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Synthesis and Characterization of the $\mathrm{GeO_4Al_{12}(OH)_{24}(OH_2)_{12}}^{8+}$ Polyoxocation

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Introduction

There is considerable interest in the aluminum polyoxocation $\mathrm{AlO_4Al_{12}(OH)_{24}(OH_2)_{12}}^{7+}$ (Al$_{13}$) due to its use in the development of pillaring agents and new microporous solids and its similarity to minerals of geochemical significance.[1−6] The Al$_{13}$ molecule consists of a central tetrahedral AlO$_4$ unit that is surrounded by 12 edge-sharing AlO$_6$ moieties arranged in a structure similar to the Baker−Figgis ϵ-Keggin isomer.[7−9] This structure polymerizes in solution to form larger polyoxo complexes[10,11] and ultimately forms solids that recrystallize to form bayerite.[4]

It has been shown conclusively that Ga^{III} can substitute for Al^{III} at the central tetrahedral site in the Al$_{13}$ molecule and that the resulting $\mathrm{GaO_4Al_{12}(OH)_{24}(OH_2)_{12}}^{7+}$ (GaAl$_{12}$) cation is generally more stable than the Al$_{13}$.[4,5] This substitution also has a large effect upon the rates of steady oxygen exchange between sites in the polyoxocation and bulk solution,[12−14] and these differences in lability cannot be explained by simple reference to the structural differences between the two.[5] The GaAl$_{12}$ and Al$_{13}$ cations exhibit cubic symmetry and have 12 equivalent bonded water molecules (η^1-OH$_2$), two structurally distinct sets (μ_2-OH^a; μ_2-OH^b) of 12 hydroxyl bridges, and four four-coordinated oxo groups (μ_4-O). Of these oxygen sites, only the μ_4-O groups are inert with respect to exchange with the bulk solution.[12−14]

During our investigations into these polyoxocations[12−14] we experimented with the introduction of more highly charged cations into the central tetrahedral site of the Al$_{13}$ cation. Substitution of other ions for the central aluminum, including germanium by the Schönherrs' group,[18] has been reported before;[5,15−18] however, the most recent review by Parker et al.[5] determined that conclusive evidence had been presented only for the substitution of gallium for aluminum. In this paper we report a reliable method for the synthesis of the GeAl$_{12}$ polyoxocation and the first conclusive structural characterization of its selenate salt through single-crystal X-ray diffraction and ^{27}Al MAS NMR spectroscopy. The GeAl$_{12}$ analogue of the Al$_{13}$ cation is particularly interesting because, although the size of the central Ge^{IV} is equal to that of Al^{III}, the GeAl$_{12}$ has a +8 molecular charge rather than the +7 charge displayed by both the Al$_{13}$ and GaAl$_{12}$[19] polyoxocations.

Experimental Section

A standard solution of approximately 0.27 M AlCl$_3$ was made by the dissolution of 63.455 g of fresh AlCl$_3$·(H$_2$O)$_6$ in 1 L of deionized water. An aliquot of 300 mL of this solution was slowly titrated at 85.3 °C against 178 mL of a 1.125 M standard NaOH solution containing 0.058 mol (0.9432 g) of GeO$_2$. This ensured that, at completion, an OH:Al ratio of approximately 2.1:1 would coincide with a Ge:Al ratio of approximately 1:10, in each case a slight excess over the theoretical ratio required for strict stoichiometry. The resulting solution was filtered hot and quenched in 200 mL of deionized water. Subsequently, 200 mL of a 0.2 M sodium selenate decahydrate solution was carefully added to give a SeO$_4$:(Al + Ge) molar ratio of 8:1 and further water added to give a total volume of 1.2 L.

Colorless tetrahedral crystals began to form after approximately 1 week, and they were harvested after 10 days. Single-crystal X-ray diffraction measurements were made with the use of a Bruker SMART 1000 diffractometer with a molybdenum source (λ = 0.71073 Å) at 90(2) K. Data collection,[20] data reduction,[20] solution,[21] and refinement[22] were routine. One of the oxygens bonded to Se(O10) is disordered with respect to a mirror plane, and one molecule of water (O15) showed large thermal motion and was refined at half its normal occupancy. The Flack parameter refined to 0.06(3), indicating the correct choice of hand. The crystallographic data are provided in Table 1.

