolated and is thought to have an average *n* value of 25. It was proposed that the core contained tetrahedrally co-ordinated iron atoms, whereas those near the surface were thought to be octahedrally co-ordinated.[36] This was later challenged, however, Magini[37] concluding that all of the iron was octahedrally co-ordinated, and this view is the generally accepted one.

Further evidence for the possibility of the synthesis of an $[Fe^{III}O_4Fe^{III}{}_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ tridecamer upon the hydrolysis of iron(III) salt solutions comes through an examination of the hydrolytic behaviour of combined iron-(II) and -(III) solutions. Hydrolysis of iron(II) solutions leads to precipitation of $Fe(OH)_2$ at a hydrolysis ratio of $OH^- : Fe^{2+} = 2:1$. However, when iron-(II) and -(III) solutions are combined and hydrolysed, spinel phases are also formed.[38–40] For solutions having $0 \leqslant x \leqslant 0.1$ [*x* being the fractional iron(II) content on a mole basis], upon hydrolysis both spinel and goethite phases have been found to coexist initially. Upon aging, however, the spinel phase rapidly disappears leaving only the goethite phase in solution. For $0.1 \leqslant x \leqslant 0.25$, protoferrihydrite has been found to form, in addition to two types of spinel particles. For $x > 0.25$, only one type of spinel phase is seen to occur.[41] These results show that an increase in the amount of Fe^{II} favours the formation of the spinel phase. The observation of the initial spinel phase for solutions having $0 \leqslant x \leqslant 0.1$, followed by its transformation to goethite, indicates that although it may readily be formed in these solutions it is unstable and a phase transformation or a dissolution followed by the precipitation of the second phase occurs quickly. This suggests strongly that the formation of $[Fe^{III}O_4Fe^{III}{}_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ions in solution upon the hydrolysis of iron(III) salt solutions would be possible, but also that they would likely be quite unstable and could quickly decompose.

In summary, the hydrolytic behaviour of iron(III) is extremely similar to that of gallium(III), with gels being formed in both cases between $OH^- : M^{3+}$ ratios of 2.5 and 3.0:1, and analogous hydroxide oxide phases [α-$MO(OH)\cdot H_2O$] between ratios of 3.0 and 4.0:1. In addition, when sulfate groups are present during hydrolysis, $[H_3O][M_3(OH)_6(SO_4)_2]$ phases (jarosite or gallium alunite type) can form to some extent in both cases. Iron(III) and gallium(III) are both spinel 'parents' and are known to form γ-M_2O_3 phases. In addition, the hydrolysis of mixed iron(II)–iron(III) systems results in the precipitation of spinel particles, which can be said to have tridecameric sub-units. In view of these similarities between gallium and iron solutions, and the fact that gallium forms a Ga_{13} polyoxocation, a study of the base hydrolysis of iron(III) solutions was undertaken to attempt to ascertain whether iron forms a $[Fe^{III}O_4Fe^{III}{}_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion.

Even if iron forms a tridecameric unit, experimental difficulties arise in trying to confirm this. Nuclear magnetic resonance studies cannot be undertaken because iron is paramagnetic. X-Ray techniques would be valuable, but in view of the expected instability of the oligomers it would not be surprising if amorphous solids predominate (in fact, as discussed below, this is the case). The infrared spectra of salts containing the Al_{13} (and $GaAl_{12}$) cation have bands in the 800–400 cm^{-1} region which are characteristic for the tridecameric unit.[42] While infrared spectra of salts obtained from the base-hydrolysed iron solutions may not be as well resolved, because of the presence of amorphous material, they might still provide some evidence that tridecameric units exist. Spectra obtained in a similar way for salts obtained from hydrolysed gallium solutions (which are known to contain a Ga_{13} tridecamer) would probably provide an even better comparison, since the hydrolytic behaviours of gallium and iron are very similar, while that of aluminium is somewhat different. For this reason, the infrared spectra of Ga_{13} sulfate salts were also obtained; they have not previously been published. Clay mineral pillaring studies were also attempted, as these can confirm whether species of the right 'height' to be the tridecameric unit are present in solution; such measurements were also carried out on hydrolysed, mixed iron(III)–iron(II) solutions.

