

# The Effects of Hydrolysis and Oligomerization upon the NMR Shieldings of $\text{Be}^{+2}$ and $\text{Al}^{+3}$ Species in Aqueous Solution

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The  $^9\text{Be}$  and  $^{27}\text{Al}$  NMR shieldings have been calculated for the species  $\text{Be}(\text{OH})_4^{+2}$ ,  $\text{Be}(\text{OH})_3\text{OH}^{+1}$ ,  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$ ,  $\text{Be}_2(\text{OH})_2(\text{OH}_2)_4^{+2}$ ,  $\text{Be}_2(\text{OH})(\text{OH}_2)_6^{+3}$ ,  $\text{Al}(\text{OH})_6^{+3}$ ,  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$ , and  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  using a 6-31G\* basis set and the gauge-including atomic orbital (GIAO) method. Our results indicate that although hydrolysis deshields the Be and Al nuclei, oligomerization shields them. Since experiment indicates that the most stable  $\text{Be}^{+2}$  and  $\text{Al}^{+3}$  species in aqueous solution at moderate concentration and pH are  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  and  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$ , respectively, which are both hydrolyzed and oligomerized, their shieldings are little different from those of their unhydrolyzed, unpolymerized parent species  $\text{Be}(\text{OH})_4^{+2}$  and  $\text{Al}(\text{OH})_6^{+3}$ . The calculated deshielding of  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  with respect to  $\text{Be}(\text{OH})_4^{+2}$  is only 0.8 ppm (compared to 0.61 ppm observed experimentally) while the calculated deshielding of  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  compared to  $\text{Al}(\text{OH})_6^{+3}$  is 2.1 ppm (compared to 3.5 ppm observed experimentally). The corner sharing Be dimer,  $\text{Be}_2(\text{OH})(\text{OH}_2)_6^{+3}$  is about 0.1 ppm more strongly shielded than  $\text{Be}(\text{OH})_4^{+2}$ . The hydrolyzed monomeric species  $\text{Be}(\text{OH})_3\text{OH}^{+1}$  and  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  are calculated to be deshielded by 1.97 and 8.8 ppm, respectively, vs their parent ions. Such species may be observable at very low concentration, but their quadrupole coupling constants are large and they may have large linewidths. Calculated changes in average  $^1\text{H}$  NMR shieldings for the hydrolyzed, oligomerized species derived from aqueous  $\text{Be}^{+2}$  are also in accord with experimental NMR data. Calculated energetics for the formation of oligomeric species from the hydrolyzed ions are consistent with the greater relative stability of oligomerized species in the Be case compared to Al. © 1998 Academic Press

## INTRODUCTION

It is well known that hydrolysis of  $\text{Be}^{+2}$  in aqueous solution leads to the formation of oligomeric products, even for very dilute solutions (1). Oligomeric species also result from the hydrolysis of  $\text{Al}^{+3}$ , but at reasonably low concentrations monomeric species are also observed (2). Early  $^{17}\text{O}$  NMR studies using low magnetic fields were able to distinguish water coordinated to cations such as  $\text{Al}^{+3}$  from bulk water but were unable to characterize any hydrolysis products (3). Later  $^1\text{H}$  NMR studies on aqueous  $\text{Be}^{+2}$  were able to characterize a number of hydrolyzed and polymerized species (4), including

one consistent with a formulation as “[ $\text{Be}(\text{OH})_3$ ]” or  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$ . However, the  $^9\text{Be}$  NMR from the same study showed only a single narrow peak, identified with the parent ion  $\text{Be}(\text{OH})_4^{+2}$ , on top of a possible broader resonance. Fortunately the species  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  has recently been synthesized (as its picrate salt) and characterized by both x-ray diffraction and  $^9\text{Be}$  solution NMR (5). It was found to be deshielded by only 0.61 ppm, with respect to  $\text{Be}(\text{OH})_4^{+2}$ .

