Aluminium-27 Nuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 5.[1] Slow Hydrolysis using Aluminium Metal

By **J. W. Akitt** * and **Alan Farthing**, The School of Chemistry, The University of Leeds, Leeds LS2 9JT

Aluminium-27 n.m.r. spectra are presented of solutions prepared by the relatively slow hydrolysis of $AlCl_3$ solutions with aluminium metal in the presence of mercury. The ways in which the spectra change with temperature or concentration are described and changes are also noted to occur as a function of magnetic field strength. It is not possible to give an unequivocal answer as to what is the nature of the species present in these solutions but there seem to be a variety of ions present which are quite easily interconvertible, contain octahedrally co-ordinated Al, and are associated in some way with fragments which resemble $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}) since some tetrahedrally co-ordinated Al always seems to be present. Thus it is suggested that structures may consist of partial Al_{13} units with octahedral units disposed as flexible chains and/or forming cross links.

We have shown in the previous paper[1] that rapid hydrolysis or hydrolysis at lower temperature appears to proceed *via* a series of equilibria which are attained relatively quickly and involve only three species [equation (1)], but that the final product, which we call

$$[Al(OH_2)_6]^{3+} \rightleftharpoons [Al_2(OH)_2(OH_2)_8]^{4+} \rightleftharpoons [AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+} \quad (1)$$

Al_{13}, is unstable in the still acidic medium and can undergo slow transformation, probably by a variety of pathways, to form other species. This conclusion explains why, in an early phase of this work,[2] we found that the use of different hydrolysing reagents gave solutions with very different ^{27}Al n.m.r. spectra. Different reagents take different times for complete reaction so that the resulting spectra are related to different stages of the later transformation reactions. The precise nature of the species formed in these reactions, if definable, is of interest since aluminium-containing minerals form a major part of the environment and processes such as weathering to form soils may well involve similar species. We have therefore studied one of the reactions in some detail and have chosen the reaction between aluminium metal and, principally, aluminium chloride solution since this produces solutions which contain no interfering cations and are closely related to solutions produced commercially (though by methods which are not in fact divulged by the manufacturers) which are used to manufacture refractory alumina fibres and as underarm deodorants, and so are of a general and personal interest.

EXPERIMENTAL

Hydrolysis with aluminium metal seems to be best performed on the laboratory scale by adding aluminium wire (AR) to refluxing aqueous $AlCl_3$ solution to which a few drops of mercury have been added. It is important to add the metal in some 10 approximately equal portions, waiting until one has almost completely dissolved before the next is added. If this is not done an insoluble precipitate and/or colloidal suspension may form and the stoicheiometry of the resulting solution is then uncertain. The given procedure produces a solution which contains very little particulate or colloidal material although sufficient may be present for the solution to appear hazy. If mercury is not added, the hydrolysis becomes very prolonged. If metal foil is used instead of wire, the reaction is much faster and can be made to go at lower temperatures. On the other hand, attempts to use powdered metal failed as there seem to be wetting problems and reaction does not occur. Some hydrolyses were performed with other AlX_3 salts to study anion effects ($X = ClO_4^-$, Br^-, NO_3^-, and $\frac{1}{2}SO_4^{2-}$).

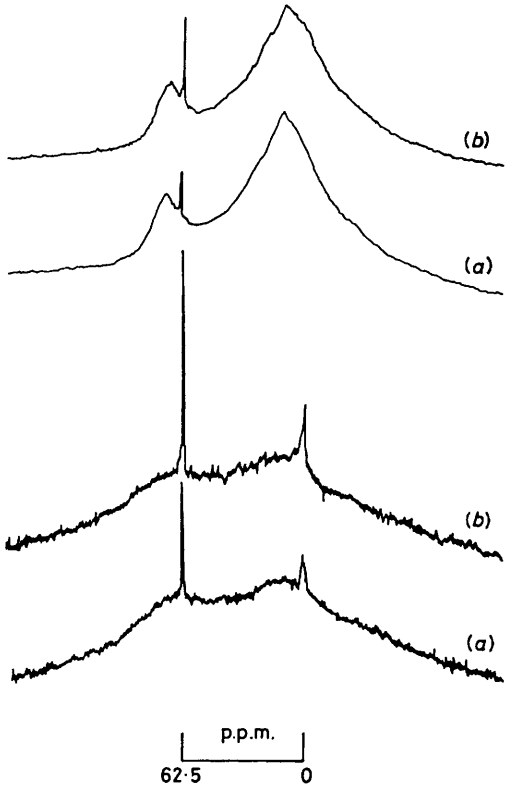

FIGURE 1 The ^{27}Al n.m.r. spectra at 23.45 MHz and 27 °C (lower pair) or 77 °C (upper pair) of solutions hydrolysed to $m = 2.5$ with (*a*) AR wire and (*b*) GPR foil, all 1 mol dm^{-3} in Al. The sharp resonance on the right (high field) is due to $[Al(OH_2)_6]^{3+}$ at 0 p.p.m. and that on the left is due to the AlO_4 central unit in Al_{13} and is situated at 62.5 p.p.m.

