

Solid State Aluminum-27 NMR Studies of Tridecameric Al-Oxo-Hydroxy Clusters in Basic Aluminum Selenate, Sulfate, and the Mineral Zunyite

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Aluminum forms a number of tridecameric (Al_{13}) cluster compounds in which O^{2-} , OH^- , F^- , and H_2O are ligands. Examples are the basic aluminum salts (chloride, selenate, and sulfate, Refs. (1, 2)) and the mineral zunyite (3). The basic aluminum salts are formed by partial hydrolysis of $Al(H_2O)_6^{3+}$ by base, have commercial utility, and have recently been the subject of several studies using aluminum-27 NMR spectroscopy, both in solution (4, 5) and in the crystalline solid state (1, 6).

The basic aluminum salts all contain a central AlO_4 unit, surrounded by twelve six-coordinate Al atoms. Early solution NMR studies readily detected signals arising from AlO_4 in the tridecamer (4), but only under certain conditions (at high temperature) could resonances attributable to the octahedral aluminums be observed, due presumably to their large quadrupole coupling constants (e^2qQ/h). Similarly, detection of the octahedral aluminums in the basic chlorides and sulfates in the solid state has until now not been successful (6). In contrast, solid state NMR studies using "magic-angle" sample spinning (MASS) (7) of the mineral zunyite, a basic aluminum silicate having the structure $[Al_{13}(OH, F)_{16}F_2]Si_5O_{20}Cl$, have recently revealed quite narrow lines for both four- and six-coordinate aluminum (1).

In this paper, we present ^{27}Al MASS, variable-angle sample-spinning (VASS) (8) and static NMR spectra of basic aluminum selenate, sulfate, and the mineral zunyite, obtained at several magnetic field strengths, which has allowed us to determine e^2qQ/h and isotropic chemical-shift values for both Al(4) and Al(6) sites in all three systems. We discuss the likely origins for the large differences in e^2qQ/h between Al(6) sites in zunyite (~ 2.5 MHz) and the basic aluminum selenate and sulfate (~ 10 MHz). Availability of e^2qQ/h (and asymmetry parameter, η) information will be shown elsewhere to permit evaluation of rotational correlation times for the Al_{13} clusters in solution, and thereby to permit estimation of oxygen-17 e^2qQ/h values in such systems (9).

The basic aluminum selenate and sulfate were obtained as $Na[AlO_4 \cdot Al_{12}(OH)_{24}(OH_2)_{12}] (XO_4)_4 \cdot YH_2O$ ($X = Se$ or S and $Y \sim 13$, Ref. (2)) from

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Professor G. Johansson, and very similar results were obtained from samples of more recent vintage, prepared in this laboratory. Zunyite was a sample from Zuni Mine, Colorado, and was kindly provided by Dr. Peter J. Dunn of the Smithsonian Institution. Aluminum-27 NMR spectra were recorded on "home-built" spectrometers at either 130.3 MHz (11.7 T), 93.8 MHz (8.45 T), or 39.2 MHz (3.52 T), as described elsewhere (10). Chemical shifts were measured with respect to an external solution of 1 M $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$ in H_2O .

Our first attempts at observation of both Al(4) and Al(6) sites in the basic aluminum salts involved studying by MASS the basic selenate and sulfate at the highest magnetic field strength readily available to us (11.7 T) in order to reduce the second-order broadening of the $(\frac{1}{2}, -\frac{1}{2})$ transition as much as possible. Results for the basic sulfate are given in Fig. 1A. One sharp resonance at 62.7 ± 0.3 ppm is seen, corresponding to the AlO_4 subunit of the tridecamer, in good agreement with the solution chemical shift of 62.5 ppm (5). Also present are a series of broad peaks, extending from -160 to 110 ppm. The Al(4) resonance remains fairly sharp at 8.45 and 3.52 T, Figs. 1B and C, but it becomes progressively shielded, the apparent chemical shift decreasing from 62.0 ± 0.4 to 59.8 ± 1 ppm, due to second-order quadrupolar effects. However, far more dramatic changes occur for the second set of spectral features, which arise from the Al(6) sites, such that they become much broader at low field, in accord with previous observations of this system, and the basic aluminum chloride, by Müller *et al.* (1, 6). Essentially the same results are seen with the basic selenate.

