in $[Tc(SR)_2(DMPE)_2]^+$ is bound more strongly than Tc–As in $[Tc(SR)_2(DIARS)_2]^+$.

Tc–S bond lengths of 2.29 Å for Tc^{III} and 2.41 Å for Tc^{II} have been observed for *trans*-$[Tc(SR)_2(DIARS)_2]^{+/0}$ and are equivalent to those observed for $[Tc(SR)_2(DMPE)_2]^{+/0}$. The contraction of Tc–As with decreasing Tc oxidation state indicates significant π-character in this bond.

The absorption spectra of *trans*-$[Tc(S\text{–}alkyl)_2(DIARS)_2]^+$ show two intense visible bands which correspond to, but are higher in energy than, those of *trans*-$[Tc(S\text{–}alkyl)_2(DMPE)_2]^+$ and are assigned as S → Tc CT transitions. *cis*-$[Tc(S\text{–}aryl)_2(DIARS)_2]^+$ possesses three intense visible bands which are again assigned to S → Tc transitions and which are similar to those observed in the analogous DMPE system. The UV region is populated by As → Tc CT bands and $\pi \rightarrow \pi^*$ ligand transitions when the sulfur substituent is aromatic.

All of the *trans*-$[TcX_2(DIARS)_2]^{+/0}$ complexes we have examined (X = Cl, Br, SCH_3, $SCH_2C_6H_5$) are easier to reduce than their DMPE congeners, with differences in $E^{\circ\prime}$ values ranging from 85 to 170 mV (Tc(III/II)) and from 20 to 150 mV (Tc(II/I)). However, *cis*-$[Tc(SC_6H_5)_2(DIARS)_2]^{+/0}$ is 23 mV (Tc(III/II)) and 110 mV (Tc(II/I)) more difficult to reduce than *cis*-$[Tc(SC_6H_5)_2(DMPE)_2]^{+/0}$.

The spectroscopic and electrochemical results together suggest that, in these *trans*-$[Tc(S\text{–}alkyl)_2D_2]^+$ complexes, DIARS is a more effective π-acceptor than DMPE. The origin of this enhanced π-acidity seems to be the aromatic backbone in DIARS. However, for the *cis*-$[Tc(S\text{–}aryl)_2D_2]^+$ complexes DIARS is a poorer π-acceptor than DMPE, presumably due to the rigidity of the DIARS ligand and its implications for M–L $d\pi$–$p\pi$ overlap in the cis configuration.

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Registry No. **1**, 139168-01-7; **2**, 129370-83-8; *trans*-$[^{99}Tc(OH)(O)(DIARS)_2](PF_6)_2$, 139168-00-6; *trans*-$[^{99}Tc(SCH_2C_6H_5)_2(DIARS)_2]PF_6$, 139168-02-8; *trans*-$[^{99}Tc^{II}(SCH_2C_6H_5)_2(DIARS)_2]^0$, 129370-77-0; *cis*-$[^{99}Tc^{II}(SC_6H_5)_2(DIARS)_2]^0$, 139240-61-2; *cis*-$[^{99}Tc(SC_6H_5)_2(DIARS)_2]PF_6$, 139240-63-4; *trans*-$[^{99}Tc(SC_6H_5)_2(DIARS)_2]PF_6$, 139168-03-9; *trans*-$[^{99}Tc^{II}(SCH_3)_2(DIARS)_2]^0$, 129423-99-0; *cis*-$[^{99}Tc^{IV}(SC_6H_5)_2(DIARS)_2]^{2+}$, 139168-04-0; *trans*-$[^{99}Tc^{I}(SCH_2C_6H_5)_2(DIARS)_2]^-$, 139168-05-1; $NH_4{}^{99}TcO_4$, 34035-97-7.

Supplementary Material Available: For *trans*-$[Tc(SCH_3)_2(DIARS)_2]PF_6$ and *trans*-$[Tc(SC_6H_5)_2(DIARS)_2]$, Tables A, C–F, and H–K, containing experimental crystallographic data, complete bond lengths and angles, thermal parameters, hydrogen parameters, and least-squares planes (9 pages); Tables B and G, listing calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

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Characterization of the $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ Polyoxocation by MAS NMR and Infrared Spectroscopies and Powder X-ray Diffraction

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Powder X-ray diffraction studies of the selenate salts of the $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ polyoxocation ($GaAl_{12}$) have confirmed unambiguously that it is structurally analogous to the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ species (Al_{13}). Lines in the solid-state MAS NMR spectra of $GaAl_{12}$, in which a gallium rather than an aluminum atom sits in the central tetrahedral position, are much sharper than those for the Al_{13} species. At least in part, this is because the $GaAl_{12}$ structure is less distorted than the Al_{13} ion. Line widths in the solution phase NMR spectra of the Al_{13} ion (and perhaps the $GaAl_{12}$ ion) are also affected by exchange broadening. Changes in the infrared spectra between ca. 900 and 400 cm^{-1} which result from replacing the central tetrahedral aluminum in Al_{13} with gallium, thereby forming $GaAl_{12}$, and also the changes which occur upon deuteration have been studied, and an assignment of the bands in this region has been proposed.

