Metal Substitution in Keggin-Type Tridecameric Aluminum−Oxo−Hydroxy Clusters

Wallace O'Neil Parker, Jr.,* Roberto Millini, and Imre Kiricsi†

Department of Physical Chemistry, Eniricerche S.p.A., 20097 San Donato (MI), Italy

Received May 29, 1996[⊗]

The species resulting from a typical preparation for metal-substituted hybrids of the Keggin tridecamer, Al_{13} or $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, were examined by performing ^{27}Al NMR on the solutions during aging and by studying the precipitated sulfate salts via solid state ^{27}Al NMR and powder X-ray diffraction (XRD). Aqueous mixtures (0.25 mol L^{-1}) of $AlCl_3$ and another metal ion (M), in a 12:1 mole ratio (Al:M), where M = Fe^{3+}, Zn^{2+}, Ga^{3+}, In^{3+}, Sn^{2+}, La^{3+}, and Bi^{3+}, were subjected to forced hydrolysis by addition of NaOH (1.0 mol L^{-1}) until OH/(Al + M) = 2.25, and the kinetics of Al_{13} formation and disappearance with aging at 80 °C was monitored by ^{27}Al NMR spectroscopy. Al_{13} units polymerize on aging with an apparent rate constant (k) of $4.8(8) \times 10^{-2}$ h^{-1} to form a species referred to as AlP_2. Only the solutions containing Ga^{3+} and Sn^{2+} exhibited faster Al_{13} conversion rates. $GaAl_{12}$ forms quickly at 80 °C (k = 0.54 h^{-1}) and is more stable than AlP_2. Sn^{2+} apparently promotes AlP_2 formation (k = 0.38 h^{-1}). XRD and solid state NMR reveal that only the Ga hybrid can be prepared by this method. No hybrid formation was evidenced using M = Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, In^{3+}, La^{3+}, or Ce^{3+} at 25 °C or M = Co^{2+} or La^{3+} under reflux conditions. Isostructural (cubic symmetry) single crystals were obtained for the sulfate salts of Al_{13} and $GaAl_{12}$. Single-crystal XRD analysis of these two polyoxocations provides the first rigorous comparison between them and shows they have very similar structures. The main crystallographic data for Al_{13} and $GaAl_{12}$ are as follows: $Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot 10H_2O$, cubic, $F\bar{4}3m$, a = 17.856(2) Å, Z = 4; $Na[GaO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot 10H_2O$, cubic, $F\bar{4}3m$, a = 17.869(3) Å, Z = 4. Thus, the greater thermal stability of $GaAl_{12}$ cannot be rationalized in terms of the overall geometric considerations, as suggested by others. Solid state NMR also shows the coordination symmetries of the outer 12 Al nuclei in both clusters to be similar.

Introduction

Recently, great interest has developed for the Keggin-type aluminum polyoxocation $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, hereafter referred to as Al_{13}, as a pillaring agent to produce PILCs (pillar interlayered clays).[1] Due to its low thermal stability, Al_{13} is not an ideal pillar since industrially used PILC catalysts need frequent regeneration.

Poor thermal stability has been suggested to correlate with cluster structure.[2,3] Al_{13} has a central Al atom surrounded by twelve edge-sharing (AlO_6) octahedra. The central tetrahedral Al atom is smaller than the cavity formed by the outer Al nuclei. Thermal stability might be increased by substituting the central Al atom with a larger metal atom to reduce the distortions of the surrounding octahedra (we will refer to these isomorphously substituted polyoxocations as Keggin hybrids). The incorporation of many different metal ions (M = La^{3+}, Mg^{2+}, and all the transition metals) into the Keggin ion has been claimed. Usually there is no distinction between which type of Al substitution occurs (tetrahedral or octahedral). In our view, convincing physical evidence for MAl_{12} hybrids has been reported only in the case of Ga^{3+}.[2−5] The reports of V^{3+} ions,[6] Fe^{3+},[7−9] Re^{3+} ions,[10] La^{3+},[11] and the transition M in general[12] are based on chemical rather than structural analyses. Workers generally characterize the PILCs rather than the pillars.

Typical substitution schemes involve thermal treatments of aqueous solutions of the mixed metal salts under hydrolysis conditions. Even without substitution, Al_{13} is converted to other (more thermally stable) species. This means that in many PILC syntheses, Al_{13} is a minor species or totally absent.[13−15] Usually it is the hydrolyzed analog of Al_{13} that serves as the initial pillaring agent.[16] Recently, Nazar and co-workers[17,18] identified the initial thermal decomposition product of Al_{13} as AlP_2, thought to be formed by condensation of two Keggin ions that have each lost a monomer ($Al_{24}O_{72}$). This higher molecular

† Present address: Jozsef Attila Univ., H-6720 Szeged, Rerrich B.t. 1, Hungary.