A species formulated as “ $\text{Al}(\text{OH})^{+2}$ ” and thought to be the monomer, deshielded by 3.5 ppm with respect to  $\text{Al}(\text{OH}_2)_6^{+3}$ , has recently been characterized by  $^{27}\text{Al}$  solution NMR (6a). A species with a deshielding reported as about 4.2 ppm was earlier formulated as a “ $\text{Al}_2(\text{OH})_2^{+4}$ ” dimer (6b). A related species, formulated as “AlF,” is deshielded by only 0.7 ppm from  $\text{Al}(\text{OH}_2)_6^{+3}$  (6c). In the course of a study of water exchange on  $\text{Al}(\text{OH}_2)_6^{+3}$  and related species (7) we calculated the  $^{27}\text{Al}$  NMR shieldings of the species  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  and found that it was deshielded with respect to  $\text{Al}(\text{OH}_2)_6^{+3}$  by about 9 ppm, rather than 3.5 ppm. This suggested that the species studied experimentally was not the monomer, and we therefore decided to consider alternative oligomeric species.

Consequently we have calculated the structures, energetics, NMR shieldings, and nuclear quadrupole coupling constants for a series of hydrolysis and oligomerization products of the aqueous  $\text{Be}^{+2}$  and  $\text{Al}^{+3}$  ions.

## COMPUTATIONAL METHODS

Modern quantum chemical methods are able to reproduce structures and reaction energies very accurately for small molecules composed of light atoms in the gas phase (8, 9). The basic procedure for gas phase molecules is to solve an approximate version of the Schrödinger equation, typically the Hartree–Fock or the Kohn–Sham equation, to high accuracy.

Evaluating the properties of species in solution is much more difficult, but is a current focus of interest in quantum chemistry (10, 11). For solution species the most serious problem is the representation of the interaction of the solute with the solvent. This is particularly true for the case of ions. There are several general schemes for evaluating the structures, energetics, and properties of ions in solution, including (1) a polarizable con-

**TABLE 1**  
**The  $^9\text{Be}$ ,  $^{17}\text{O}$ , and  $^1\text{H}$  NMR Shieldings (in ppm) Calculated for Be Aquo and Hydroxo Complexes Using the 6-31G\* Basis Set, the GIAO Method, and 6-31G\* Optimized Geometries**

Molecule	$\sigma^{\text{Be}}$	$\sigma^{\text{O}}$	$\sigma^{\text{H}}$
$\text{Be}(\text{OH}_2)_4^{+2}$	119.98 115.33 <sup>a</sup> 112.66 <sup>b</sup>	313.4–321.7 (H <sub>2</sub> O)	27.2–27.5 (H <sub>2</sub> O) av. 27.3
$\text{Be}(\text{OH}_2)_3\text{OH}^{+1}$	118.01 113.32 <sup>a</sup> 111.21 <sup>b</sup>	312.0–315.0 (H <sub>2</sub> O) 325.1 (OH)	28.3–28.9 (H <sub>2</sub> O) 31.1 (OH) av. 29.0
$\text{Be}_2(\text{OH})_2(\text{OH}_2)_4^{+2}$	119.10	318.3 (OH) 328.7 (H <sub>2</sub> O)	28.2 (H <sub>2</sub> O) 30.1 (OH) av. 28.8
$\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$	119.21	321.9 (OH) 315.7 (H <sub>2</sub> O)	28.1 (H <sub>2</sub> O) 30.7 (OH) av. 29.0
$\text{Be}(\text{OH}_2)_4 \dots 6\text{H}_2\text{O}^{+2}$	119.41	310.2–317.4 (central H <sub>2</sub> O)	23.4–29.4 (H <sub>2</sub> O)
$\text{Be}(\text{OH}_2)_3\text{OH} \dots 6\text{H}_2\text{O}^{+1}$	117.78	300.8–317.2 (central H <sub>2</sub> O) 329.6 (OH)	24.6–29.4 (H <sub>2</sub> O) 30.3 (OH)
$\text{Be}_2(\text{OH})(\text{OH}_2)_6^{+3}$	120.06	319.1 (OH) 300.7–302.7 (H <sub>2</sub> O)	27.2–28.3 (H <sub>2</sub> O) 30.2 (OH) av. 28.1
$\text{Be}(\text{OH})_4^{-2}$	117.61	313.3–314.0 (OH)	35.4 (OH)

<sup>a</sup> 6-311G(2d, p).