Experimental

Aqueous iron-(III) and -(II) solutions were prepared by dissolving $Fe(ClO_4)_3{\cdot}xH_2O$ (Alfa, 17.4% water), $FeCl_3{\cdot}6H_2O$ (Fisher) or $FeCl_2{\cdot}4H_2O$ (Aldrich) in deionized/distilled water. Gallium(III) solutions were prepared using anhydrous $GaCl_3$ (GFI, 99.9%). The latter solutions had been partially hydrolysed through the evolution of HCl gas upon the exposure of the $GaCl_3$ to water vapour in the air. These gallium solutions were both forward- and back-titrated with base (NaOH) and acid (HCl), respectively, and the titration curves compared to those of solutions prepared using standardized $Ga(NO_3)_3$ solutions. Acid (HCl) was added to the $GaCl_3$ solutions as required to correct for the self-hydrolysis. The resulting iron(III) and gallium(III) solutions were standardized gravimetrically through the precipitation of the metal quinolin-8-olate salts.[43]

These $GaCl_3$ and $Fe(ClO_4)_3$ solutions (*ca.* 0.1 mol dm^{-3} for Ga^{III} and 0.05 mol dm^{-3} for Fe^{III}) were base hydrolysed through the slow addition of *ca.* 0.2 mol dm^{-3} NaOH with vigorous stirring until $OH^-:M^{3+}$ ratios of *ca.* 2.25:1 had been reached. It was ensured that no sulfate ions were present in solution during these hydrolyses, as they could result in jarosite-type phases. The iron(III) solutions were cooled in ice throughout this procedure. The gallium solutions were left at room temperature until they were no longer visibly turbid, typically just a few minutes. Following this the pH of each solution was measured, and Na_2SO_4 (or Na_2SeO_4, Na_3PO_4 or Na_2HAsO_4) counter ion solutions that had been adjusted to pH values equivalent to those of the hydrolysed solutions (to prevent further hydrolysis) were added dropwise until $XO_4:M$ ratios (X = S, Se, As or P) of *ca.* 0.3–2.0:1 had been reached. The resulting salts were left for several days (or longer) and then collected by centrifugation, washed five times with deionized/distilled water and allowed to dry in air at room temperature.

The crystalline gallium sulfate phase believed to contain the Ga_{13} unit (as discussed in the Results section) was formed by hydrolysing a 0.2 mol dm^{-3} gallium chloride solution to an $OH^-:Ga^{3+}$ mole ratio of 2.25:1. This solution was left at room temperature until no longer visibly turbid. A pH-corrected sodium sulfate solution (0.2 mol dm^{-3}) was then added dropwise to the hydrolysed gallium solution to give an $SO_4^{2-}:Ga^{3+}$ mole ratio of 0.5:1. The resulting colloidal suspension was left for several weeks, and the powder that precipitated was separated from the remaining colloidal precipitate by careful decantation.

Gallium-71 (122.03 MHz) magic angle spinning (MAS) NMR spectra of sulfate salts prepared from the hydrolysed gallium(III) solutions were obtained using a Bruker MSL-400 spectrometer, with the magic angle accurately set through the use of the ^{79}Br resonance of KBr. The resonance positions reported are with respect to the band of $[Ga(H_2O)_6]^{3+}$ solution at $\delta = 0$.

Powder X-ray diffraction (XRD) studies of the sulfate (and other counter ion) salts of the hydrolysed metal(III) solutions were carried out using a Norelco X-ray diffractometer with either graphite-monochromated Fe-Kα ($\lambda = 1.936$ Å) or Cu-Kα ($\lambda = 1.5418$ Å) radiation, as indicated. In an attempt to overcome the problem of peak intensities deviating from their theoretical values due to preferred orientation, all of the samples were very finely ground, and were not tightly packed into the sample holders. Diffraction patterns were typically run from 5 to 90° in 2θ, utilizing a step width of 0.01° in 2θ and a scan time of 7 s per step.