Introduction

The development of new types of microporous solids through the intercalation of charged metal polymers by various types of layered inorganic solids[1-5] has led to an increased interest in the types of oligomers formed upon the base hydrolysis of metal ions in solution. Our work in this area has concentrated thus far on the study of the base hydrolyses of aqueous aluminum, gallium, and mixed gallium–aluminum solutions.[6-8] It is well-known that the base hydrolysis of aqueous Al^{3+} solutions results in the formation, among other species, of the tridecameric $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ cation (i.e. Al_{13}).[9] This Al_{13} ion consists of a central tetrahedral aluminum surrounded by 12 edge-linked octahedrally coordinated aluminums,[9] arranged in an analogous fashion to the Baker–Figgis ϵ-isomer[10] of the well-known Keggin structure (the Baker–Figgis α-isomer) which occurs in the heteropoly oxometalates.[11-13] Our previous results have indicated that, upon base hydrolysis, aqueous Ga^{3+} solutions form, among other species, a $GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ unit (i.e. Ga_{13}), which appears to be isostructural with the Al_{13} species. In addition, our study of the base hydrolysis of gallium and aluminum solutions mixed in a 1:12 ratio[8] supported the previous suggestion made by Thomas et al.,[14] on the basis of a single NMR peak, that a $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ ion (i.e. $GaAl_{12}$) could be formed. While the size of this $GaAl_{12}$ species appears to be similar to that of the Al_{13} ion, its exact structure has yet to be determined.

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Solution NMR revealed sharper octahedral aluminum peaks for the $GaAl_{12}$ than the Al_{13} ion, which suggests that the former is more symmetric, but it also may be that exchange broadening plays a role in determining the widths of the NMR peaks of these ions. It is also possible that the $GaAl_{12}$ species is not a Baker–Figgis ϵ-isomer, as the Al_{13} ion is. Its structure could be that of one of the four other Baker–Figgis isomers, perhaps that of the Keggin unit itself, and that might be responsible for the differences in NMR peak widths. Therefore, one of the purposes of the work reported in this paper was to use X-ray powder diffraction studies of the selenate salts of these two cations (single crystals have been difficult to prepare) to confirm, if possible, the structure of the $GaAl_{12}$ species. Also, no solid-state MAS NMR spectra of compounds containing the $GaAl_{12}$ ion have been reported. A comparison of the NMR line widths in solution and in the solid state might reveal information about the relative importance, for the two ions, of differences in symmetry and differences in the exchange kinetics in solution. In addition, a detailed study of the characteristic bands in the infrared spectra of these ions between ca. 900 and 400 cm^{-1} has been carried out. This was done to determine the applicability of infrared spectroscopy to the study of the structures of similar cations in which NMR intractable nuclei had been substituted.

Experimental Section

Aqueous 0.2M Al^{3+} and Ga^{3+} solutions were prepared by dissolving $AlCl_3{\cdot}6H_2O$ (Aldrich, 99%) and $GaCl_3$ (Aldrich, 99.99+%) in deionized/distilled water, and their concentrations were determined gravimetrically through precipitation of the 8-hydroxyquinoline complexes, as previously described.[6,7]

The Al_{13} ions (among other species in solution) were prepared by base hydrolyzing the 0.2 M Al^{3+} solutions to OH/Al mole ratios of ca. 2.25 by the slow addition of 0.2 M NaOH, under conditions of vigorous stirring. The solutions were heated at 80 °C until they were no longer visibly turbid and then cooled in an ice bath. The $GaAl_{12}$ ions were prepared by mixing 0.2 M Al^{3+} and Ga^{3+} solutions in a 12:1 mole ratio and adding 0.2 M NaOH to an OH/M ratio of 2.25. The resulting $GaAl_{12}$ solutions, which were extremely turbid, were then refluxed at the boiling point for 2 days, after which NMR studies showed that there was no longer any trace of the Al_{13} species.[8]

Crystals of the Al_{13}– and $GaAl_{12}$–sulfates and –selenates were prepared by the dropwise addition of 0.2 M solutions of aqueous sodium sulfate (Fisher Chemicals) or sodium selenate (Aldrich) (which had been pH adjusted to those of the base-hydrolyzed metal ion solutions), to these solutions. This was done to the point that SO_4^{2-}/M or SeO_4^{2-}/M mole ratios ranging from 0.5 to 3.0 had been reached. The resulting suspensions were then left for several days, and the crystals which formed (single and powder) were separated from the amorphous colloidal precipitate by careful decantation.

Powder X-ray diffraction (XRD) studies were carried out using a Norelco X-ray diffractometer with graphite-monochromated Fe Kα radiation (λ = 1.936 Å). 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 glass base sample holders. Diffraction patterns were run from 5 to 90° in 2θ, utilizing a step width of 0.01° in 2θ and a scan time of 7 s/step.