The ^{27}Al MAS NMR spectra were acquired at 104.26 MHz with a Chemagnetics CMX 400 Infinity spectrometer. The samples were spun at 15−17.2 kHz in sealed 4.0 mm (o.d.) ZrO$_2$ rotors. Spectra were acquired with 0.5−1.0 μs pulses (ν_{RF} = 42 kHz) and a 0.1 s pulse delay. Chemical shift and quadrupolar-coupling parameters were estimated from comparison with central-transition line shapes calculated with the method described by Massiot et al.[23] Fits were judged by relative positions of edges and horns in the powder patterns. Chemical

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Table 1. Crystal Data and Structure Refinement for $[GeO_4Al_{12}(OH)_{24}(H_2O)_{12}](SeO_4)_4 \cdot 14H_2O$

empirical formula	$H_{62}Al_{12}GeO_{70}Se_4$
fw	1894.69
temp	90(2) K
cryst syst	tetragonal
space group	$I\bar{4}m2$ (119)
unit cell dimens	$a = 13.0322(7)$ Å $c = 17.2087(13)$ Å
vol	2922.7(3) Å^3
Z	2
ρ_{calc}	2.153 mg/m^3
μ	3.345 mm^{-1}
reflns collected	27190
indep reflns	1829 [R(int) = 0.0757]
obsd reflns ($I > 2\sigma(I)$)	1764
$R(F)^a$ ($F_o^2 > 2\sigma(F_o^2)$)	0.063
$\omega R2^a$	0.147

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $\omega R2 = \sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]^{1/2}$.

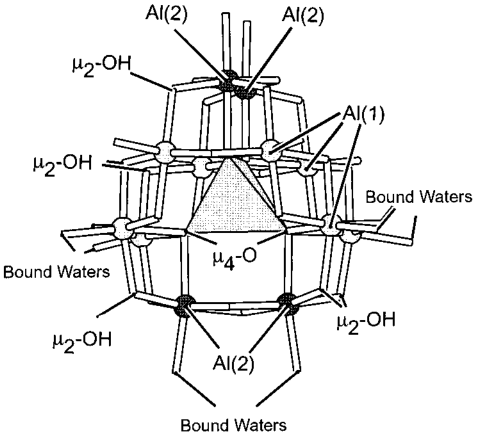

Figure 1. Representation of the $GeO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{8+}$ polyoxocation ($GeAl_{12}$), with some sites labeled to be consistent with Table 2. The structure has a tetrahedral $^{IV}GeO_4$ unit surrounded by 12 $^{VI}AlO_6$ octahedra in two crystallographically inequivalent sites. There are four ^{IV}Al(1) sites and eight ^{VI}Al(2) sites in a structural unit.

Table 2. Comparison of Selected Bond Lengths for Al_{13}, $GaAl_{12}$ Sulfate, and $GeAl_{12}$ Selenate Salts[a]

	bond lengths (Å)			
moiety	M = Al	M = Ga	M = Ge	oxygen type
^{IV}M−O	1.831(4)	1.879(5)	1.809(8)	μ_4-O
^{VI}Al−O	2.026(4)	2.009(6)	2.1039 Al(1)	μ_4-O
^{VI}Al−O	2.026(4)	2.009(6)	2.079 Al(2)	μ_4-O
^{VI}Al−O	1.857(6)	1.852(6)	1.854(6) Al(1) 1.843(6) Al(2)	μ_2-OH^a
^{VI}Al−O	1.857(6)	1.869(7)	1.841−1.869	μ_2-OH^b
^{VI}Al−O	1.961(4)	1.962(6)	1.928 Al(1)	η^1-OH$_2$ (bound water)
^{VI}Al−O	1.961(4)	1.962(6)	1.910 Al(2)	η^1-OH$_2$ (bound water)

[a] Data for Al_{13} and $GaAl_{12}$ are from Parker et al.,[5] and data for the $GeAl_{12}$ are from this paper.

shifts were referenced relative to $\delta(^{27}Al) = 0$ ppm for the $Al(H_2O)_6{}^{3+}$ ion in the form of an external sample of $Al(NO_3)_3(aq)$.