Clay mineral pillaring studies were carried out for the hydrolysed iron(III) as well as for mixed iron(III)–iron(II) solutions (the mixed-valence solutions were prepared using chloride rather than perchlorate salts) to determine the approximate size of any intercalated polyoxocations, with respect to the phyllosilicate sheets. The hydrolysed solutions were added dropwise to vigorously stirred suspensions (*ca.* 1% w/w) of Na-STx-1 (a Na^+-exchanged montmorillonite), to solution loadings of *ca.* 10 milliequivalents metal per g STx-1 (the metal concentration was calculated on the assumption that the metal was still present in solution as the M^{3+} or M^{2+} form, which is obviously a simplification). The suspensions were then washed with distilled water five times, and thin films of the pillar interlayered clay minerals were prepared. To examine their d_{001} spacings, both before and after thermal treatments, oriented thin films were prepared on quartz or glass slides, as appropriate. Powder X-ray diffraction patterns (Fe-Kα source) of the slides were run from 4 to 22° in 2θ employing a step width of 0.02° in 2θ and a step scan time of 4 s.

Fourier-transform infrared (FTIR) spectra of CsI pellets of the gallium and iron sulfate and selenate salts were run on a Mattson Galaxy 4030 spectrometer at a resolution of 2 cm^{-1}.

Results

While the Ga_{13} cation is known to exist in hydrolysed aqueous solutions,[24,44] it is much less stable than the Al_{13} unit and it has not been proven that the gallium tridecamer can exist in the solid state. To investigate what phases do form when salts are formed from such gallium solutions, and to have spectra of the Ga_{13} salts to compare to those of iron salts formed from hydrolysed iron(III) salt solutions, powder XRD, infrared and MAS NMR studies were carried out.

Powder XRD Studies of Salts prepared from Hydrolysed Gallium(III) *Solutions.*—Salts of hydrolysed gallium solutions were prepared using sulfate, selenate, phosphate and arsenate counter ions. Only sulfate was found to yield crystalline products, and only poorly crystalline powders resulted. It was critical that the pH of the sulfate counter ion solution be lowered to that of the hydrolysed gallium solution (through the addition of dilute HCl), otherwise the precipitate would be the gallium hydroxide oxide. Powder XRD patterns of these gallium sulfate salts revealed there to be generally two crystalline phases present, the ratios of which depended on the synthetic technique. One phase had a powder XRD pattern[45] that clearly matched that of the $[H_3O][Ga_3(OH)_6(SO_4)_2]$ salt[33] which is isostructural with the aluminium sulfate mineral, alunite.[46] This gallium alunite phase was found to occur in much larger quantities when the $SO_4^{2-}:Ga^{3+}$ ratio was fairly high (*e.g.* above 1:1), or if the gallium solution had been heated during hydrolysis and not been allowed to cool before the sulfate solution was added. In some cases it was the only crystalline phase formed, although some amorphous material was always present.

The second crystalline phase observed produced mainly low-angle X-ray reflections [Fig. 2(*a*)] in a pattern that was somewhat similar to that calculated[45] and observed [Fig. 2(*b*)]