Deuterated crystals of the Al_{13}–sulfate were also prepared for infrared studies, to attempt to determine if any bands could be ascribed to $(Al–OH)_{O_h}$ and $(Al–OH_2)_{O_h}$ rather than $(M–O)_{T_d}$ and $(Al–O)_{O_h}$ vibrations. Freshly sublimed anhydrous $AlCl_3$ was dissolved in D_2O (Aldrich 99.9%). Anhydrous sodium carbonate (MCB Reagents, oven dried at 260 °C) was dissolved in D_2O and added dropwise to the boiling, vigorously stirred $AlCl_3$ solution, until an OH/Al ratio of ca. 2.25 had been reached. The clear base–hydrolyzed Al solution was then cooled in ice. Anhydrous sodium sulfate (also oven dried at 260 °C) was dissolved in D_2O, and added to the Al solution until an SO_4^{2-}/Al ratio of ca. 2.0 had been reached. The resulting solution, which quickly became cloudy, was then left until crystallization was complete (approximately 1 week), after which the crystals were collected and washed with D_2O.

Fourier transform infrared spectra of CsI pellets of the Al_{13}– and $GaAl_{12}$–sulfate and –selenate salts and the deuterated Al_{13}–sulfate salt were run on a Mattson Galaxy 2000 spectrometer at a resolution of 2 wavenumbers.

Gallium-71 (122.03 MHz) and aluminum-27 (104.20-MHz) MAS NMR spectra of the $GaAl_{12}$– and Al_{13}–sulfate salts were run on 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 $Ga(H_2O)_6^{3+}$ and $Al(H_2O)_6^{3+}$ aqueous solution bands, which are defined as occurring at 0 ppm.

Results

Powder X-ray Diffraction Studies. To prove that the $GaAl_{12}$ species is isostructural with the Al_{13} species, and to examine the exact differences in symmetry in the two cases, single crystals of the sulfate or selenate salts of the $GaAl_{12}$ species would ideally be required. An attempt to obtain single crystals of the $GaAl_{12}$ species has not yet been successful in either case, however, as twinning has been found to be a problem.

Comparisons of X-ray powder diffraction patterns of the sulfate salts of the $GaAl_{12}$ and Al_{13} species were found to be impracticable, as the Al_{13} solutions are known to produce at least three different types of sulfate crystal structures depending on the solution pH, and it was found to be virtually impossible to crystallize samples consisting of only one phase. The phases which have been found to be present are as follows: (1) the monoclinic[9,15] crystals $[Al_{13}O_4(OH)_{25}(H_2O)_{11}][SO_4]_3{\cdot}xH_2O$, in which each tridecamer is believed to have lost one proton from the form present in solution and two slightly different unit cells of which have been found to occur, with space group *P*2/*n* or *Pn*, where *a* = 14.18 Å, *b* = 11.50 Å, *c* = 17.73 Å, and β = 102.3° (*Z* = 2), or space group *P*2/*a*, or *Pa*, where *a* = 20.2 Å, *b* = 11.5 Å, *c* = 25.0 Å, and β = 103° (*Z* = 2); (2) tetrahedral crystals[16] of formula $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4{\cdot}xH_2O$, having a cubic space group $P4_232$, where *a* = 17.9 Å (*z* = 2). The Al_{13} solutions have a general tendency to crystallize in the form of the monoclinic sulfate crystals of space group *P*2/*n*, whereas the $GaAl_{12}$ solutions appear to have more of a preference to crystallize in the cubic form.

The Al_{13}–selenate salt, however,[16,17] has only been found to crystallize in the form of tetrahedral crystals of formula $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SeO_4]_4{\cdot}xH_2O$, of space group $F\bar{4}3m$ (*a* = 18.01 Å, *Z* = 2), and for this reason, the selenate salts were chosen for comparative powder XRD studies. An examination of the X-ray powder pattern calculated for the Al_{13}–selenate from the single-crystal data and that observed for the Al_{13}–selenate (Figure 1, Table I) confirms that there is only one crystalline phase present and also that although preferred orientation does occur, it is a minor problem. A comparison of the observed powder patterns for the two selenate salts confirms unequivocally that the $GaAl_{12}$ ion forms a structure analogous to that of the Al_{13}–selenate. The only definite difference observed between the two cases was that for the Al_{13}–selenate the weak 022 and 024 reflections were always present, whereas for the $GaAl_{12}$–selenate they were invariably absent. Dissolution of these $GaAl_{12}$–selenate crystals in $BaCl_2$, followed by NMR spectroscopy of solutions held at 60 °C, resulted in spectra showing no ^{27}Al peak at 62.5 ppm, and the only evidence of a tetrahedrally coordinated species was the 138 ppm ^{71}Ga peak. This confirms that the crystals could not be simply Al_{13}–selenate crystals in which the difference in peak intensities was due to preferred orientation. If single crystals of the $GaAl_{12}$–selenate cannot be prepared, Reitveld refinements may allow an accurate determination of the structural parameters and thereby allow a careful study of the symmetry differences between these structural analogues.