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

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S0020-1669(96)00635-0 CCC: $14.00

weight species (referred to as AlP_2) provides PILCs that are more hydrothermally stable than those pillared with Al_{13}.[19,20]

The lack of physical−chemical evidence for the M−Al Keggin hybrids claimed in the literature prompted us to propose an indirect solution state ^{27}Al NMR method for indicating if isomorphous substitution occurs.[21a] Hydrolysis (OH/Al = 2.25) of 0.25 mol L^{-1} $AlCl_3$ solutions at 80 °C provided convenient conditions for following the transformations, as Al^{3+} is converted to Al_{13} and then to AlP_2. Unfortunately, direct methods for verifying M−Al hybrids via NMR of the M nuclei (many being paramagnetic) are not practical. Recently, we investigated the incorporation of Fe^{3+} and Cr^{3+} ions using Mossbauer and ^{27}Al NMR spectroscopy and concluded that no isomorphous substitution occurs in the tetrahedral or octahedral positions of Al_{13} Keggin ions.[21b−e] Here, the solution state NMR method is combined with the direct solid state analysis of the precipitated products (powder XRD and ^{27}Al NMR) to verify if M−Al Keggin hybrids more stable than Al_{13} (or AlP_2) are formed. PILC stability is dependent on the stability of the pillaring agent.[22,23] Thus, only metal polyoxocations with greater stability than Al_{13} are of interest. This report accounts a multidisciplinary search for these M−Al cations using the most commonly cited M in the literature.

We must stress the following. There is no doubt that mixed oxide pillared clays, as synthesized using literature methods, can exhibit excellent catalytic properties. However, there is considerable doubt about the isomorphous substitutions of different metal ions into the Al_{13} Keggin ions.

Experimental Section

Partial forced hydrolysis, with 1.0 mol L^{-1} NaOH, of the aqueous metal halide solutions (initially 0.25 mol L^{-1}) was performed at 25 °C as previously reported .[21a] The 80 °C aged solutions (ca. 1 L) were kept in volumetric flasks in an oven, and 2 mL aliquots were withdrawn at predetermined intervals. These solutions were studied by NMR (at 25 °C where hydrolysis is very slow) within 1 h. The sulfate salts were prepared by adding 0.1 mol L^{-1} Na_2SO_4 to the cooled solution of aged Keggin ions. The pH was maintained at 4.5 by addition of dilute H_2SO_4. After a few days, the crystals formed were filtered and dried in air.

^{27}Al (78.2 MHz), ^{71}Ga (91.5 MHz), and ^{139}La (42.4 MHz) NMR spectra were obtained on a Bruker CXP-300 spectrometer. Solution state spectra were made at 25 °C as previously reported.[21a] Chemical shifts are referenced externally to aqueous solutions (1.0 mol L^{-1}) of $AlCl_3$ and $GaCl_3$ (both 0 ppm) and $La(NO_3)_3$ (2.7 mol L^{-1}, −8.5 ppm). Solid state ^{27}Al NMR spectra were collected on samples contained in 7 mm zirconia rotors using 0.4 μs (π/10) rf pulses and a 2 s recycle delay. MAS (magic angle spinning) spectra are shown in the power mode to give all positive signals.

X-ray powder diffraction (XRD) patterns were collected on a computer-controlled Phillips PW1710 vertical diffractometer equipped with a pulse−height analyzer, variable divergence slits, and a monochromator on the diffracted beam. Data were collected stepwise in the appropriate angular region, using Cu Kα (λ = 1.541 78 Å). Before elaboration, data were converted to fixed divergence slit of 1°.

Single-Crystal X-ray Data Collection and Structure Refinement. Single-crystal X-ray diffraction analyses were performed on a Siemens AED diffractometer, using Mo Kα radiation (λ = 0.710 69 Å). Unit cell dimensions and the crystal orientation matrix were determined by a least-squares fit of the setting angles of 30 strong reflections collected in the range $12 \le \theta \le 17°$. Intensity data were collected with the $\theta/2\theta$ method, with $\theta_{max} = 35°$. One intense reflection was monitored for every 50 reflections collected. Data were corrected for Lorentz and polarization effects. The main crystallographic data are provided in Table 4. The structural model adopted for the refinement of the structures of Al_{13} and $GaAl_{12}$ sulfate salts is that reported by Goerz et al.[4] Refinements were performed anisotropically for all the non-H atoms (48 parameters) with the SHELX-76 computer program.[24] Geometrical data were computed with the program PARST.[25]

$Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot 10H_2O$ (Al_{13}). A colorless regular tetrahedral crystal with an edge dimension of 0.30 mm was used for data collection and structure refinement. A total of 3415 reflections were measured, of which 669 were unique and 454 with $F > 4\sigma(F)$ were considered observed. The (008) reflection, monitored every 50 reflections, showed a 3% intensity decay after total collection. The refinement was performed by considering the cubic $F\bar{4}3m$ space group. A total of 53 parameters, including positional and anisotropic thermal parameters for all non-hydrogen atoms, were refined using full-matrix least-squares techniques. Refinement converged at $R = 0.058$ and $R_w = 0.064$, with $w = 1/[\sigma^2(F) + 0.004737F^2]$.

$Na[GaO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot 10H_2O$ ($GaAl_{12}$). A colorless regular tetrahedral crystal with an edge dimension of 0.25 mm was used for data collection and structure refinement. A total of 3444 reflections were measured, of which 672 were unique and 467 with $F > 4\sigma(F)$ were considered observed. The (222) reflection, monitored every 50 reflections, showed no intensity decay after total collection. The refinement was performed by considering the cubic $F\bar{4}3m$ space group. A total of 53 parameters, including positional and anisotropic thermal parameters for all non-hydrogen atoms, were refined using full-matrix least-squares techniques. Refinement converged at $R = 0.055$ and $R_w = 0.059$, with $w = 1/[\sigma^2(F) + 0.006064F^2]$.

Results and Discussion

^{27}Al NMR studies of aluminum clusters have one major drawback. At lower field strengths, some aluminum nuclei may not be detected. Al nuclei having large quadrupole coupling constants (QCC), as a result of low coordination symmetries, can give signals broadened beyond detection.[13] In the solution state ^{27}Al NMR experiments made here with OH/(Al + M) = 2.25, ca. 60% of the signal area is missing, based on an unhydrolyzed $AlCl_3$ reference solution. A large portion of this NMR-silent Al is part of alumina sol. Solid state ^{27}Al NMR detects nuclei with high QCCs provided that sufficiently large magnetic field strengths are used. A 14 T field strength, double the one used here, is needed to observe signals for ^{27}Al nuclei with QCC = 10.5 MHz,[26] which are representative of some nuclei in this study.

Attempted Synthesis of Al_{13} Hybrids at 25 °C. Initially, the preparation of M−Al hybrids was attempted under mild conditions (OH/(Al + M) = 2.0 to 2.5). Soluble salts of bivalent (Mg, Co, Ni, Cu, Zn) or trivalent (Fe, In, La, Ce) metal ions were used. After the reaction mixtures were stirred overnight at 25 °C, the polyoxocations were precipitated with Na_2SO_4 or Na_2SeO_4 (at pH = 4.5). ^{27}Al NMR of these solutions, before precipitation, showed no evidence of new Al species. Only the spectra of M = Co^{2+} and Cu^{2+} were different, since little or no monomeric $[Al(H_2O)_6]^{3+}$ was detected. These paramagnetic ions apparently interact strongly with free Al^{3+} ions.

The precipitates were characterized by powder XRD and ^{27}Al MAS NMR. There was no evidence of M incorporation. Only Al_{13} was found. The XRD patterns are indexable in the cubic $F\bar{4}3m$ space group, with the unit cell parameter reported in Table

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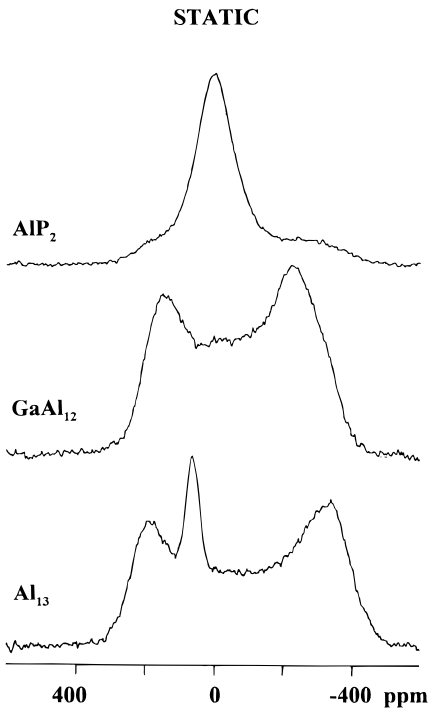

Figure 1. Solid state ^{27}Al static NMR spectra of authentic Al_{13} sulfate, authentic $GaAl_{12}$ sulfate, and AlP_2 sulfate.