<sup>b</sup> BLYP.

tinuum model, in which the polarization of the bulk solvent by the charge distribution of the solute is evaluated; (2) the supermolecule approach, in which the solute and several explicit solvent molecules surrounding it are treated quantum mechanically; and (3) simulation techniques, in which many solvent molecules interact with the solute through pair or high order potentials, calculated quantum mechanically or fitted to experiment (see Ref. (10) for representative studies). In the present study on  $\text{Al}^{+3}$  and  $\text{Be}^{+2}$  complexes we employ a supermolecule approach.

We have optimized geometries of the gas phase ions at the Hartree–Fock 6-31G\* level, without symmetry constraints for all the monomeric species, using the program GAMESS (12). For the dimeric species we have generally employed symmetry constraints, e.g.,  $D_{3h}$  for  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$ . NMR shieldings for all the species have been evaluated using the 6-31G\* basis and the GIAO (gauge-including atomic orbital) method (13) as implemented in the program GAUSSIAN94 (14). To evaluate the hydration energies of the ions we have used the Rashin and Honig (15) reformulation of the Born model, as explained further below. This is a considerably less accurate approach to solution energetics than in some of our previous studies (16), but our emphasis here is upon the NMR properties of the species considered.

For some of the species we have also calculated the NMR shieldings using the more flexible 6-311(2d, p) basis set (8) or

a density functional approach known as BLYP (17). Several groups are systematically exploring the relative value of Hartree–Fock and density functional theory for the evaluation of NMR shieldings (18), but our goal is simpler—we merely wish to establish that our calculated shielding trends are reasonably insensitive to the basis set or computational method. Electric field gradients at Be and Al have also been calculated with the 6-31G\* basis using GAMESS.

## RESULTS

Calculated  $^9\text{Be}$ ,  $^{17}\text{O}$ , and  $^1\text{H}$  shieldings for the Be species are presented in Table 1 and  $^{27}\text{Al}$  NMR shieldings for the Al species are presented in Table 2. Calculated electric field gradients and nuclear quadrupole coupling constants at Be or Al for some of the species are shown in Table 3. The calculated structures of  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  and  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  are shown in Fig. 1. The calculated Be–OH and Be–OH<sub>2</sub> bond distances in  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  of 1.592 and 1.711 Å, respectively, are in reasonably good agreement with the experimental values of 1.580–1.601 and 1.644–1.672 Å, respectively, for the range of Be–OH and Be–OH<sub>2</sub> distances (5) while the calculated Al–OH and Al–OH<sub>2</sub> distances of 1.904 and 1.970 Å, respectively, are in reasonable agreement with experimental values of 1.85–1.87 and 1.88–1.95 Å, respectively (19).

The reference for  $^9\text{Be}$  NMR in solution studies is usually  $\text{BeSO}_4(\text{aq})$  at low concentration. All evidence indicates that the dominant species in such solutions at low pH is  $\text{Be}(\text{OH}_2)_4^{+2}$ . When the pH is increased this species hydrolyzes and oligomerizes. Solubility and potentiometric studies indicate that two additional species are initially formed, “ $\text{Be}_2(\text{OH})^{+3}$ ” and “ $\text{Be}_3(\text{OH})_3^{+3}$ ” (1). We formulate these species as  $\text{Be}_2(\text{OH})(\text{OH}_2)_6^{+3}$  and  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$ . As noted above the

**TABLE 2**

**The  $^{27}\text{Al}$  NMR Shieldings (in ppm) Calculated Using the 6-31G\* Basis Set, the GIAO Method, and 6-31G\* Optimized Geometries**

Molecule	$\sigma^{\text{Al}}$
$\text{Al}(\text{OH}_2)_6^{+3}$	637.3 (632.2 <sup>a</sup> , 615.2 <sup>b</sup> , 602.6 <sup>c</sup> )
$\text{Al}(\text{OH}_2)_6^{+3} \dots 12\text{H}_2\text{O}$	631.5
$\text{Al}(\text{OH})_4^{-1}$	548.1 (522.0 <sup>b</sup> , 499.9 <sup>c</sup> )
$\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$	628.5
$\text{Al}(\text{OH}_2)_5\text{OH}^{+2} \dots 12\text{H}_2\text{O}$	620.9
$\text{Al}(\text{OH}_2)_5(\text{OH})\text{H}_3\text{O}^{+3}$	625.6
$\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$	635.2
$\text{Al}(\text{OH}_2)_3\text{F}^{+2}$	631.3
$\text{Al}_2\text{F}_2(\text{OH}_2)_8^{+4}$	638.7

<sup>a</sup> Evaluated at geometry optimized using 6-31G\* SCF energy plus Born energy.