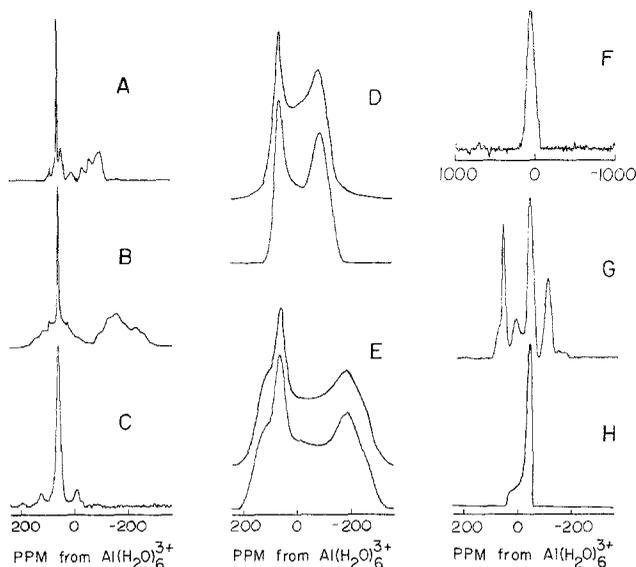


FIG. 1. Aluminum-27 NMR spectra of basic aluminum sulfate crystals. (A) 11.7 T, MASS NMR. (B) 8.45 T, MASS NMR. (C) 3.52 T, MASS NMR. (D) 11.7 T, static spectrum (below) together with its computer simulation (top). (E) 8.45 T, static spectrum (below), together with its computer simulation (top). (F) 3.52 T, static spectrum. (G) 11.7 T, 75° VASS NMR spectrum. (H) Simulation of the Al(6) centerband in (G).

These results clearly indicate that the Al(4) sites in the basic aluminum salts all have quite small quadrupole coupling constants, while for the Al(6) sites, the couplings are much larger. For the Al(4) sites, the second-order quadrupole-induced shifts (δ) from the isotropic value are related to e^2qQ/h as

$$\delta \text{ (ppm)} \approx 6(1 + \eta^2/3)(e^2qQ/h\nu_0)^2 10^3 \quad [1]$$

where ν_0 is the Larmor frequency ($1I$). For $\eta = 0$, least-squares analysis of the shift data using Eq. [1] yields $e^2qQ/h = 0.8$ MHz for the basic aluminum sulfate.

The results for the basic aluminum selenate are very similar, reflecting the fact that although the two compounds have differences in their crystal symmetries (2), the dimensions of the $\text{Al}_{13}\text{O}_{40}$ groups in them are almost identical. For the selenate we obtained apparent chemical shifts of 62.7 ± 0.3 ppm (11.7 T), 62.0 ± 0.4 ppm (8.45 T), and 58.5 ± 1.0 ppm (3.52 T), yielding $e^2qQ/h = 1.0$ MHz. Note that although η is unknown, uncertainties in its value can cause at most a 15% error in determination of the quadrupole coupling constant. The isotropic chemical shifts of the two compounds, after correction for quadrupole effects, are 62.8 ± 0.3 ppm (sulfate) and 62.9 ± 0.3 ppm (selenate).

The overall breadth of the broad component in Fig. 1A suggested to us that the quadrupole coupling constants for the Al(6) sites in the tridecamer are very large. In such situations it may be preferable to use variable-angle sample-spinning techniques, or even static samples. Because of the apparent magnitude of e^2qQ/h , VASS spectra were expected to contain complex sideband patterns. Thus we first obtained static spectra of the basic selenate and sulfate at 11.7, 8.45, and 3.52 T, and results for the sulfate are shown in Figs. 1D–F.