Table 1. Unit Cell Parameter for Al_{13} Salts Precipitated from Al + M Solutions

sample	*a* (Å)	sample	*a* (Å)
$Al_{13}-SeO_4$	18.067(6)	$Al_{13}-SeO_4 + Zn$	18.070(8)
$Al_{13}-SeO_4 + Cu$	18.067(7)	$Al_{13}-SeO_4 + La$	18.074(5)
$Al_{13}-SeO_4 + Ni$	18.064(7)	$Al_{13}-SeO_4 + Ce$	18.068(6)
$Al_{13}-SeO_4 + Mg$	18.061(6)	$Al_{13}-SO_4 + La$	17.856(6)
$Al_{13}-SeO_4 + Co$	18.059(8)	$Al_{13}-SO_4 + Ga$	17.859(5)

1. This is well-known for the selenate salt of Al_{13}[27] but is unprecedented for the sulfate salt. In fact, different polymorphic structures of the sulfate salt can be obtained, depending on solution pH. Normally, it tends to crystallize in the monoclinic *P*2/*n* (*Pn*) or *P*2/*a* (*Pa*) space groups, but tetrahedral crystals may be obtained with the cubic $P4_232$ space group. Under our conditions (and in the presence of La^{3+} ions) the sulfate salt of Al_{13} crystallized as large tetrahedral crystals in the cubic $F\bar{4}3m$ space group with $a = 17.856(6)$ Å, isostructural with the selenate salt. Single-crystal XRD of this material (see below) was made to allow a direct structural comparison with other metal-substituted Al_{13} compounds.

Solid state ^{27}Al NMR spectra of authentic Al_{13} (sulfate salt examined by single-crystal XRD) were obtained with the highest field available to us, both static (Figure 1) and with MAS (Figure 2) at the highest spin rates possible. The highly symmetrical T_d-Al of Al_{13} (QCC = 1.2(1) MHz, Table 2) gives a sharp signal near 63 ppm, even under modest NMR conditions.[28] This sharp signal readily distinguishes Al_{13} from other clusters, although broad T_d-Al signals are sometimes mistakenly assigned to Al_{13}.[14,16,29] Our 7 T field strength and 6.5 kHz MAS rate (Figure 2) cannot fully detect the 12 O_h-Al nuclei of Al_{13}, since they have highly distorted coordination symmetries and thus large QCCs.[2,28,30] A QCC of 10.7(1) MHz (Table 2) was obtained from the static spectrum in Figure 1. The large second-order quadrupolar effect gives a broad signal for these O_h-Al (ca. 800 ppm) modulated by spinning sidebands. This MAS spectrum (Figure 2), although it represents only a small part of the O_h-Al nuclei, will be used here as a "fingerprint" to detect eventual modifications of O_h-Al nuclei in Al_{13}.

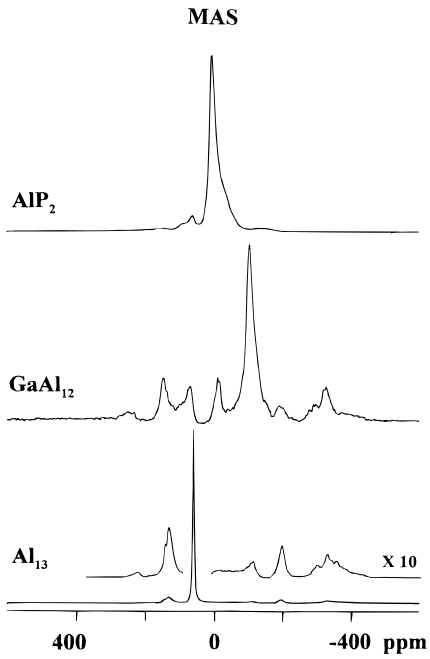

Figure 2. Solid state ^{27}Al MAS NMR spectra (power mode) of authentic Al_{13} sulfate, $GaAl_{12}$ sulfate, and AlP_2 sulfate. Spin rate = 6.5 kHz.