<sup>b</sup> 6-311(2d, p) GIAO at 6-31G\* optimized geometry.

<sup>c</sup> BLYP GIAO calculation with 6-31G\* basis set at 6-31G\* optimized geometry.

TABLE 3

Calculated Values of the Electric Field Gradient at Be and Al,  $eq_M$  (in au), and the Be and Al Nuclear Quadrupole Coupling Constants,  $e^2q_MQ_M/h$  (in MHz)

Molecule	$eq_M$	$e^2q_MQ_M/h$
$Be(OH_2)_4^{+2}$	0.0062	0.07
$Be(OH_2)_3OH^{+1}$	0.0885	1.02
$Be_2OH(OH_2)_6^{+3}$	0.0368	0.42
$Be_3(OH)_3(OH_2)_6^{+4}$	0.0331	0.38
$Al(OH_2)_6^{+3}$	0 ( $T_h$ symmetry)	0
$Al(OH_2)_5OH^{+2}$	0.4144	12.46
$Al_2(OH)_2(OH_2)_8^{+4}$	0.1930	5.80

Note. Nuclear quadrupole moments from Ref. (21).

$^9Be$  NMR of  $Be_3(OH)_3(OH_2)_6^{+3}$  in solution was determined to be 0.61 ppm, vs the  $Be(H_2O)_4^{+2}$  reference, which compares well with the calculated difference in Table 1 of 0.77 ppm. The monomeric species  $Be(OH_2)_3OH^{+1}$  is more strongly deshielded, with a difference from the reference parent ion of 1.97 ppm. The edge sharing dimer  $Be_2(OH)_2(OH_2)_4^{+2}$  is deshielded by 0.88 ppm compared to the reference while the corner sharing dimer  $Be_2(OH)(OH_2)_6^{+3}$  (in which each Be is bonded to one -OH and three  $-OH_2$ ) is actually shielded by 0.08 ppm compared to the reference.

We have considered the stability of our calculated shielding differences with respect to the basis set and computational method. The calculated shielding difference between  $Be(OH_2)_4^{+2}$  and  $Be(OH_2)_3OH^{+1}$  only changes from 1.97 to 2.01 ppm if we expand the basis set to 6-311(2d, p), while increasing to 2.41 ppm if we use the BLYP rather than the HF method. The use of BLYP rather than HF often leads to somewhat increased chemical shifts (18). In any case, the effect of more flexible basis and density functional rather than HF methodology on the shielding difference is fairly small. We have also considered the effect of some increase in the size of the model molecule. If we coordinate six  $H_2O$  molecules to each of the monomeric species to form supermolecules (i.e.,  $Be(OH_2)_4(OH_2)_6^{+2}$  and  $Be(OH_2)_3OH(OH_2)_6^{+1}$ , their  $^9Be$  shielding difference is reduced only slightly to 1.65 ppm. Thus the  $Be(OH_2)_3OH^{+1}$  species is clearly much more strongly deshielded than either its parent or the hydrolyzed dimer.

The changes in shielding for the Be compounds are all quite small, since the changes in electron density at Be are small and the energetic separation of occupied and empty orbitals is large. Nonetheless, the trends are the same as those observed for Al or for nuclides forming more covalent compounds, such as Si. Substitution of  $-OH_2$  by  $-OH$  deshields the nuclide, while oligomerization of the species increases its shielding. For example, the  $Be(OH)_4^{-2}$  ion, formed in highly alkaline solution, is calculated to be deshielded by about 2.4 ppm, compared to  $Be(OH_2)_4^{+2}$ . There even seems to be the same dependence of the shielding on ring size, as found in silicates and siloxanes (20), with the 2-ring  $Be_2(OH)_2 \dots$  species showing a slightly

smaller shielding than the 3-ring  $Be_3(OH)_3 \dots$  species. The  $Be_2(OH)(OH_2)_6^{+3}$  species is actually shielded compared to the parent unhydrolyzed species since only one  $-OH_2$  has been replaced by  $-OH$ , and that  $-OH$  is in a bridging position.