At 11.7 T the observed lineshape and breadth are at first glance surprisingly similar to those expected for a single species with $e^2qQ/h \sim 10$ MHz and $\eta \sim 0$, and there is no well-resolved signal from the four-coordinate site. This apparent anomaly is, however, resolved at 8.45 T, Fig. 1E, where the width of the Al(6) resonance increases, and the Al(4) component is readily observed. Simulations of both spectra (shown directly above the experimental spectra) yield $e^2qQ/h = 10.2 \pm 0.5$ MHz, $\eta = 0.2 \pm 0.1$, and $\sigma_i = 8 \pm 5$ ppm (Table 1) for the Al(6) sites. Essentially identical results were obtained for the basic aluminum selenate (Table 1; spectra not shown). As expected, at 3.52 T, only the resonance from the AlO_4 subunit is observed, Fig. 1F, since the broadening of the Al(6) sites is ~ 100 kHz. We have thus observed, for the first time, the solid state ^{27}Al NMR spectra of the Al(6) sites in the $\text{Al}_{13}\text{O}_{40}$ tridecamer of basic aluminum selenate and sulfate. The Al(6)/Al(4) ratio of about 9:1 obtained from the computer simulations indicates that the intensity of the Al(4) resonance is increased by excitation of the satellite transitions because of the small e^2qQ/h value involved (12).

Finally, we show in Fig. 1G the 75° -VASS NMR spectrum of the basic aluminum sulfate at 11.7 T. Centerband peaks for the Al(4) and Al(6) sites are observable, and the corrected isotropic shift for Al(6) of 11 ± 3 ppm determined from the VASS spectrum (using $e^2qQ/h = 10.2$ MHz, $\eta = 0.2$) is in good agreement with that deduced from the static spectrum, Figs. 1D and E.

We now turn our attention to the basic aluminum silicate, zunyite $[\text{Al}_{13}(\text{OH}, \text{F})_{16}\text{F}_2]\text{Si}_5\text{O}_{20}\text{Cl}$, which consists of an Al_{13} cluster much as in the basic aluminum

TABLE I

Quadrupole Coupling Constants, Asymmetry Parameters, and Isotropic Chemical Shifts for Basic Aluminum Selenate, Sulfate, and Silicate (Zunyite)

Site	e^2qQ/h (MHz) ^a	η^b	σ_i (ppm) ^c
Basic aluminum selenate, Na[AlO ₄ · Al ₁₂ (OH) ₂₄ (H ₂ O) ₁₂](SeO ₄) ₄ · 13H ₂ O			
Al(4)	1.0 ± 0.2 ^d		62.9 ± 0.3
Al(6)	10.3 ± 0.5 ^e	0 ± 0.1	8 ± 5
Basic aluminum sulfate, Na[AlO ₄ · Al ₁₂ (OH) ₂₄ (H ₂ O) ₁₂](SO ₄) ₄ · 13H ₂ O			
Al(4)	0.8 ± 0.2 ^d		62.8 ± 0.3
Al(6)	10.2 ± 0.5 ^e	0.2 ± 0.1	8 ± 5
Zunyite (basic aluminum silicate), [AlO ₄ · Al ₁₂ (OH, F) ₁₆ F ₂](Si ₅ O ₂₀)Cl			
Al(4)	0.6 ± 0.1 ^f		72 ± 1.0
Al(6)	2.2 ± 0.5 ^d		8 ± 1.0

^a Quadrupole coupling constant, in megahertz.

^b Asymmetry parameter of electric field gradient tensor.

^c Isotropic chemical shift, in ppm from an external sample of 1 M Al(H₂O)₆Cl₃ in H₂O at 23°C.

^d Obtained from the field dependence of the chemical shift, assuming $\eta = 0$.

^e Obtained by computer simulation of the static ²⁷Al NMR lineshape at 11.7 and 8.45 T.

^f Obtained from observation of the satellite transitions in MASS spectra, assuming $\eta = 0$.

selenate or sulfate, and an unusual tetrahedral Si₅ silicate unit, containing linear Si–O–Si bonds (3, 13). ²⁷Al MASS NMR spectra of zunyite have been reported previously by von Lampe *et al.* (1), who were the first to note that both Al(4) and Al(6) sites could be observed in this material (at about 70 MHz), while under essentially the same conditions the Al(6) sites in the basic chloride and sulfate were broadened beyond detection.