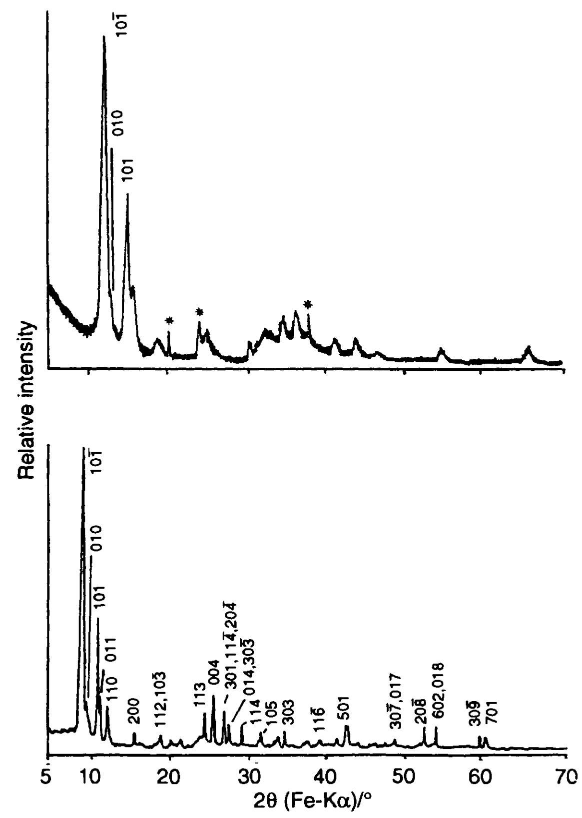

Fig. 2 Powder XRD patterns for Ga_{13} sulfate (above) and Al_{13} sulfate (below). Peaks due to the gallium alunite phase in the upper pattern are indicated by an asterisk

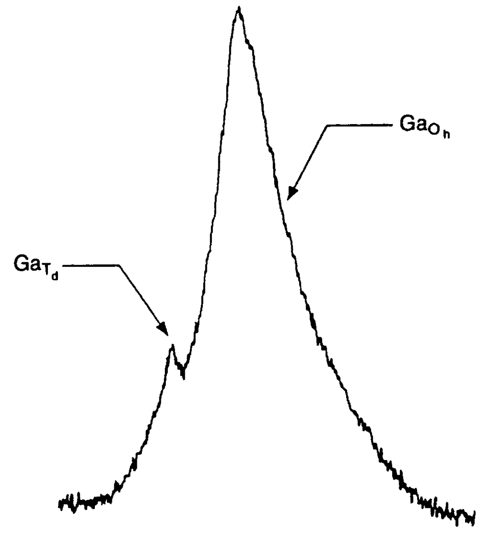

Fig. 3 Observed ^{71}Ga MAS NMR spectrum of the gallium sulfate salt

for the monoclinic[7,10] $[Al_{13}O_4(OH)_{25}(H_2O)_{11}][SO_4]_3 \cdot xH_2O$, which has a space group of *P*2/*n* or *Pn*, and $a = 14.18$, $b = 11.50$, $c = 17.73$ Å and $\beta = 102.3°$ ($Z = 2$). It was not possible to obtain any crystalline phases having powder XRD patterns[45] similar to that of the cubic form ($P4_232$, $Z = 2$, $a = 17.9$ Å)[8] of $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4 \cdot xH_2O$. This is unfortunate as such crystals would have had more intense bands at higher diffraction angles, and would have been much more helpful for confirming analogous phases.

Although this second crystalline phase had a powder XRD pattern similar to that of the Al_{13} sulfate discussed, it was sufficiently different that obviously no firm identification could be made on this basis alone. The combination of the poorly crystalline character of this gallium sulfate phase, and the fact that the gallium alunite phase was also invariably present to a small extent, also ruled out elemental analyses and powder Rietveld refinements as tools for confirming the presence of and determining the precise structure of the Ga_{13} ion.

^{17}Ga *MAS NMR Spectra of the Gallium-Sulfate Salts.*—A gallium-71 MAS NMR spectrum was run of the gallium sulfate salt which through XRD studies was found to contain the crystalline phase believed to be isostructural with the Al_{13} sulfate, in addition to a small amount of the gallium alunite phase. Two strong bands were observed, one at a high enough chemical shift to indicate a tetrahedral environment and the second in the appropriate position for an octahedral environment (Fig. 3). This latter band was strongly skewed to lower chemical shift, suggesting another band underneath. Since the lineshapes for such quadrupolar nuclei are complex, depending on the quadrupolar coupling constants, the spinning ratios and flip angles, curve fitting is difficult and therefore the locations of the centres of the bands could not be determined exactly.