We also show in Table 1 calculated  $^{17}O$  and  $^1H$  NMR shieldings for the Be species. O NMR shieldings have not been determined for this system but we present calculated values in Table 1 for completeness. Note that the  $^{17}O$  NMR shieldings for the OH and  $H_2O$  groups depend fairly strongly upon the particular molecule. Proton NMR studies on the hydrolysis of aqueous  $Be^{+2}$  (4) show three resonances (A, B, and C in Fig. 1 of Ref. (4)) which were assigned on the basis of intensities to Be species with 4, 3, and 2 waters per Be, i.e.,  $Be(OH_2)_4^{+2}$ ,  $Be_2(OH)(OH_2)_6^{+3}$ , and  $Be_3(OH)_3(OH_2)_6^{+3}$ , respectively. The calculated average  $^1H$  shieldings for these species are 27.3, 28.1, and 29.0 ppm, with the parent ion most deshielded, which are quite consistent with the experimental results. This lends further support to the assignment of the trimer as an important species in solution.

The first point to notice in the calculated Al NMR shieldings in Table 2 is that we obtain a value for the shielding difference of Al in  $Al(OH_2)_6^{+3}$  and  $Al(OH)_4^{-1}$  which is quite close to the value of 80 ppm observed experimentally (see, e.g., (6a)). Using 6-31G\* SCF geometries for the free gas-phase ions and the GIAO method with a 6-31G\* basis set the calculated difference is 89 ppm. Correcting the calculated Al-O distances in  $Al(OH_2)_6^{+3}$  and  $Al(OH_2)_4^{-1}$  for the Born energy (which

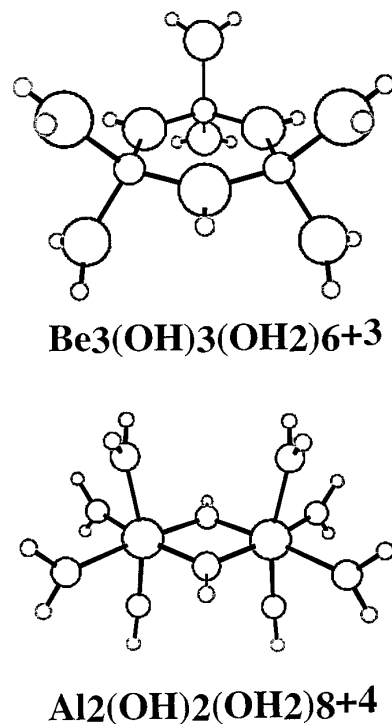


FIG. 1. Calculated geometries for the oligomeric species  $Be_3(OH)_3(OH_2)_6^{+3}$  and  $Al_2(OH)_2(OH_2)_8^{+4}$ . Atoms in order of decreasing size are Al, O, Be, and H.

contracts both ions but has a much larger effect for  $\text{Al}(\text{OH}_2)_6^{+3}$  we obtain a difference of about 84 ppm, as indicated in Table 2. Deprotonation of  $\text{Al}(\text{OH}_2)_6^{+3}$  to form the monomeric species  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  deshields the Al by about 9 ppm. In the dimeric species  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$ , however, the Al is deshielded by only 2.1 ppm compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ . Thus, we can see that deprotonation and oligomerization have effects on the shielding which are of opposite sign and similar size. This indicates that the species “ $\text{Al}(\text{OH})^{+2}$ ” reported by Faust *et al.* (6a) as deshielded by 3.5 ppm compared to  $\text{Al}(\text{OH}_2)_6^{+3}$  was primarily the dimer. Akitt and Mann (6b) reported a species deshielded by about 4.2 ppm compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ , which they identified as the  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  dimer. It is possible that the experimental value of Ref. (6a) actually represents an average of the monomer and dimer contributions.