Such solutions were hydrolysed to different values of m (m = OH added/Al present, which in this case is equal to

$3Y/(1 + Y)$ where Y is the moles of Al dissolved per mole of AlX_3) and were examined by ^{27}Al n.m.r. at 27 and *ca.* 80 °C over a period of two years after storage under a variety of conditions. Spectra were obtained mainly at 23.45 MHz as described previously,[1] although the resonances were in general broad and the baseline was often difficult to locate so that quantitative data could not be obtained with the same accuracy. Some improvement was obtained by printing out the first 40 or so data points of the free induction decay (FID) and extrapolating the peak-to-peak amplitude excursion to zero time using a combination of sinewave fitting and inspection. The amplitude so obtained could be compared with that of a resonance from a standard solution containing only $[Al(OH_2)_6]^{3+}$. Where the spectrum consisted of a single predominant resonance this technique gave results which were reproducible to within 5%. Where two overlapping resonances were present, it was not possible to detect modulation of the FID envelope and the error in such cases is likely to be much greater and perhaps also dependent on the spectrometer phase setting at a particular time, although it was usually possible to account for 80—90% of the aluminium present. Some spectra were also obtained at 62.86 MHz on a CAMECA instrument and at 104.23 MHz on a Bruker WH 400.

RESULTS

Typical spectra of hydrolysed aluminium solutions with $m = 2.5$ are shown in Figures 1, 2, and 3, the latter two

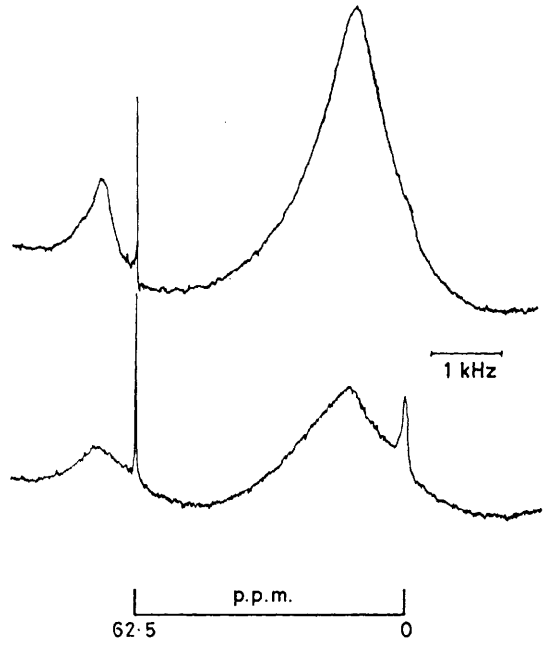

FIGURE 2 The ^{27}Al n.m.r. spectra at 62.86 MHz and 27 °C (lower) or 77 °C (upper) of a solution 1 mol dm^{-3} in Al hydrolysed to $m = 2.5$ with AR wire

sets being obtained at high fields. The spectra are very temperature dependent. It is immediately obvious that they contain four visible resonances: one narrow one due to $[Al(OH_2)_6]^{3+}$ at 0 p.p.m. which broadens due to exchange with $[Al_2(OH)_2]^{4+}$ at the higher temperatures; one narrow one due to the AlO_4 unit in Al_{13} at 62.5 p.p.m.; one broad one due to octahedrally co-ordinated Al, and one broad one due to tetrahedrally co-ordinated Al. The broad resonances contain the majority of the intensity. Up to 90% of the aluminium is visible at 27 °C and probably all can be seen at 80 °C.*

We also found that the form of these spectra was very concentration dependent. Samples were made up with different aluminium concentrations and the resulting high-temperature spectra are shown in Figure 4. The features to