To estimate e^2qQ/h values for both Al(4) and Al(6) for comparison with the results obtained above, we recorded MASS NMR spectra of zunyite at 11.7, 8.45, and 3.52 T, and typical results are shown in Figs. 2A–C. Our results are consistent with those of von Lampe *et al.* (1) and show an Al(4) resonance at 72 ± 1 ppm, together with a much broader resonance due to Al(6) which appears at 6.6 ± 0.5 ppm (11.7 T), 4.0 ± 1 ppm (8.45 T), 0 ± 1 ppm (7 T, Ref. (1)), and –10 ± 3 ppm (3.52 T). Weighted least-squares analysis of these results using Eq. [1] yields $e^2qQ/h = 2.2 ± 0.5$ MHz (assuming $\eta = 0$). The Al(4) resonance does not show any measurable second-order quadrupole-induced shift at various fields and hence e^2qQ/h could not be obtained from Eq. [1]. However, we were able to measure directly the overall spectral breadth by following the spinning sidebands of the satellite transitions as a function of carrier offset, yielding an e^2qQ/h of 0.6 ± 0.1 MHz. This value is close to the 0.8–1.0 MHz found with the basic selenate and sulfate, due presumably to the highly “buried” nature of the AlO₄ subunit, and lack of influence of the peripheral ligands on e^2qQ/h . We shall now attempt to more fully analyze these results in terms of the structures of the species involved.

For octahedral aluminum, it has been suggested by others (14) that there is a

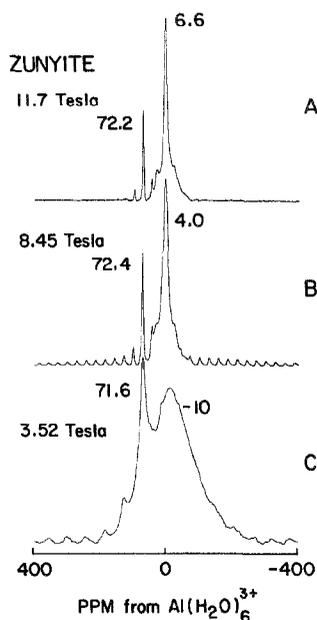


FIG. 2. Aluminum-27 MASS NMR spectra of basic aluminum silicate (zunyite) crystals at (A) 11.7 T, (B) 8.45 T, and (C) 3.52 T. The spectrum in A is $\sim 1^\circ$ from the "magic-angle." This broadens the spinning sidebands (SSB) which arise from the satellite transitions, seen clearly in (B).

good correlation between the quadratic elongation of the octahedron, which has been used as a measure of polyhedral distortion, and e^2qQ/h values. The longitudinal strain $|\alpha|$ has been defined as

$$|\alpha| = \sum_{i=1}^6 |\ln(l_i/l_0)| \quad [2]$$

where l_i are the individual Al–O bond lengths and l_0 is the ideal bond length for a perfect octahedron having the same volume as the actual coordination polyhedron. For Al(6) in the basic selenate we obtain $|\alpha| = 0.164$ from the X-ray distances (2), which yields an e^2qQ/h of 9.5 MHz, which is in good agreement with the e^2qQ/h value obtained in the present study. Such type of distortion has been suggested by von Lampe *et al.* to be a significant contributor to the field gradients in the basic aluminum sulfate and chloride. However, for zunyite we obtain $|\alpha| = 0.120$, which corresponds to an e^2qQ/h value of 7.3 MHz, almost three times that observed experimentally. We thus tend to favor a second possible explanation for the very large differences in e^2qQ/h found between the basic sulfate (selenate) and zunyite, which rests on a symmetry argument.

Zunyite, to a first approximation, has three OH^- (or F^-) ligands per Al(6), together with three shared O^{2-} groups, which are all in a *facial* arrangement. For such a *fac*- MA_3B_3 grouping, the results of point dipole calculations yield, perhaps surprisingly, a zero electric field gradient at the metal (M) site, assuming that the bonds coincide with the cubic axes of an octahedron and that all M–A bonds have

the same length, as do all M–B bonds. The calculation is independent of the charges on A or B (15). Thus, generation of a field gradient at Al(6) in zunyite may be thought of as due to deviations from the perfect *fac*-Al(OH)₃(O)₃ bonding scheme, due presumably to coordination of one O²⁻ to Al(4) while the other two are shared with Si(4) in the Si₃ anion. In the basic sulfate, there are four OH⁻, one O²⁻, and one H₂O ligand, which (as noted by von Lampe *et al.*) yields a large field gradient at aluminum.

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