However the relationship between ^{71}Ga and ^{27}Al NMR chemical shifts for compounds having only oxygen in the first metal co-ordination sphere has recently been found to be $\delta(^{71}\mathrm{Ga}) \approx 2.83\ \delta(^{27}\mathrm{Al})$.[47] The ^{27}Al MAS NMR spectrum of Al_{13} sulfate salts typically consists of one band at δ *ca.* 60–64,[42,48–50] which is due to the tetrahedrally co-ordinated Al in the tridecamer. No octahedral peak is generally observed for the octahedrally co-ordinated aluminiums in the tridecamer, however for the $GaAl_{12}$ sulfate of analogous structure (wherein gallium is in the central tetrahedral position) the Al_{O_h} band is clearly seen, and occurs at δ 9.[42] The reason for the absence of an Al_{O_h} band in the Al_{13} sulfate salts is not understood, and therefore it cannot be predicted whether or not one would be seen for a Ga_{13} analogue.[45] In solutions containing isolated Al_{13} ions the ^{27}Al NMR peak due to the octahedrally co-ordinated aluminiums can be seen (at elevated temperatures only) and occurs at δ 9–11.[39,51] On the basis of these peak positions, and the relationship between ^{71}Ga and ^{27}Al chemical shifts, the ^{71}Ga NMR peaks for a Ga_{13} salt would be expected to fall at δ *ca.* 171–180 for the central tetrahedral gallium, and the band (if seen) for the octahedrally co-ordinated galliums at between δ 25 and 31. On the basis of these predicted chemical shifts, the two stronger bands in the ^{71}Ga NMR spectrum appear to be in appropriate regions to represent, respectively, the tetrahedrally and octahedrally co-ordinated galliums in the tridecamer. Therefore it is felt that it can be safely concluded that the Ga_{13} ion is present in this particular sulfate salt, and that the powder XRD pattern which is similar to that of the monoclinic form of the Al_{13} sulfate must therefore be due to a Ga_{13} sulfate which is similar in structure to the above-mentioned Al_{13} sulfate.

The second, very broad octahedral ^{71}Ga MAS NMR signal which appears to underlie the stronger one probably arises from the presence of another phase. Gallium alunite was known to be present, and it is quite likely that a signal would be observed for the gallium nuclei in this structure as their environments would not be particularly distorted. It is also known that sulfate groups act somewhat in a shielding manner, as can be seen from the negative chemical shifts of some of the aluminium sulfates.[52] Therefore the tentative assignment of this high-field band to the gallium alunite phase is made. One way to confirm this would be to synthesise gallium alunite in its pure form (single crystals, not powder that could contain amorphous impurities) and to obtain the ^{71}Ga MAS NMR spectrum. Unfortunately attempts to carry out this synthesis, which employed various published methods,[33,53] were not successful.

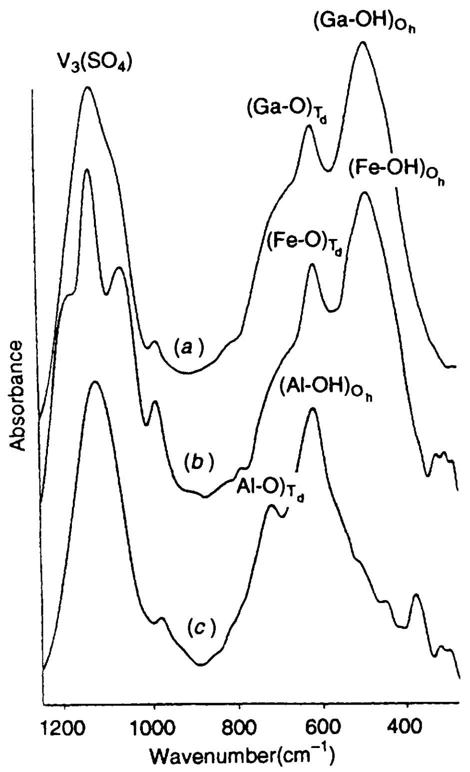

Fig. 4 Infrared spectra of CsI pellets of sulfate salts of hydrolysed solutions of Ga^{III} (*a*), Fe^{III} (*b*) and Al^{III} (*c*)