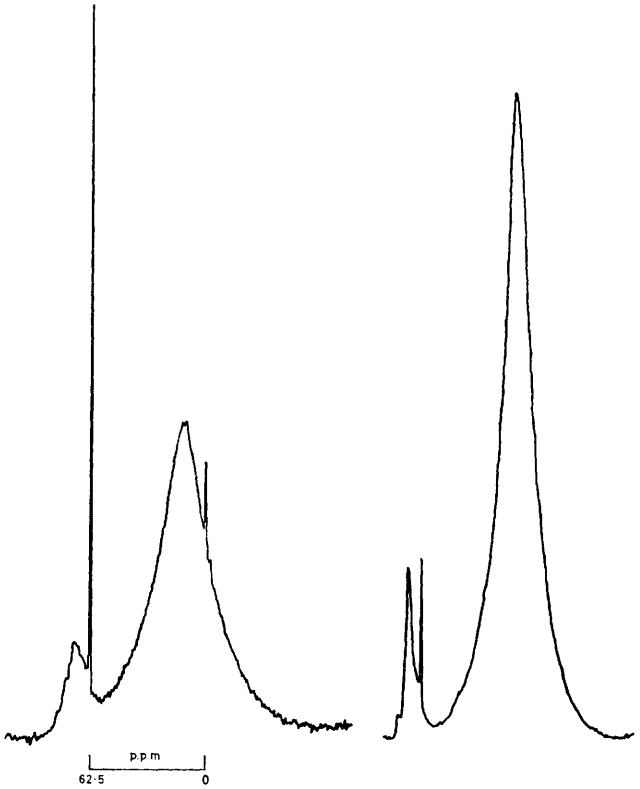

FIGURE 3 The ^{27}Al n.m.r. spectra at 104.23 MHz and 27 °C (left) and 77 °C (right) of a solution hydrolysed to $m = 2.5$ with AR wire. It is of interest that this solution was prepared at a different time and by a different operator to that shown in Figure 1 and the variability of the Al_{13} content should be noted. The scale is the same for both spectra

note here are that as the concentration is increased the broad resonance in the tetrahedral region changes little in intensity, Al_{13} is reduced in intensity, and the resonance in the octahedral region increases in intensity, changes in shape, and suffers a chemical shift. The overall signal intensity seems proportional to concentration up to about 1.5 mol dm^{-3} and the rate of increase falls off thereafter, only 30% of the Al being visible in the 5 mol dm^{-3} solution. The changes noted are reversible on dilution. One solution was also examined at high concentration (obtained by evaporation under vacuum) and high field. The spectra were somewhat different in form and the octahedral region was resolved into two components although, as in the previous preparation, much aluminium was not visible. These results are summarised quantitatively in the Table.

Anion Effects.—Aluminium bromide and perchlorate

* It is worth noting that these spectra provide an object example of the dangers inherent in curve-fitting. The 23.45-MHz spectra can be fitted very satisfactorily for their noise level on the basis of two almost equal broad components, whereas the high-field spectra show that this is an entirely erroneous solution.

solutions can be hydrolysed to $m = 2.5$ and have the same spectrum as the chloride solution. Aluminium nitrate can only be hydrolysed to $m = 1.5$ when reaction ceases. The

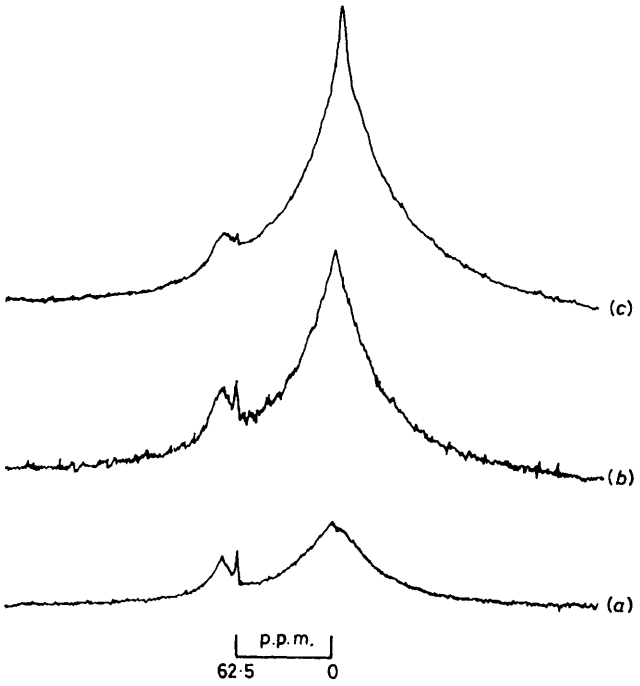

FIGURE 4 The ^{27}Al n.m.r. spectra at 23.45 MHz and 77 °C of solutions hydrolysed to $m = 2.5$ at the total Al concentrations (*a*) 1, (*b*) 3, and (*c*) 5 mol dm^{-3}