We have considered several other interpretations for the small experimental shielding difference of “ $\text{Al}^{+3}$ ” and “ $\text{Al}(\text{OH})^{+2}$ .” First, we expanded the basis set from 6-31G\* to 6-311(2d, p) and replaced the Hartree–Fock approach by BLYP. These changes increased the difference in shielding of  $\text{Al}(\text{OH}_2)_6^{+3}$  and  $\text{Al}(\text{OH})_4^{-1}$  by 5–10 ppm. This indicates that the Hartree–Fock approach we have employed for all the species probably slightly *underestimates* the Al NMR shielding differences. Next we considered the effect of the Born energy upon the equilibrium geometry and the consequent change in the shielding. This effect is large and easy to evaluate for  $\text{Al}(\text{OH}_2)_6^{+3}$ , because of its high symmetry. For  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  the effect is harder to evaluate because of the lower symmetry but will certainly be of smaller magnitude because of the smaller charge (the Born energy scales as the charge squared). If we consider the Born energy effect only for  $\text{Al}(\text{OH}_2)_6^{+3}$ , reducing its shielding by about ppm, this effect would decrease the shielding difference of parent and hydrolyzed monomer to about 5 ppm. This is a lower limit since we have not corrected for  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  shielding for this Born effect, and our shielding difference is still larger than experiment. Incorporation of  $\text{Al}(\text{OH}_2)_6^{+3}$  or  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  into supermolecules with 12 waters reduces the  $^{27}\text{Al}$  shielding of each species but changes their shielding difference by only about 1 ppm. Associating the  $\text{H}_3\text{O}^+$  produced by the hydrolysis reaction with the  $\text{Al}(\text{OH}_2)_5\text{OH}^{+2}$  as a fragment of a second hydration sphere actually further deshields the hydrolyzed species, increasing its shielding difference compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ . Thus, the most reasonable explanation for the small shielding difference of the “ $\text{Al}^{+3}$ ” and “ $\text{Al}(\text{OH})^{+2}$ ” species is that the “ $\text{Al}(\text{OH})^{+2}$ ” species is the dimer  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$ .

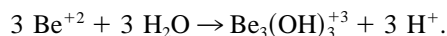
In the same way the  $\text{Al}(\text{OH}_2)_5\text{F}^{+2}$  species is calculated to be deshielded by about 6 ppm compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ , while the experimental difference of “ $\text{Al}^{+3}$ ” and “ $\text{AlF}^{+2}$ ” species is only about 0.7 ppm (6c). Indeed, the dimeric species  $\text{Al}_2\text{F}_2(\text{OH}_2)_8^{+4}$  is actually calculated to be shielded compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ . This suggests that “ $\text{AlF}^{+2}$ ” actually occurs mainly in the form of the dimer. Replacement of -OH- by -F- increases the Al shielding, in both the monomer and the dimer.

**TABLE 4**  
Calculated Energetics (in Hartree Atomic Units) for Hydrolysis and Polymerization Reactions in Solution

Reaction	$\Delta E_{\text{SCF}}$	Born hydration energy	Estimated $\Delta E_{\text{solution}}$
$3 \text{Be}(\text{OH}_2)_4^{+2} \rightarrow \text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3} + 3 \text{H}_2\text{O} + 3\text{H}^+$	+0.8318	-0.807	0.025
$3 \text{Be}(\text{OH}_2)_3\text{OH}^{+1} \rightarrow \text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3} + 3 \text{H}_2\text{O}$	+0.2348	-0.276	-0.041
$2 \text{Be}(\text{OH}_2)_3\text{OH}^{+1} \rightarrow \text{Be}_2(\text{OH})_2(\text{OH}_2)_4^{+2} + 2 \text{H}_2\text{O}$	+0.0948	-0.095	0.00
$2 \text{Al}(\text{OH}_2)_5\text{OH}^{+2} \rightarrow \text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4} + 2 \text{H}_2\text{O}$	+0.3917	-0.314	+0.078

As seen in Table 3, the nuclear quadrupole coupling constants at Be are quite small for  $\text{Be}(\text{OH})_4^{+2}$  but are somewhat larger for the oligomeric species,  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$ , and much larger for the monomer  $\text{Be}(\text{OH}_2)_3\text{OH}^{+1}$ . The increased coupling constants for the hydrolyzed species would produce larger linewidths and make accurate determination of their NMR shieldings difficult. A similar change is seen between the parent, hydrolyzed, and oligomerized Al species. Consequently seeing the hydrolyzed monomeric species in solution NMR will be difficult.