Table 2. Isotropic Chemical Shifts (δ), Quadrupolar Coupling Constants (QCC), and Asymmetry Parameters (η) Calculated by Computer Simulation of Solid State ^{27}Al NMR Spectra for Sulfate Salts of Al_{13}, $GaAl_{12}$, and AlP_2

		T_d-Al			O_h-Al			
		δ (ppm)	QCC (MHz)	η	δ (ppm)	QCC (MHz)	η	ref
Al_{13}	static	70	*a*	0.6	7	10.7	0.1	*b*
	MAS	64	1.2	1				*b*
	MAS	63	0.8		8	10.2	0.2	*c*
$GaAl_{12}$	static				11	9.6	0.2	*b*
AlP_2	static				18.3	4.2	0.6	*b*
	MAS	70	2.2	0		5	0	*d*

[a] Value of 2.6 MHz is found, but this reflects a large dipolar interaction as well. [b] This work, made with WinFit (Bruker) line shape analysis program. Error in fit is ±10% of the value shown. [c] Reference 28, QCC of T_d-Al (error ±25%) from the field dependence of the chemical shift; QCC of O_h-Al (error = ±5%) from simulated static line shape. [d] Reference 18, QCC of T_d-Al from the field dependence of the chemical shift; QCC of O_h-Al estimated from the ratio of solution state line widths.

Attempted Synthesis of Al_{13} Hybrids at 80 °C. All substitution attempts were made directly by partially hydrolyzing (OH/(Al + M) = 2.25) mixed aqueous solutions of $AlCl_3$ and MCl_3 (or NO_3) (Al/M = 12 and total concentration = 0.25 mol L^{-1}). The aging kinetics was followed by solution state ^{27}Al NMR, via the sharp T_d-Al signal intensity of Al_{13} (63 ppm), until all samples contained little or no Al_{13} (ca. 48 h). Since the amount of NMR-silent species actually decreases slightly with time for the solutions shown in Figure 3, Al_{13} disappearance is not attributed to Al sol formation. Thus, Keggin hybrid formation (MAl_{12} or M_{13}) might occur in cases where Al_{13} decay (at 80 °C) is faster than that known for AlP_2 formation. However, both substitution of the central T_d-Al of Al_{13} and polymerization of Al_{13} units (to form AlP_2 or higher species) cause the loss of the 63 ppm signal. Only analysis of the solid

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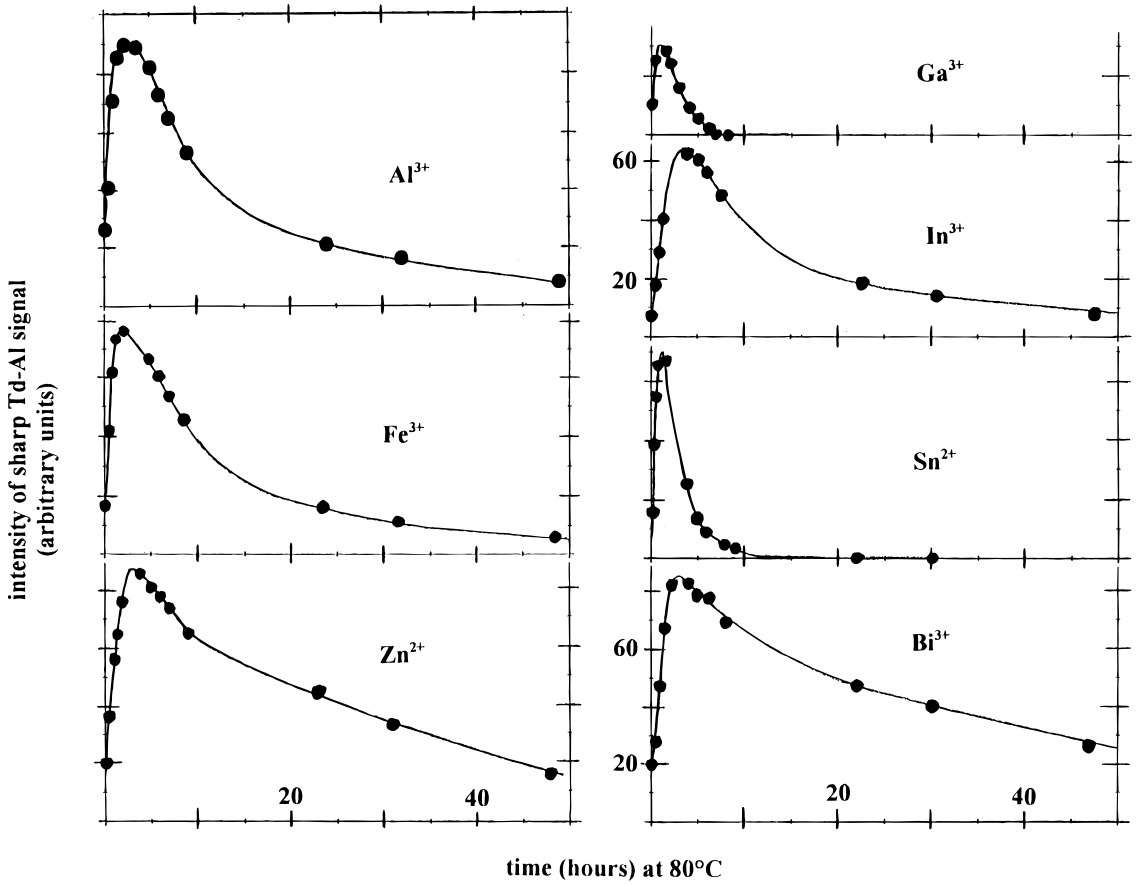