spectrum of the resulting solution was markedly different from that of the others, although a broad resonance of low intensity indicative of the presence of tetrahedral aluminium was observed. A solution of the nitrate can however be prepared either with $m = 2.4$ using the organic phase hydrolysis [3] or with $m = 2.5$ by dissolving freshly precipitated aluminium hydroxide in aluminium nitrate solution, although the latter is not a clean preparation on the laboratory scale. Attempted hydrolysis of an aluminium sulphate solution gives much precipitate and the solutions obtained continue to precipitate solid on standing. Sulphate anion is of course known to complex Al^{3+} and is also a good reagent for preparing crystalline products of Al_{13} and $[Al_2(OH)_2(OH_2)_8]^{4+}$ so that it cannot be regarded as inert.[4-6] No resonances other than those of $[Al(OH_2)_6]^{3+}$ and of the sulphate complex could be observed, although any broad resonances would of course be masked by these intense and narrow ones. One solution was produced with the composition $Al(OH)_{1.6}(SO_4)_{0.7}$ and *ca.* 1 mol dm^{-3} in Al which had the unusual property of producing a precipitate on heating which re-dissolved on cooling, a type of behaviour which had been observed in the very early days.[7]

Temperature of Hydrolysis.—It was found possible to carry out hydrolyses with aluminium metal at much lower temperatures than with $Na_2[CO_3]$, where the high temperature seems to be essential to allow rapid re-dissolution of the $Al[OH]_3$ initially formed and before this is converted spontaneously into insoluble forms. The reaction rate was increased by using metal foil and solutions with [Al] = 1 mol dm^{-3}, $m = 2.5$ were made at temperatures as low as 40 °C. The proportion of Al_{13} increased as the temperature of preparation was lowered and attained 70% of the total Al below 60 °C. Such solutions resembled those hydrolysed with $Na_2[CO_3]$ in that the remaining Al was undetectable and that prolonged heating caused the same general changes to occur.[1] Addition of a small quantity of $Na_2[SO_4]$ solution to a fresh preparation (see below) gave needle-like crystals of Al_{13} sulphate which differed from any we had produced previously. Normally $Na_2[CO_3]$-hydrolysed solutions give tetrahedral crystals containing the cations $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ and Na^+,[5] and these can be recrystallised to give plates containing only the cation, Al_{13}^{6+}. Assay of the needles was consistent with the presence of '$Al_{13}^{5.5+}$.' Weissenberg photographs showed that the unit cell was closely similar to that of Al_{13}^{6+} but was disordered in one dimension. This might indicate the loss of some protons and the presence of extra hydrogen bonding between Al_{13} units in these crystals and may be related to spontaneous changes in cell dimensions observed by Johannson.[6]

Crystallisation from Hydrolysed Solutions.—In order to attempt to identify the species present in these solutions it would be of obvious interest to prepare solid or crystalline materials which could be examined by analysis or *X*-ray

Summary of the ^{27}Al n.m.r. results

Spectrometer frequency/ MHz	Temp./°C	Concentration/ mol dm^{-3}	Chemical shifts/ p.p.m.		Linewidths [a]/ Hz		Ratio $\frac{\text{(octahedral Al)}}{\text{(tetrahedral Al)}}$ [b]
			tetrahedral	octahedral	tetrahedral	octahedral	
23.45	27	1	70.0	11.3		1 800 [c]	4 (estimated)
	77	1	70.2	12.0	360	1 360	13
	77	3	69.8	11.3	320	880	12
	77	5	69.8	6.5	300	760	27
62.86	27	1	71.4	6.0, 12.4 [d]	760	2 300	8.3
	77	1	71.2	12.0	490	1 550	8.6
	27	6	71.0	7.2, 12.0 [d]	(?)	1 600	
	77	6	71.2	12.2	800	1 200	
104.23	30	1	71.7	11.6	1 330	3 328	8.5
	80	1	69.7, 75.3 [e]	10.7	456	1 840	14.9

[a] Results ±20% except for 104-MHz spectra which are ±10%. [b] This ratio may also be dependent upon magnetic field strength. It is in any case very sensitive to small errors in determining the area of the tetrahedral resonance, and so to the placement of the baseline level. [c] Estimated from high-field half of the line and very approximate. [d] Doublet. [e] Small component at 75.3 p.p.m.