MAS NMR Studies. The solid state ^{71}Ga and ^{27}Al MAS NMR spectra of the $GaAl_{12}$–sulfate salt are presented in Figure 2. To allow direct comparison, the ^{27}Al MAS NMR spectrum of Al_{13} (which has been reported elsewhere[18-20]) is shown in Figure 3. The peak positions and line widths are summarized in Table II. In the case of the Al_{13} complex, the spectrum was similar to that previously reported; only one peak was visible, in a position (60.9

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Table I. Calculated d_{hkl} and Relative Intensity (I_{rel}) Values for the Al_{13}–Selenate and Observed Values for the Al_{13}– and $GaAl_{12}$–Selenate Salts

	calculations		observations			
	Al_{13}–selenate		Al_{13}–selenate		$GaAl_{12}$–selenate	
hkl	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}
111	10.3981	48.87	10.4	35.7	10.3	45.2
002	9.0050	44.69	8.97	23.8	8.95	37.5
022	6.3675	3.24	6.37	1.3		
113	5.4302	11.93	5.42	8.7	5.41	10.3
222	5.1990	100.00	5.20	100.0	5.10	100.0
004	4.5205	20.87	4.51	19.7	4.49	6.6
133	4.1318	15.02	4.13	11.1	4.13	3.6
024	4.0272	2.27	4.03	1.4		
224	3.6763	10.88	3.676	11.4	3.672	6.6
115; 333	3.4660	49.60	3.465	53.7	3.462	34.7
044	3.1837	18.92	3.189	20.6	3.183	13.4
135	3.0442	14.26	3.044	14.2	3.041	9.4
006; 244	3.0017	2.56	3.003	1.9	3.000	4.3
226	2.7151	21.14	2.716	18.8	2.714	14.3
444	2.5995	2.54	2.598	4.4	2.600	2.2
117; 155	2.5219	2.56	2.521	6.0	2.52	2.6
046	2.4975	0.03				
246	2.4067	4.52	2.408	4.6	2.404	2.7
137; 355	2.3447	18.54	2.346	11.7	2.345	10.8
266	2.0659	1.42	2.07	1.05	2.08b	2.4
048	2.0136	2.75	2.007	0.9	1.984	4.6
119; 357	1.9769	19.95	1.98	11.3	1.976	7.7
248	1.9651	1.08				
088	1.5919	7.48	1.594	4.6	1.595	4.1
179; 1,3,11	1.5735	5.67	1.573	3.1	1.575	3.12
288; 4,4,10	1.5676	1.35				
379; 3,3,11	1.5276	1.53	1.527	0.7	1.522	2.5
2,6,10	1.5221	5.68	1.523	2.6		
199	1.4107	2.82	1.408	2.9	1.41	<0.5
688; 0,8,10; 2,4,12	1.4063	3.72				

Table II. ^{71}Ga and ^{27}Al NMR Peak Positions and Full Widths at Half-Height for Hydrolyzed Al and $GaAl_{12}$ Aqueous Solutions and Sulfate Salts

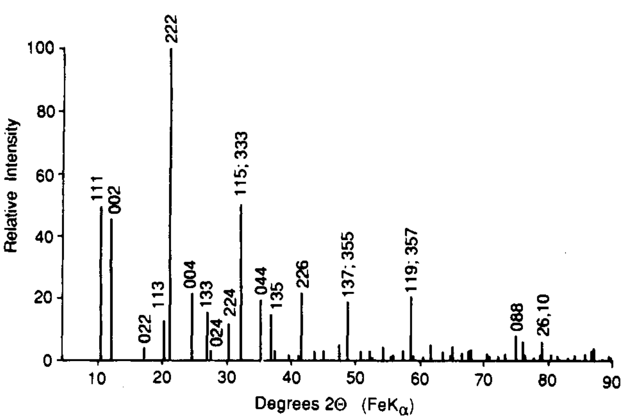
	M_{T_d}	$(Al_{12})_{O_h}$	$(Al_{monomeric})_{O_h}$
	(a) Solutions		
hydrolyzed Al			
^{27}Al	62.5 ppm (20 Hz)	7–11 ppm (3900 Hz)	0 ppm
hydrolyzed $GaAl_{12}$			
^{27}Al		16–18 ppm (2100 Hz)	0 ppm
^{71}Ga	137.8 ppm (95 Hz)		
	(b) Solids		
Al_{13}–sulfate			
^{27}Al	60.9 ppm (550 Hz)		N/A
$GaAl_{12}$–sulfate			
^{27}Al		9.0 ppm (1990 Hz)	N/A
^{71}Ga	128 ppm (6130 Hz)		N/A

ppm, 550 Hz fwhh) appropriate for the central tetrahedral aluminum in the Baker–Figgis ϵ-structure. Also, as reported elsewhere,[18-20] no peak was observed which could be ascribed to the outer octahedrally coordinated aluminums, and the reason for this is not completely understood.