Figure 3. 80 °C aging profiles showing the formation and disappearance of Al_{13} as monitored (at 25 °C) by the intensity of the sharp T_d-Al NMR resonance at 63 ppm.

Table 3. Apparent First-Order Rate Constants (k_{app}) for Disappearance of Al_{13} During Aging of Partially Hydrolyzed Al + M (12:1 Mole Ratio) Solutions at 80 °C (Starting Aqueous $AlCl_3$ Concentration = 0.25 mol L^{-1})

M(aq)	k_{app} ($\times 10^2$ h^{-1})[a]	M(aq)	k_{app} ($\times 10^2$ h^{-1})[a]
$AlCl_3$	4.8(8)	$In(NO_3)_3$	4.8
$FeCl_3$	5.8	$SnCl_2$	38
$ZnCl_2$	3.7	$La(NO_3)_3$	4.1
$Ga(NO_3)_3$	54	$Bi(NO_3)_3$	2.6

[a] Error margin estimated to be ±15% of the value given.

product (XRD, NMR), obtained by precipitation, can permit a distinction between substitution (with M) and conversion (to AlP_2 or other species).

Aging of freshly hydrolyzed $AlCl_3$ at 80 °C, under our reproducible conditions,[21a] causes Al_{13} to be converted to AlP_2 with an apparent first-order rate constant of 4.8(8) × 10^{-2} h^{-1}. This is slightly faster than the rate (0.036 h^{-1}) observed by Nazar and co-workers[17] for a "pure" Al_{13} solution (0.035 mol L^{-1}) aged at 85 °C. Unlike our solutions, which contain all of the hydrolysis products (even NMR-silent Al sol), their solutions contained only Al_{13}.

The time course for Al_{13} formation and the subsequent decay during 80 °C aging of the freshly hydrolyed Al + M solutions is shown in Figure 3 along with that for $AlCl_3$. The profiles for M = La^{3+} (not shown) and most of the M shown are the same as that observed for $AlCl_3$. Al_{13} decay rates are given in Table 3. Only the M = Ga^{3+} and Sn^{2+} solutions exhibited a faster conversion than that for the pure $AlCl_3$ solution. The presence of Bi^{3+} slightly retards conversion.

The solutions with M = Ga^{3+} and La^{3+} were also examined by ^{71}Ga and ^{139}La NMR, respectively. In the case of M = Ga^{3+}, initially there is competition for polyoxocation formation. Al_{13} and $GaAl_{12}$[2] form simultaneously, as seen (Figure 4) by the

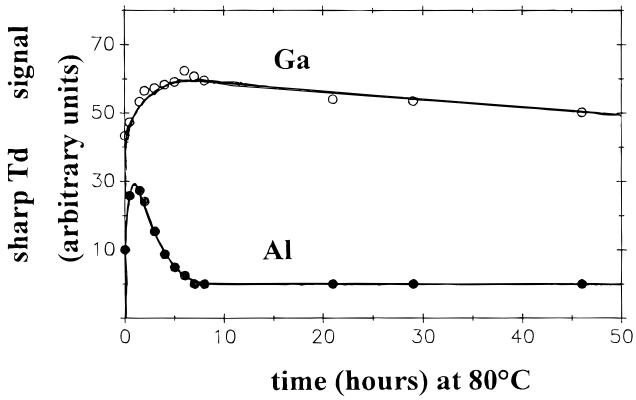

Figure 4. 80 °C aging profiles showing the intensity variations of the sharp ^{27}Al and ^{71}Ga NMR resonances of T_d-Al (63 ppm) and T_d-Ga (137 ppm) with time, for the M = Ga^{3+} solution.

increase in the sharp T_d-Al resonance of Al_{13} (63 ppm) and the sharp T_d-Ga of $GaAl_{12}$ (137 ppm). Within 7 h at 80 °C, all of the Al_{13} was converted to the more stable Ga hybrid, with no AlP_2 formation evident. Slow decay of $GaAl_{12}$ also occurred. No changes in the ^{139}La NMR spectra (shift = 6.9 ppm or area) were observed during the aging of the M = La^{3+} solution. This (and the other observations) confirms that no La incorporation occurs. Substitution with La^{3+} was also attempted under reflux conditions. AlP_2 and $La_2(SO_4)_3$ were the sole products, of the precipitated salts, as evidenced by NMR (^{27}Al, ^{139}La).