diffraction. A large number of possible reagents were investigated but the only one which was found to give solid products was sodium sulphate, which gave an amorphous but separable precipitate in good yield. Partial crystallisation was tried in an attempt to effect a separation but the substances which precipitated always had very similar compositions with m close to 2.52 and the ratio $[Al]/[SO_4]$ = 4.22. This should be compared with the values for Al_{13}^{6+} sulphate, namely 2.54 and 4.33. Excess of sodium sulphate solution caused the precipitates to re-dissolve although most of the Al was not then detectable by n.m.r. The composition of the precipitates is obviously close to that of an Al_{13} salt and is similar to that of felsöbanyite.[8-12] An X-ray powder pattern did contain lines observed for the latter mineral but these were much fainter than other intense lines of unknown origin which were present.

Other Methods of Hydrolysis.—Those which we have already reported [2] all give spectra which differ from one another and from those described here, although they all exhibit the same broad features to a greater or lesser degree. It is worth noting however that some commercially produced oxychlorides have the property that no Al_{13} is detectable in a freshly made solution at 27 °C but that its resonance appears if the solution is heated to *ca.* 80 °C and then remains when the solution is allowed to cool, although it slowly decays in intensity and eventually disappears. The spectra of commercially produced oxychlorides are also very sensitive to concentration and some have an additional resonance in their spectra 45 p.p.m. to high field of $[Al(OH_2)_6]^{3+}$ which is evident in the 62.86-MHz spectra. Such solutions invariably form glass-like solids on standing. They obviously contain another species of ion which must differ substantially from anything that we have *observed* in our laboratory preparations and which can affect the ageing properties of the solutions containing them.

Long Term Storage of Oxychloride Solutions.—Concentrated solutions (*ca.* 5 mol dm^{-3}) of oxychlorides such as are described here may remain stable and fluid apparently indefinitely, *i.e.* for at least the three years covering the period of these studies, and their n.m.r. spectra will be unchanged during this time. Others may throw down a precipitate with an accompanying increase in the intensity of the $[Al(OH_2)_6]^{3+}$ resonance. Others may remain clear but increase in viscosity to become thick, barely pourable syrups or even solid glasses. With the one exception noted above, we have not been able to relate these changes to any preparative or spectroscopic feature. We have however found it possible to obtain ^{27}Al n.m.r. spectra of the viscous solutions. The increase in viscosity does cause much of the aluminium resonance to broaden to the point where it cannot be detected but some 20% can still be observed even in samples which have set to a glass in the n.m.r. sample tube. These spectra do not seem to change with age once sufficient time has elapsed. We thus appear to be observing cationic aluminium species which are still mobile and so must exist within a less mobile and presumably cross-linked network which provides the viscous framework and which can become more rigid with time.

DISCUSSION

The spectra described here obviously contain a wealth of information about the species present in these solutions although it is not at present possible to interpret them in terms of structure. However, as we shall show, some idea of the sort of material present can be obtained. The broad intense resonance in the octahedral region must almost certainly contain several components. At the higher temperatures used and [Al] = 1 mol dm^{-3} the linewidth of this band increases with increasing magnetic field strength at a rate which would be consistent with the presence of two broad overlapping components *ca.* 6 p.p.m. apart. The rate of increase appears to be much greater at ambient temperature, although its value is less certain because of the overlap in the 23.45-MHz spectra. The resonances here appear to be 12—18 p.p.m. apart. Thus either the shift is temperature dependent or one component is not visible at higher temperature, although this latter suggestion is not in accord with the observation that the intensity increases rather than decreases with temperature. However, we have seen a resonance of 7 p.p.m. which decreases in intensity with temperature in some samples, particularly commercially produced ones. The results can best be rationalised if we assume that one component broadens and disappears due to exchange and lends its intensity to another portion of the spectrum. The Al_{13} component of course provides more intensity in the octahedral region at high temperature [2] although this forms a relatively small portion of these spectra and