Results and Discussion

Crystal Structure. Figure 1 shows a diagrammatic representation of the $GeAl_{12}$ polyoxocation, with the ϵ-Keggin-like structure. The Al_{13} and $GaAl_{12}$ ϵ-Keggin-like molecules each have cubic ($\bar{4}3m$) symmetry and octahedrally coordinated aluminum ions in crystallographically equivalent sites surrounding the central tetrahedral ion. In contrast substitution of Ge^{IV} into the central position produces a tetragonal distortion corresponding to a slight expansion in both axial and equatorial directions and an overall symmetry of $I\bar{4}m2$. The 12 octahedral aluminum ions in the $GeAl_{12}$ occupy two distinct sets of sites: four are axial Al(2) ions with mirror symmetry, and eight are equatorial Al(1) ions with no crystallographic symmetry (Figure 1). The presence of two aluminum sites in the germanium-centered molecule doubles the number of μ_2-OH sites. Interestingly, in contrast to the gallium and aluminum compounds studied previously[12−14] there are now two μ_2-OH^a sites, one coordinated to each of the two Al(1) or two Al(2) aluminum atoms and adjacent to two μ_4-oxo groups. The two μ_2-OH^b units are coordinated to one aluminum atom from each of the Al(1) sites and an Al(2) site but adjacent to only one μ_4-oxo group. This symmetry distortion produces geometric differences between Al(1) and Al(2) to terminal bound waters and to the μ_4-O site. The $\langle ^{IV}Ge-O\rangle$ bond lengths in the center of the structure are 1.809 Å, slightly shorter than the 1.831 Å $\langle ^{IV}Al-O\rangle$ previously measured for the Al_{13} sulfate salt,[5] and much shorter than the $\langle ^{IV}Ga-O\rangle$ bonds (1.879 Å) in the $GaAl_{12}$ analogue.[5] This difference is probably due to the increased charge of the central Ge^{IV} relative to the Al^{III} and Ga^{III}. The shorter bond lengths between the μ_4-O and the more highly charged central atom result in a less symmetrical molecule exhibiting two octahedral aluminum atom sites where the $\langle Al(1)-(\mu_4\text{-}O)\rangle$ bond length is longer at 2.103 Å than the corresponding bond from the Al(2) site (2.079 Å). Bond lengths between octahedral aluminum and the hydroxyl bridges are comparable between the Al_{13} and $GeAl_{12}$ structures, but bonds to water are longer in the $GeAl_{12}$ than in either the $GaAl_{12}$ or Al_{13} molecules. A comparison of bond lengths between the $GeAl_{12}$, $GaAl_{12}$, and Al_{13} is given in Table 2.

The presence of two aluminum sites has a considerable influence on the bond angles between octahedral units. The Al(1) sites are located slightly further away from the central tetrahedron, but Al(2) sites are almost unchanged from the $GaAl_{12}$ molecule. This distortion has the result of reducing the angle through one of the shared oxygen atoms (O4) between the two aluminum sites. The effect that these structural differences have on the rates of oxygen exchange in this molecule are currently under investigation.

The selenate molecules are located between adjacent $GeAl_{12}$ molecules in the crystal structure. The selenate position is between a set of two Al(2) metals at the axial position on one $GeAl_{12}$ molecule and a set of one Al(1) and one Al(2) site on the adjacent $GeAl_{12}$ molecule. The Se(1)−Al(2) distances (4.89 Å) are slightly shorter than Se(1)−Al(1) distances (5.13 Å).

^{27}Al Solid-State NMR Spectroscopy. The ^{27}Al MAS NMR spectrum of the $GeAl_{12}$ selenate salt (Figure 2a) contains signals from two distinct resonances that are characterized by very large quadrupolar coupling constants (C_q). For comparison, we show also spectra from the similarly prepared selenate salts of $GaAl_{12}$ (Figure 2b) and Al_{13} (Figure 2c). The spectrum of Al_{13} contains a distinct peak at +61 ppm that arises from the central, tetrahedral aluminum,[23] whereas only very small peaks at this position occur in the spectra of the $GaAl_{12}$ and $GeAl_{12}$ samples, indicating that they contain small quantities of the Al_{13} polyoxocation as an impurity. We cannot ascertain whether the Al_{13} impurity substitutes for the $GeAl_{12}$ in the structure or occurs as a separate Al_{13} selenate salt. The spectra from $GaAl_{12}$ and Al_{13} yield quadrupolar coupling and chemical shift parameters similar to those previously reported.[4,24−26]

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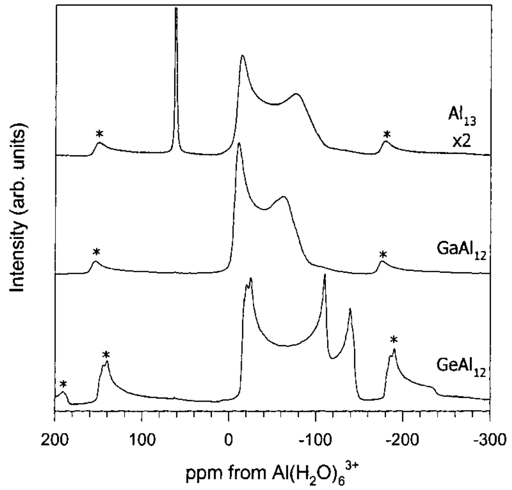

Figure 2. ^{27}Al MAS NMR spectra of the selenate salts of (a) GeAl$_{12}$ (ν_{rot} = 17.2 kHz); (b) GaAl$_{12}$ (ν_{rot} = 15.4 kHz); and (c) Al$_{13}$ (ν_{rot} = 15.4 kHz). Data acquired at 104.26 MHz, pulse lengths of 1 μs (a) and 0.5 μs (b and c), relaxation delays of 0.1 s (a) and 0.1 s (b and c), 1000−12000 acquisitions, 200 kHz digitization rate.