AlP_2[17,18] was obtained by refluxing hydrolyzed $AlCl_3$ (OH/Al = 2.25) for 2 days, until complete disappearance of Al_{13}. The ^{27}Al MAS NMR spectrum (Figure 2) contains a broad T_d-Al and a relatively sharp O_h-Al signal, with observed shifts of 60 and 4 ppm, respectively. Clearly, the O_h-Al of AlP_2 have higher symmetry (smaller QCC) than those of Al_{13}, since a

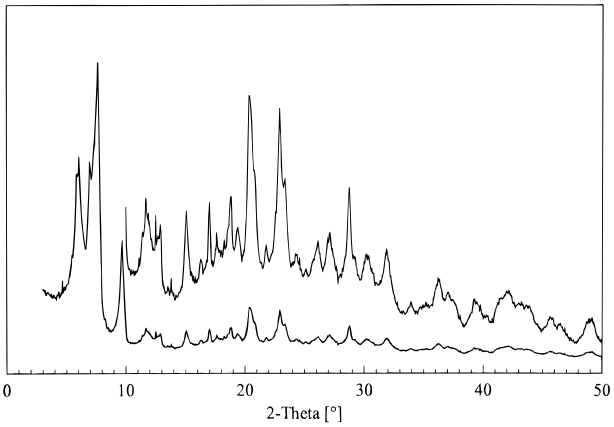

Figure 5. Powder XRD pattern of AlP_2 sulfate.

signal resembling the central transition is seen in the MAS spectrum (Figure 2). Calculation of QCCs for static spectra confirm this (Table 2). Also, visual comparision of the static spectra of the two clusters (Figure 1) reveals the T_d-Al of AlP_2 to be much less symmetrical than that of Al_{13}.[18] In Figure 2, the T_d-Al signal of AlP_2 is broader than that of O_h-Al. This is contrary to the findings of Nazar et al. (Table 2, ref 18), which is not readily explained by their use of a higher magnetic field strength. Perhaps exchange phenomena are important. Thus, AlP_2 (or similar species with higher molecular weight, e.g., AlP_3) as synthesized here is not exactly the same as that prepared by others.[18] However, we will refer to our product as AlP_2, even though it apparently contains small amounts of other polymeric hydroxides.

The powder XRD pattern of AlP_2 is shown in Figure 5. It is a rather complex pattern that reveals the presence of a significant amount of amorphous material, together with the AlP_2 crystalline phase. All of the attempted substitutions gave powdered precipitates with XRD patterns similar to that of AlP_2 except for Ga^{3+}, which gave the pattern for cubic $GaAl_{12}$−SO_4.

Solid state NMR shows that after 2 days at 80 °C all of the solutions contained mainly AlP_2, except for M = Ga^{3+}. Complete conversion to AlP_2 occurred only for M = Sn^{2+}. This metal ion apparently enhances the condensation of Al_{13}, perhaps by chemically linking Al_{12} units. Solid state ^{27}Al NMR spectra of authentic $GaAl_{12}$ (determined by single-crystal XRD) are shown in Figures 1 and 2. The O_h-Al signals exhibit large quadrupolar broadening effects similar to those of Al_{13} (Table 2) and give a distinct MAS signal pattern with a prominent modulated side band at −100 ppm under our conditions. This spectrum is more highly resolved at a 9.4 T field strength[2] as second-order quadrupolar effects are reduced.

Single-Crystal Structural Analysis. Single-crystal structural analysis was performed on Al_{13} sulfate, obtained by slow crystallization of the solution containing La^{3+} ions treated at 25 °C, and on $GaAl_{12}$ sulfate, obtained from the solution containing Ga^{3+} ions treated at 80 °C. These two structures, both of cubic cell symmetry, provide the first rigorous comparision between these two polyoxocations since, for the first time, crystals of the sulfate salt of Al_{13} were obtained. Emphasis was placed on verifying if the geometrical considerations can justify the higher thermal stability of $GaAl_{12}$, as suggested by others.[2,3] The main crystallographic data are reported in Table 4, selected geometrical data in Table 5. To facilitate the comparison with previously published crystallographic data of the cubic selenate salt of Al_{13}[27] and of the cubic sulfate salt of $GaAl_{12}$,[4] we have maintained the same atom-labeling scheme.