Infrared Spectra of Iron and Gallium Sulfate and Selenate Salts.—The infrared spectrum of the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion has recently been examined and the low-wavenumber bands assigned.[42,45] The Al–O vibrations were assigned as follows: 729, (Al–O)$_{T_d}$; 627, (Al–OH)$_{O_h}$; 546, (Al–O)$_{O_h}$; and 492 cm^{-1}, (Al–OH$_2$)$_{O_h}$ stretch. The relative positions of the infrared bands would be expected to vary significantly between an $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and an isostructural $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion, primarily due to the different masses of aluminium and gallium. Comparisons between the infrared spectra of γ-Al_2O_3 and γ-Ga_2O_3 found the M–O stretching vibrations to occur approximately 100 cm^{-1} lower for the gallium spinel,[54] and on this basis the bands for Al_{13} and Ga_{13} tridecamers, which can be considered to be sub-units of the γ-M_2O_3 structure, would likely occur at similarly lower wavenumbers for the Ga_{13} unit.

The gallium sulfate salt that was characterized by ^{71}Ga MAS NMR and powder X-ray diffraction studies and was therefore known to contain the Ga_{13} unit, in addition to some of the gallium alunite phase, was found to exhibit the infrared spectrum shown in Fig. 4(*a*). There are two strong bands present at wavenumbers that would be appropriate for (Ga–O)$_{T_d}$ and (Ga–OH)$_{O_h}$ bands in a $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion (605 and 471 cm^{-1}), and in addition there appears to be a broad underlying band. The band at *ca.* 605 cm^{-1} could not have been due to the ν_4 vibration of SO_4^{2-} as it was not observed to shift in position when the counter ion was changed to selenate. This spectrum did not, however, exhibit the other (weaker) stretching bands that were seen for the Al_{13} sulfate and selenate salts [*i.e.* the (Al–O)$_{O_h}$ and the (Al–OH$_2$)$_{O_h}$ bands]. This is probably due to the gallium sulfate salt being very poorly crystalline and amorphous matter also being present, while the Al_{13} sulfates and selenates examined previously were all highly crystalline.[42] When sulfate ions were added to a hydrolysed aluminium solution and the resulting colloidal precipitate was collected without time being allowed for crystallization, the infrared spectrum of the amorphous phase exhibited predominantly the (Al–O)$_{T_d}$ and (Al–OH)$_{O_h}$ bands [Fig. 4(*c*)], which is very similar to that seen for the gallium sulfate salt, except, of course, for the changes in wavenumbers. The designation of the higher-wavenumber band to a (Ga–O)$_{T_d}$ vibration is reinforced by the observation that this band was not observed when the hydrolysed gallium solutions were allowed to age for fairly long times before the sulfate solutions were added. The time required for this infrared band to disappear was slightly longer than that required for the Ga$_{T_d}$ NMR signal to disappear (*e.g.* 1 d at 50 °C). This time difference is not surprising as the NMR signal could disappear as soon as the tetrahedral symmetry had been altered sufficiently (^{71}Ga being quadrupolar), and this would occur well before a change in co-ordination number had occurred. The infrared spectrum would likely not be influenced as readily by such changes.

The very broad infrared band underlying the two relatively sharp bands may be due to the poorly crystalline gallium alunite phase that was known to be present. Unfortunately, no infrared spectrum appears to have been published for such a gallium phase. Single crystals would be required in order to obtain a reliable spectrum (powder would not be acceptable as other X-ray amorphous phases could readily be present) and as previously discussed it was not found to be possible to synthesise these.

When an iron(III) solution was hydrolysed, and a sulfate salt thereof was prepared immediately, the infrared spectrum was virtually identical to that of the gallium sulfate salt just discussed; bands assigned as (Fe–O)$_{T_d}$ and (Fe–OH)$_{O_h}$ occurred at 606 and 465 cm^{-1} [Fig. 4(*b*)]. In addition, there is a very broad underlying band, similar to that which was attributed to gallium alunite in the spectra obtained for the sulfate salt precipitated from the hydrolysed gallium solutions. As iron is also known to form an alunite type of phase (jarosite), $[H_3O][Fe_3(OH)_6(SO_4)_2]$, this result was not unexpected. The overall appearance of the two spectra show that gallium and iron behave in a very similar manner. The kinetics in the case of iron is much faster, however; the tetrahedral (Fe–O)$_{T_d}$ band disappeared if the hydrolysed solution was allowed to age for more than a few seconds before the sulfate solution was added, even when all of the solutions were cooled in ice. This suggests that a tridecamer is formed upon the hydrolysis of iron(III) salt solutions, but that it is extremely unstable and very quickly decomposes. The major difference seen between the spectra of the gallium and iron(III) sulfate salts was the degree of splitting of the $\nu_3(SO_4^{2-})$ bands, indicating differences in structural arrangements between the polyoxocations and the sulfate groups.