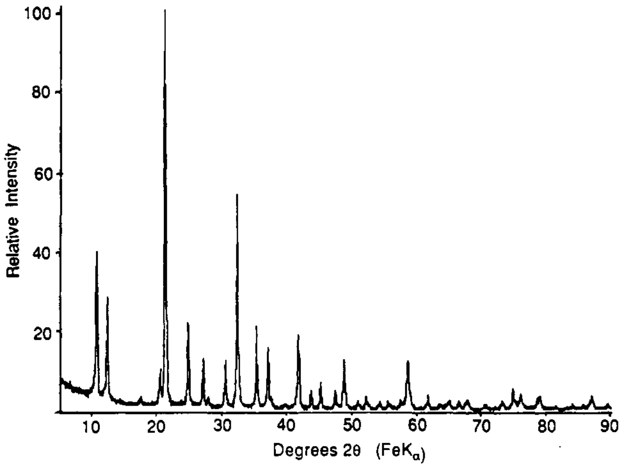
The MAS NMR spectra of the $GaAl_{12}$–sulfate salt, however, revealed not only a ^{71}Ga peak which had a chemical shift appropriate[8,21] to tetrahedrally coordinated gallium (128 ppm, 6130 Hz fwhh) but also an ^{27}Al peak which can be attributed to octahedrally coordinated aluminum (9.0 ppm, 1990 Hz fwhh). This observation of an octahedral Al peak in the solid-state NMR spectrum of the $GaAl_{12}$ unit is very interesting. Since it is known from the powder diffraction studies (see above) that the $GaAl_{12}$ and the Al_{13} ions are both Baker–Figgis ϵ-isomers, it suggests that the octahedrally-coordinated aluminums must be in a more symmetrical environment in $GaAl_{12}$ than in Al_{13}. It is known that the Al_{13} species is distorted inward,[9,15,16] and this suggests that the central tetrahedral Al is too small for an ideal fit. It appears that having gallium, a larger species, in the central tetrahedral position has formed a less distorted structure.

If peaks were being broadened due to chemical exchange in solution in addition to quadrupolar broadening due to reduced

a) Al_{13}-selenate: Calculated XRD Powder Pattern



b) Al_{13}-selenate: Observed XRD Powder Pattern



c) $GaAl_{12}$-selenate: Observed XRD Powder Pattern

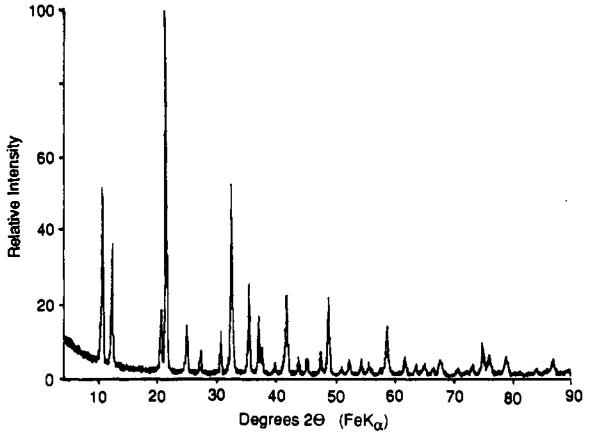


Figure 1. Powder X-ray diffraction patterns (FeKα): (a) calculated for the Al_{13}–selenate (a few major reflections are indicated by their *hkl* indices); (b) observed for the Al_{13}–selenate; (c) observed for the $GaAl_{12}$–selenate.

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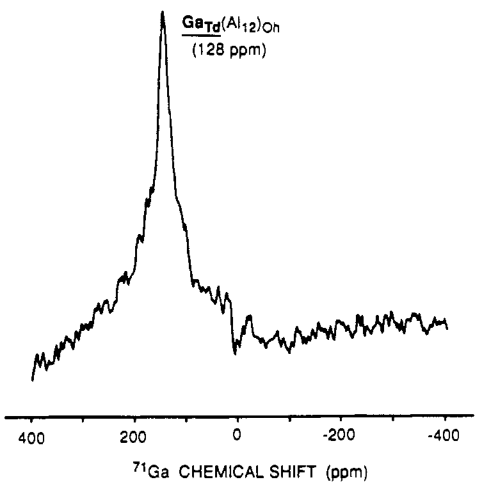
[21] Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987; p 265.