Although the two octahedral Al signals from GeAl$_{12}$ cannot be fully resolved, their essential line shape parameters can be obtained from the MAS NMR spectrum, because the two sites exhibit distinct quadrupolar coupling parameters. The observed center band (0 ppm to −150 ppm region) contains two powder patterns, one of which gives a low-frequency horn positioned near −110 ppm and the other near −140 ppm. The asymmetry of the respective electric-field gradients (EFGs) can be estimated from the shape of these features to be $\eta = 0$ for that at −110 ppm and $\eta = 0.05$ (±0.01) for that at −140 ppm. With this information, the best simulation of the high-frequency region (−10 to −30 ppm) is obtained by assigning the sharp downfield feature (−17 ppm) to the high-frequency horn of a powder pattern containing the peak at −110 ppm, giving $\delta = 13(1)$ ppm, $C_q = 11.95(5)$ MHz, $\eta = 0$ (component *a*). The other features at −20 and −24 ppm can be simulated by, respectively, the discontinuity and high-frequency horn for a powder pattern with slight asymmetry consistent with the feature at −140 ppm: $\delta = 15(1)$ ppm, $C_q = 13.50(5)$ MHz, and $\eta = 0.05$ (component *b*). At the 17.2 kHz spinning rate, the low-frequency edge of this powder pattern also overlaps the $n = -1$ spinning sideband.

Figure 3 shows the observed spectrum and a sum of the two central transition MAS powder patterns calculated using these parameters, with an intensity ratio for the components *a*:*b* of 1:2 (including all spinning sidebands). On the basis of this observation, we assign the resonance with the smaller coupling constant (component *a*) to the Al(1) site identified in the X-ray structure (Figure 1). This interpretation is supported by the similar chemical shifts obtained from the two powder patterns. Any other assignment scheme for the fine structure in the −10 to −30 ppm region requires very different chemical shifts for the two sites, which are topologically very similar. A possible alternative assignment of the peaks at −29 and −110 ppm to component *a* yields chemical shifts of +2 ppm (*a*) and +20 ppm (*b*), but C_q values that differ from those given above by less than 5%. The C_q's observed for GeAl$_{12}$ are significantly larger than those for Al$_{13}$ (10.3 MHz) and GaAl$_{12}$ (9.7 MHz). These differences could not be explained by simple point charge models (e.g., see ref 27). Further analysis awaits more detailed quantum chemical calculations.

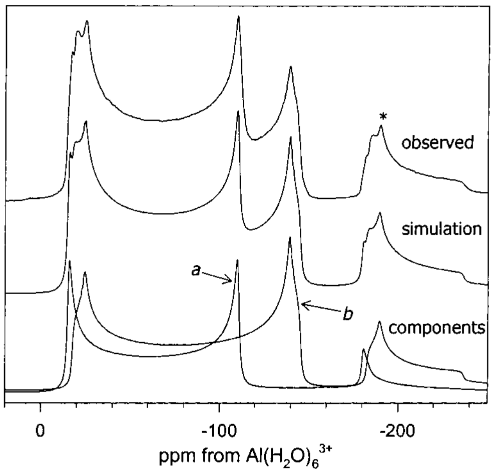

Figure 3. Observed (top) and simulated (middle) ^{27}Al central transition MAS NMR line shapes for the GeAl$_{12}$ selenate salt (ν_{rot} = 17.2 kHz). The simulation is a sum of two powder patterns (bottom, *a* and *b*) in an intensity ratio of 1:2. Component *a*: $\delta = 13(1)$ ppm, C_q 11.95(5) MHz, $\eta = 0$. Component *b*: $\delta = 15(1)$ ppm, C_q 13.50(5) MHz, $\eta = 0.05(1)$.

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Supporting Information Available: Crystallographic data in CIF format for [GeO$_4$Al$_{12}$(OH)$_{24}$(OH$_2$)$_{12}$](SeO$_4$)$_4$·14H$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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