Clay Mineral Pillaring Studies utilizing Hydrolysed Iron Solutions.—Iron-pillared clays have been reported in the literature, however they have not been prepared by using polyoxocations made through iron(III) hydrolysis as pillars. Attempts to do this have seemingly failed.[55,56] The predominant approach that has been taken has been to intercalate trinuclear acetatohydroxoiron(III) ions $\{[Fe_3(OCOCH_3)_7(OH)]NO_3\}$ followed by calcination to iron oxide pillars.[57–60]

Hydrolysed Iron(III) *Solutions.*—Pillaring studies were undertaken for iron(III) perchlorate solutions that had been hydrolysed to $OH^-:Fe^{3+}$ mole ratios of *ca.* 2.25:1. The solutions were used as rapidly as possible, but regardless there was a fair time lag involved in terms of how fast the clay suspension could be added to the hydrolysed solution (or *vice versa*), as well as how fast the solutions of the pillar interlayered clay minerals could be washed by centrifugation. In the case of Ga_{13} the stability of the pillar interlayered clay minerals in solution was much less than those of Al_{13}; degeneration to a chloritic type of phase occurred quite rapidly.[45] As the proposed Fe_{13} ion appeared to have an extremely poor thermal stability in comparison to the Ga_{13} ion, it would seem likely that this instability for the pillared clay minerals in solution would be paralleled.

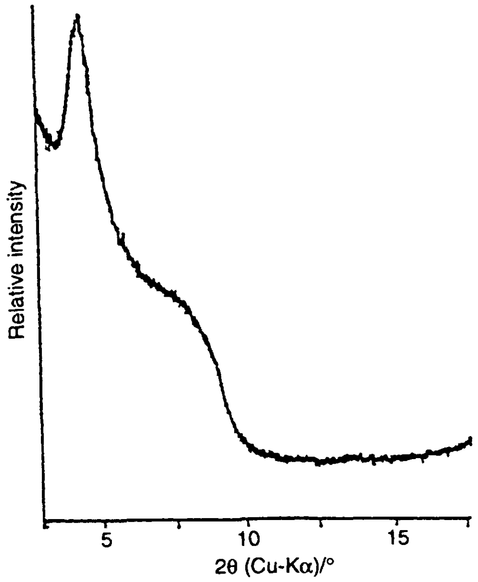

Fig. 5 Powder XRD pattern for Fe^{II}/Fe^{III}-pillared montmorillonite

Regardless of the pillaring technique, degree of loading, rate of addition of solutions, rate of aging of iron(III) solutions, *etc*., the final iron(III) material had d_{001} basal spacings of *ca*. 14.5–15.0 Å. This meant that there had either not been an Fe_{13} ion intercalated, or if there had been, decomposition had occurred too rapidly to allow its detection by XRD studies.

Hydrolysed Iron(II)*-doped Iron*(III) *Solutions*.—The studies[41] by Jolivet *et al*. of the hydrolysis of iron(III) solutions doped with varying amounts of Fe^{II} showed that the addition of small amounts (< 10%) had the effect of creating spinel particles in addition to goethite [α-FeO(OH)·H_2O], upon hydrolysis to a OH^- : Fe ratio of 3 : 1. These spinel particles were observed to transform to goethite fairly rapidly, however. For higher iron(II) contents only spinel particles were formed, and they did not undergo subsequent phase transformation.[41] These results suggest that if Fe_{13} polyoxocations could form upon the hydrolysis of iron(III) solutions, but were extremely unstable and quickly decomposed, then the addition of very small amounts of Fe^{II} might serve to stabilize the tridecameric unit somewhat. Addition of too large amounts, however, could complicate matters by causing the tridecamers formed to coalesce and thereby form a spinel phase. For these reasons, pillaring studies involving varying degrees of iron(II) loading were undertaken.