Incorporation of Ga produces an expansion of the central tetrahedron, with the four Ga−O(2) bond lengths of 1.879(5) Å being slightly smaller than those found by Goerz et al. (1.892(6) Å) and significantly longer than the typical tetrahedral Ga−O bond distance (e.g., 1.82 Å in β-Ga_2O_3). However, in spite of the larger dimension of the central tetrahedral atom, the geometries of the surrounding octahedra are almost unaffected (Table 5). In fact, the increase of the M_T−O(2) distance produces a contraction of the Al_O−O(2) bond from 2.026(4) to 2.009(6) Å, while no significant differences exist among the bond angles of the two polyoxocations, which generally agree within the standard deviations.

Table 4. Crystallographic Data for Al_{13} and $GaAl_{12}$ Sulfate Salts

	$Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_2\cdot 10H_2O$	$Na[GaO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_2\cdot 10H_2O$
fw	1626.49	1669.23
space group	$F\bar{4}3m$ (No. 216)	$F\bar{4}3m$ (No. 216)
a (Å)	17.856(2)	17.869(3)
V (Å^3)	5693.2(11)	5705.6(17)
Z	4.00	4.00
T (°C)	25.00	25.00
radiation, λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69
ρ_{calcd} (g cm^{-3})	1.898	1.943
μ (cm^{-1})	5.025	9.473
R^a	0.058	0.055
$R_w{}^b$	0.064	0.059

^{a} $R = \sum(|F_o - F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 5. Selected Geometrical Data for Al_{13} and $GaAl_{12}$ Sulfate Salts

	M_T = Al	M_T = Ga
M_T−O(2) × 4	1.831(4)	1.879(5)
Al_O−O(1) × 2	1.857(6)	1.852(6)
Al_O−O(2)	2.026(4)	2.009(6)
Al_O−O(3)	1.961(4)	1.962(6)
Al_O−O(4) × 2	1.857(6)	1.869(7)
O(2)−M_T−O(2′) × 6	109.5(2)	109.5(2)
O(1)−Al_O−O(1′)	78.0(2)	77.5(2)
O(1)−Al_O−O(2) × 2	95.4(2)	95.3(2)
O(1)−Al_O−O(3) × 2	92.3(2)	92.7(2)
O(1)−Al_O−O(4) × 2	94.2(2)	94.5(2)
O(1)−Al_O−O(4′) × 2	171.6(2)	171.1(3)
O(2)−Al_O−O(3)	170.1(2)	169.6(3)
O(2)−Al_O−O(4) × 2	82.0(2)	81.5(2)
O(3)−Al_O−O(4) × 2	91.3(2)	91.4(2)
O(4)−Al_O−O(4′)	93.3(2)	93.2(2)
Al_O−O(1)−Al_O′	101.4(2)	102.1(3)
Al_O−O(2)−M_T × 3	123.6(2)	122.6(3)
Al_O−O(2)−Al_O′ × 3	92.3(2)	93.7(2)
Al_O−O(4)−Al_O′	103.7(2)	103.3(3)

Conclusions

Metal ion substitution of Al in Al_{13} was attempted using Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, In^{3+}, La^{3+}, and Ce^{3+} at 25 °C and using Fe^{3+}, Zn^{2+}, Ga^{3+}, In^{3+}, Sn^{2+}, La^{3+}, and Bi^{3+} at 80 °C. Only the $GaAl_{12}$ hybrid was evidenced by NMR and XRD methods under our experimental conditions. Metal ion substitutions of Al_{13} that are claimed in the literature frequently involve the modification of condensed Al_{13} clusters (AlP_2-type species) or polymeric hydroxides, not Al_{13}. The higher thermal stability of $GaAl_{12}$ (compared to Al_{13}), observed both in solution and in PILCs, cannot be justified from the structural considerations of the solid polyoxocations. This conclusion was possible, for the first time, by comparision of the single-crystal XRD data for the isostructural forms (cubic symmetry) of these two polyoxocations.

Supporting Information Available: Listings of crystallographic data and tables of positional and anisotropic thermal parameters for Al_{13} and $GaAl_{12}$ sulfate salts (6 pages). Ordering information is given on any current masthead page.

IC960635S