a) ^{71}Ga MAS NMR



b) ^{27}Al MAS NMR

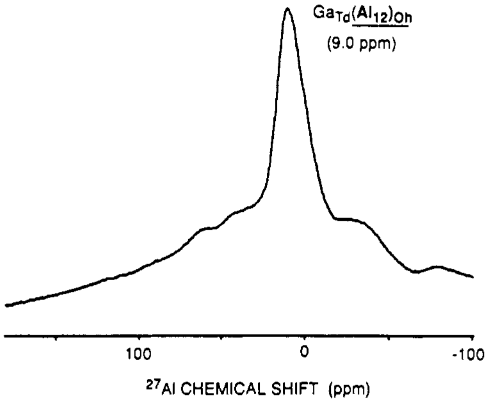


Figure 2. ^{27}Al and ^{71}Ga MAS NMR of the GaAl$_{12}$–sulfate salt: (a) ^{27}Al; (b) ^{71}Ga. Note: the ^{27}Al spectrum exhibited a sideband which fell at approximately 60 ppm and could thus be interpreted as due to the presence of a small amount of tetrahedral aluminum. When these crystals were dissolved and solution NMR were run, however, no evidence was seen of any tetrahedral aluminum, and thus it appears that the peak is in fact a sideband.

symmetry, one would expect the ratio of the widths of the $\mathbf{Ga}_{T_d}\mathrm{Al}_{12}$ peak for the GaAl$_{12}$ species and the $\mathbf{Al}_{T_d}\mathrm{Al}_{12}$ peak for the Al$_{13}$ species (i.e. fwhh ($\mathbf{Ga}_{T_d}\mathrm{Al}_{12}/\mathbf{Al}_{T_d}\mathrm{Al}_{12}$)) to be smaller for the solution case than for the solid case. This would be expected as the shorter lifetime of the Al$_{13}$ species in solution implies that faster exchange is occurring; this would result in the peaks being broadened to a larger degree than those in the GaAl$_{12}$ case. Such exchange broadening would not be manifested in the solid state case, of course. A comparison of the widths of the $\mathbf{Al}_{T_d}\mathrm{Al}_{12}$ peak in the Al$_{13}$ unit and the $\mathbf{Ga}_{T_d}\mathrm{Al}_{12}$ peak in the GaAl$_{12}$ unit, in both the solid-state (i.e. sulfate salts) and solution-state (i.e. discrete ions) spectra, suggests very strongly that this is indeed the case; the observed peaks in the solution spectra of the Al$_{13}$ species are partially broadened through exchange. The ratios are

$$\text{solution:} \quad \mathrm{fwhh}(\mathbf{Ga}_{T_d}\mathrm{Al}_{12}/\mathbf{Al}_{T_d}\mathrm{Al}_{12}) = 4.75$$

$$\text{solid state:} \quad \mathrm{fwhh}(\mathbf{Ga}_{T_d}\mathrm{Al}_{12}/\mathbf{Al}_{T_d}\mathrm{Al}_{12}) = 11.15$$

It is quite possible that the peaks observed for the GaAl$_{12}$ species are also broadened (to some lesser extent) by exchange, but from these results it is not possible to determine this. It would be reasonable to assume that exchange broadening is even more important for the Ga$_{13}$ polyoxocation, which exhibits an extremely short lifetime in solution and extremely broad NMR lines.[6]

Infrared Spectroscopic Studies. The infrared spectra of the Al$_{13}$– and GaAl$_{12}$–sulfate and –selenate salts (CsI pellets) are shown in Figure 4. The band positions for the Al$_{13}$ salts are similar to those reported in tabular form by Waters and Henty, who also studied the Raman spectra.[22] However, the additional information obtained from the spectra of the GaAl$_{12}$ compounds has resulted in several differences in assignments, as discussed below.

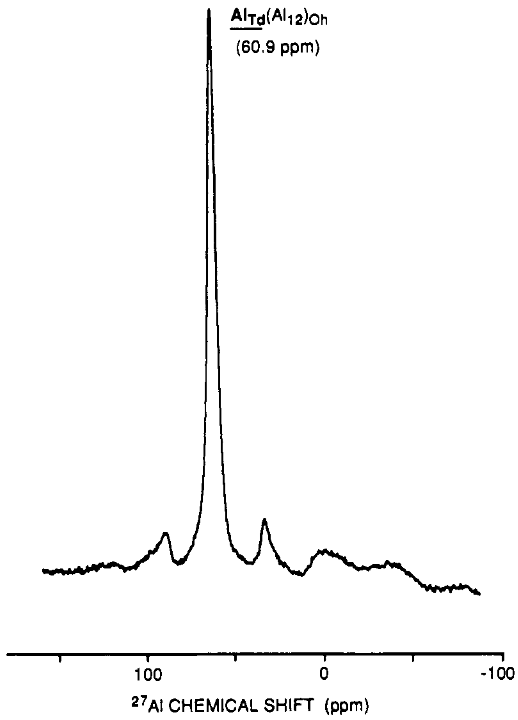


Figure 3. ^{27}Al MAS NMR of crystals of the Al$_{13}$–sulfate salt.