Iron(III) chloride solutions were combined with varying percentages (mole basis) of iron(II) chloride, hydrolysed to an OH^-:(Fe^{II} + Fe^{III}) mole ratio of 2.25:1, and then used as pillaring solutions. All of the solutions were cooled in an ice-bath throughout the procedures. Montmorillonite suspensions (1–2% w/w) were added dropwise to the hydrolysed solutions until loadings of about 10 milliequivalents per g had been achieved. These pillar interlayered clay mineral sols were then washed five times by centrifugation, and subsequently air dried. The timing of all the steps in this process was critical, and the results varied substantially as a function of this. The resulting pillared material in some cases, however, exhibited XRD patterns having d_{001} spacings of between 19.2 and 19.6 Å (Fig. 5). This was virtually identical to the spacing of the Ga_{13} pillared materials,[61,62] and reinforced the hypothesis that Fe_{13} ions could be formed. This occurred only in cases where the iron(II) content was 2–3 mol %, and when all steps involved were carried out very rapidly. In all other cases lower d_{001} spacings were observed, typically about 14.5–15.0 Å, essentially the same as observed for the iron(III) system.

Infrared investigations were also attempted for salts of these mixed-valence iron polyoxocations, however the combination of Fe^{II} and Fe^{III} produced only a very broad band at low wavenumbers, and thus no co-ordination numbers could be assigned for the Fe^{III} *versus* Fe^{II}.

Conclusion

Gallium-71 MAS NMR and powder X-ray diffraction studies of sulfate salts prepared using hydrolysed gallium(III) solutions are reported for the first time, and they confirm that the rather unstable $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion which is known to form in solution can also exist in the solid state. The sulfate crystals were not well crystallized, however, and a gallium alunite phase was always present. The infrared spectra of these sulfate salts contain two strong bands between 250 and 800 cm^{-1}; one of these was assigned to a $(Ga–O)_{T_d}$ asymmetric stretch, and the second is thought to be due to a $(Ga–OH)_{O_h}$ stretch. In addition, a broad band which could be due to the gallium alunite, or $[H_3O][Ga_3(OH)_6(SO_4)_2]$, phase that was also known to be present underlies the two peaks.

Infrared spectra of the sulfate salts of freshly prepared, base-hydrolysed iron(III) perchlorate solutions were virtually identical to those for the gallium system, indicating that similar species must be present, and suggesting that Fe_{13} ions had indeed been formed. These ions were found, however, to have extremely short lifetimes in solution, much shorter than the Ga_{13} ions, which in turn are far less stable than the Al_{13} ions. Clay mineral pillaring studies that utilized these hydrolysed iron(III) solutions as intercalant did not reveal a d_{001} basal spacing of *ca*. 19.2–19.6 Å, as did the hydrolysed gallium(III) solutions. This is probably due to the iron species decomposing during the pillaring procedure. Interestingly, when iron(III) solutions were doped with *ca*. 2–3 mol % Fe^{II} and then hydrolysed the clay mineral intercalates did in some cases have basal spacings of *ca*. 19.3 Å, supporting the view that $[FeO_4Fe_{12}(OH)_{24}(H_2O)_{12}]^{x+}$ ions of mixed valence had formed. Such a tridecamer would probably have an 'inverse' structure in which the Fe^{III} rather than the larger Fe^{II} would sit in the central tetrahedral position, as occurs in the Fe_3O_4 spinel (magnetite).

These results therefore suggest very strongly that analogous Fe_{13} and Ga_{13} species form upon the base hydrolyses of aqueous iron(III) and gallium(III) solutions. However, it is also clear that the proposed Fe_{13} species has not been unambiguously characterized. Unfortunately the difficulties that would have to be overcome to do so would be formidable. There does not seem to be, at present, any method of proving their existence other than the structure refinements of single crystals of their salts, and as discussed herein such crystals have not yet been formed.

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