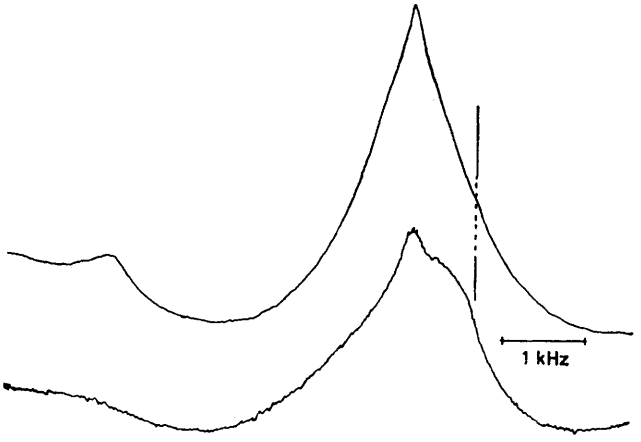

FIGURE 5 The ^{27}Al n.m.r. spectra at 62.86 MHz and 27 °C (lower) and 77 °C (upper) of the solution used to obtain Figure 2, but concentrated to [Al] = 6 mol dm^{-3} over P_2O_5. The vertical line is at 0 p.p.m.

should not discernably affect the results. There is no reason, however, why another component should not be present which behaves in a similar way and indeed this must explain the increase in the ratio (octahedral Al)/(tetrahedral Al) with temperature.

Increasing the concentration produces marked changes in the spectra, a change in chemical shift, a change in area, and a change in lineshape, all in the ' octahedral ' region. The super-Lorenzian line shape suggests that we have two components with the same chemical shift but different linewidth. The chemical shift change suggests that in addition a line with intensity at low concentration broadens beyond the limit of detection

when the concentration is increased. Thus some of the material present is restricted considerably in its motion as the concentration is increased or perhaps is subject to aggregation.

This evidence taken together seems to us to indicate the presence of at least four components in the octahedral region, excluding Al_{13}.

These arguments do of course assume that the extreme-narrowing condition is met in these spectra. The fact that the lines narrow with increasing temperature supports such an assumption. However, in the case of the larger molecules we might in fact be seeing the emergence of more complex relaxation behaviour, involving for ^{27}Al ($I = \frac{5}{2}$) three exponential rates of decay,[13] which should become important when $\tau_0 \sim 1/\omega_0$ and therefore at the higher magnetic fields used.

On the other hand, the broad resonance in the tetrahedral region is probably a singlet or at least consists of one dominant line. In order that tetrahedral Al should exist at all in these acidic solutions it is probably necessary that the AlO_4 units be surrounded by a protective shell of octahedrally co-ordinated Al, although perhaps this shell need not be so complete as in Al_{13}. The implication is that a species is present which is Al_{13}-like in structure. A possible candidate would be an ion like $[Al_2W_{18}O_{62}]^{10-}$ whose likely ^{27}Al n.m.r. spectrum we have already described,[14] or in other words an $(AlO_4)_2$-$Al_{18}O_{48}$ type of structure,* although the spectra are too complex for this to be the sole product and its octahedral Al might not be visible at 25 °C. The gel permeation chromatography (g.p.c.) results [15] show that the larger polymers cannot be a great deal larger than Al_{13}. At the same time Al_{13} has a very broad octahedral resonance; and in order to reconcile narrowed resonances with larger size we have to assume either that the larger structures are less distorted and therefore perhaps more relaxed or that parts of them are very mobile, a conclusion which could explain the exchange related features noted above. The several spectral components are not separated by g.p.c. and so must have similar sizes, and therefore a variety of structures. We have also shown [16] that although some of the material in these solutions decomposes rapidly if excess of acid is added it is much more stable than Al_{13} in the presence of small quantities of acid. Thus these slower reacting species, if Al_{13}-like, must be protected in some way. One can envisage an Al_{13} unit opening partially and then losing the attacking protons again by adding on $[Al(OH_2)_6]^{3+}$ or $[Al_2(OH)_2]^{4+}$ units more or less at random to give a larger, more open and relaxed structure containing AlO_4 units in varying proportion, and tending to the hexagonal arrangement demanded by Gibbsite. Such a scheme equally allows the condensation of Al_{13} fragments to give a family of structures of which the $Al_{20}O_{56}$ skeleton is only one particularly symmetrical example. That the various structures proposed may be easily interconvertible can be realised by unfolding a model of Al_{13} made with cardboard octahedra to find that this produces directly the backbone of the alunite structure.[17,18]

In conclusion, the outcome of this section of the work is relatively disappointing although it must be pointed out that the system does in principle seem to be resolvable. Higher magnetic fields alone will not do this, although they have proved invaluable here, and other new methods need to be brought to bear in concert with ^{27}Al n.m.r.

* This formulation avoids the single OH bridges required by the Keggin structure.

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