The bands near 1126 cm^{-1} in the sulfate salts and 883 cm^{-1} in the selenate salts must represent the ν_3 vibration of the SO$_4^{2-}$ and SeO$_4^{2-}$ ions, respectively.[23] Waters and Henty have suggested that ν_4 for SO$_4^{2-}$ lies at 612 cm^{-1}, and for SeO$_4^{2-}$, it is at 410 cm^{-1}. We agree with these assignments, although it is clear that the ν_4 band in the sulfate salts overlaps a band from a vibration of the tridecameric cation. This latter band can be seen near 627 cm^{-1} in the spectrum of both the Al$_{13}$ and GaAl$_{12}$ selenate salts. The fact that it is at virtually the same position in both the Al$_{13}$ and GaAl$_{12}$ species argues strongly against the assignment made by Waters and Henty that it involves a stretching vibration of the four bonds attached to the central tetrahedral metal atom.

An examination of the infrared spectra of the Al$_{13}$-sulfate and selenate salts (Figure 4a,c, Table III), from 1250 to 260 cm^{-1}, revealed six other bands which did not change appreciably when the anion changed and which therefore can be assigned to vibrations of the Al$_{13}$ cation. These bands were at 728–731, 545–548, 490–495, 371, 308, and 297 cm^{-1}. The 371-cm^{-1} band overlapped the ν_4(SeO$_4$) band in the selenate salts, and the bands at 308 and 297 cm^{-1} varied in intensity in different spectra, at least in part due to noise. These three lowest wavenumber bands probably represent bending vibrations; the three other bands, plus the one near 625 cm^{-1}, are in the region appropriate to Al–O stretching vibrations. The strong band reported by Bertram and Schönherr[24] at 985 cm^{-1} for their Al$_{13}$–chloride salt, attributed to an Al–OH deformation, was not evident in any of our spectra; it may arise because of the acetone-induced precipitation technique which they have used in synthesis.[25] If the observed vibrations can be considered to be relatively independent of one another, then

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(22) Waters, D. N.; Henty, M. S. *J. Chem. Soc., Dalton Trans.* **1977**, 243.

(23) Nakomoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986; p 139.

(24) Bertram, R.; Schönherr, S. *Z. Chem.* **1984**, *24*, 225.

(25) Schönherr, S.; Görz, H.; Müller, D.; Gessner, W. *Z. Anorg. Allg. Chem.* **1981**, *476*, 188.

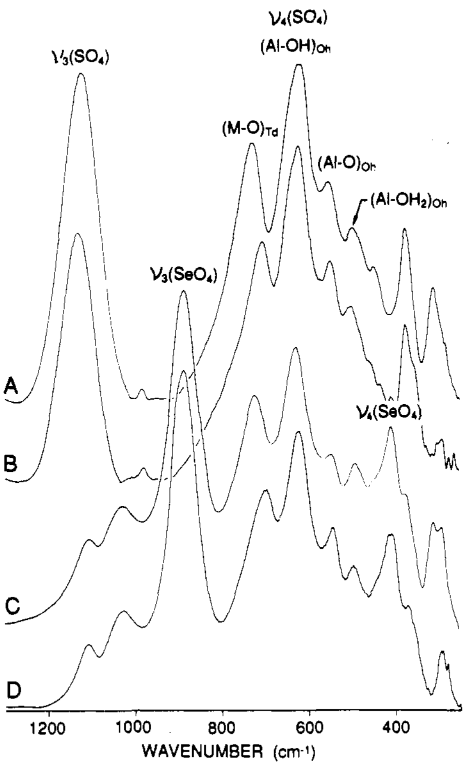


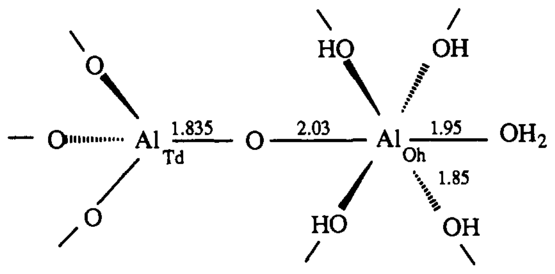
Figure 4. Infrared spectra: (a) Al^{13}–sulfate; (b) $GaAl_{12}$–sulfate; (c) Al_{13}–selenate; (d) $GaAl_{12}$–selenate.

Table III. Tridecameric Cations: Vibrational Assignments[a]

this work			Waters and Henty[b]	
Al_{13}	$GaAl_{12}$	assignt	Al_{13}	assignt
729	704	$(M–O)_{T_d}$	728	unassigned
627[c]	623[c]	$(Al–OH)_{O_h}$	625	$(Al–O)_{T_d}$
546	543	$(Al–O)_{O_h}$	542	$(Al–OH_2)_{O_h}$
492	494	$(Al–OH_2)_{O_h}$	490	unassigned
371	371	bend	380	$(Al–OH)_{O_h}$
308	308	bend	310	unassigned
297	297	bend	298	unassigned

[a] The band positions are in wavenumbers/cm^{-1}. The reported numbers are averages for the sulfate and selenate salts. [b] Reference 22. [c] This band position was determined from the selenate salts because in the sulfate salts it is overlapped by ν_4 of the anion.

it might be expected that the shorter bonds would correspond to the higher wavenumbers. From the Al–O bond lengths as determined in the single-crystal structure (average bond lengths being 1.835 Å for $(Al–O)_{T_d}$, 1.85 Å for $(Al–OH)_{O_h}$, 1.95 Å for $(Al–OH_2)_{O_h}$, and 2.03 Å for $(Al–O)_{O_h}$)[9], the tetrahedral and octahedral parts of the Al_{13} ion can be shown diagrammatically as



If the bond lengths were the only factor, then one would expect the order of the stretching vibrations to be $\nu(Al–O)_{T_d} > \nu(Al–OH)_{O_h} > \nu(Al–OH_2)_{O_h} > \nu(Al–O)_{O_h}$. However other factors, such as whether the bond is bridging or terminal, would be expected to affect the frequencies. Substitutions of Ga for Al in the tetrahedral position and of deuterium for hydrogen (which would affect some of the octahedral stretches) can be used to check the assumption of independence and to confirm the identity of some of the vibrations.

In the $GaAl_{12}$–sulfate and –selenate salts (Figure 4b,d), only the highest wavenumber band was observed to shift substantially from the case of the Al_{13} salt (from 728–731 to 702–706 cm^{-1}), confirming that it is an effectively independent $(M–O)_{T_d}$ stretch (asymmetric). This assignment has already been suggested by Bertram and Schönherr who had studied the IR spectra of the Al_{13}–sulfate and a proposed $GeAl_{12}$–sulfate.[24-26] It is different than that proposed by Waters and Henty, who suggested that the $(M–O)_{T_d}$ vibration falls at 627 cm^{-1} (see above).[22]

A comparison of the IR spectra of the Al_{13}–sulfate and its deuterated analogue revealed, as expected, no shift in the 728–731-cm^{-1} band. The 545–548-cm^{-1} band also did not change position, and therefore it must be associated with a group which does not involve an exchangeable hydrogen, i.e., the $(Al–O)_{O_h}$ vibration. This result is different from that reported by Waters and Henty;[22] they found that the 542-cm^{-1} band did shift on deuteration, although in this instance they were studying a concentrated aluminum chlorohydrate solution, not the Al_{13}–sulfate. Probably different species (monomers, dimers, etc...) were present in their solutions, and this may account for this difference. For our deuterated Al_{13}–sulfate, movements were seen in the 622–630- and the 490–495-cm^{-1} bands, the former being to 616 cm^{-1} and the latter to approximately 475 cm^{-1} (peak overlap made the exact position of this band difficult to determine). These latter two bands must involve groups which can be deuterated and, on the basis of bond lengths, likely correspond to the $(Al–OH)_{O_h}$ and $(Al–OH_2)_{O_h}$ stretches respectively. These assignments are summarised in Table III, where they are compared with those made by Waters and Henty.

The average absorbances of the observed $(M–O)_{T_d}$, $(Al–OH)_{O_h}$, $(Al–O)_{O_h}$, and $(Al–OH_2)_{O_h}$ bands for the $GaAl_{12}$– and Al_{13}–sulfate and selenate salts were found to be fairly repeatable in the relative intensity ratio 88:100:76:70, in order of decreasing wavenumber. Thus the band positions and intensities observed serve as an excellent fingerprint of the Al_{13} and $GaAl_{12}$ structures. This Al_{13} fingerprint should be quite useful, in addition to techniques such as MAS NMR and powder X-ray diffraction, in the study of Al gels which are formed through the base hydrolysis of aqueous aluminum salt solutions and the phase transformations which take place in the precipitation of the gibbsite/bayerite phases. In addition, it could be used to examine the structures of other MAl_{12} species in which NMR-intractable nuclei had been substituted. We have studies of both of these types currently underway.

Conclusions

X-ray powder diffraction, solution and MAS NMR, and infrared studies of the $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxocation have proven that it is isostructural with the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ ion. The NMR studies have indicated that although it is indeed a more symmetric structure, this difference is not to as large a degree as had been suggested by the peak width differences observed in the solution studies, thereby indicating that exchange broadening is also an important factor. Infrared studies have assigned the Al–O stretching vibrations in the tridecamer and thereby provided a further tool for characterizing structural analogues of these species.

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Registry No. $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; $Na[GaAl_{12}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4$, 139166-17-9; $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SeO_4]_4$, 62863-57-4; $Na[GaAl_{12}O_4(OH)_{24}(H_2O)_{12}][SeO_4]_4$, 139100-40-6; $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$, 112385-59-8; $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$, 12703-68-3; ^{71}Ga, 14391-03-8; sulfuric acid, aluminum salt, basic, 55892-56-3.

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(26) Schönherr, S.; Bertram, R. *Z. Chem.* **1983**, *23*, 105.