We can also evaluate approximate energetics for some hydrolysis and oligomerization reactions in solution, as shown in Table 4. For a rigorous calculation of the solution energetics we would need to evaluate the gas phase reaction energies at a higher level, perhaps Moller–Plessett 2nd order perturbation theory, calculate the vibrational frequencies for the species so as to evaluate zero-point vibrational, enthalpic, and entropic contributions, and evaluate the hydration energies using a polarizable continuum approach, as in our earlier studies (16). For the present we consider only gas phase energies at the SCF level, with the hydration energies estimated as simply the Born energies for the ions, using the method of Rashin and Honig (15). The calculated energy change for the first reaction is about 16 kcal/mol, which agrees fortuitously well with the experimental enthalpy of +16.0 kcal/mol for a reaction given by Mesmer and Baes (1) as



The other three calculated reaction energies in Table 4 indicate that the formation of the  $\text{Be}_3(\text{OH})_3(\text{OH}_2)_6^{+3}$  species from hydrolyzed  $\text{Be}^{+2}$  is somewhat more favorable than is formation of the  $\text{Be}_2(\text{OH})_2(\text{OH}_2)_4^{+2}$  species and that  $\text{Be}^{+2}$  oligomerization is considerably more favorable than is  $\text{Al}^{+3}$  oligomerization. The calculated energetics are therefore qualitatively consistent with experiment, although the accuracy of the present approach to energetics is probably not very high.

## CONCLUSION

Hydrolysis and oligomerization have opposite effects upon the shielding of  $\text{Be}^{+2}$  and  $\text{Al}^{+3}$  in aqueous solution. The small deshieldings of the oligomeric hydrolysis products of  $\text{Be}^{+2}$  and  $\text{Al}^{+3}$ , with respect to the parent cations, provide very strong evidence for the presence of these oligomeric species. If we assume that the calculated shieldings are highly accurate, it appears that the observed deshielding of " $\text{Al}(\text{OH})^{+2}$ ," may actually be a weighted average, with some contribution from the more strongly deshielded monomeric species. Calculated nuclear quadrupole coupling constants are quite large for the hydrolyzed monomeric species, suggesting that their solution linewidths may be large. SCF values for gas phase reaction energies with corrections for Born hydration effects correctly predict that  $\text{Be}^{+2}$  hydrolyzed species will oligomerize more strongly than  $\text{Al}^{+3}$  species.

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## REFERENCES

1. R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.* **6**, 1951 (1967).
2. C. R. Frink and M. Peech, *Soil Sci.* **20**, 346 (1962).
3. J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.* **32**, 553 (1960).
4. J. W. Akitt and R. H. Duncan, *J. C. S. Faraday Trans. I* **76**, 2212 (1980).
5. F. Cecconi, C. A. Ghilardi, S. Midollini, and A. Orlandini, *Inorg. Chem.* **37**, 146 (1998).
6. (a) B. C. Faust, W. B. Labioso, K. H. Dai, J. S. MacFall, B. A. Browne, A. A. Ribeiro, and D. D. Richter, *Geochim. Cosmochim. Acta* **59**, 2651 (1995); (b) J. W. Akitt and B. E. Mann, *J. Magn. Reson.* **44**, 584 (1981); (c) J. W. Akitt and J. M. Elders, *J. Chem. Soc. Faraday Trans. I* **81**, 1923 (1985).
7. B. L. Phillips, J. A. Tossell, and W. H. Casey, submitted for publication.
8. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, "Ab Initio Molecular Orbital Theory," Wiley, New York (1986).
9. J. B. Foresman and A. Frisch, "Exploring Chemistry with Electronic Structure Methods," Gaussian, Inc., Pittsburgh, Pennsylvania (1993).
10. C. J. Cramer and D. G. Truhlar (Eds.), "Structure and Reactivity in Aqueous Solution: Characterization of Chemical and Biological Systems," Am. Chem. Soc., Washington, DC (1994).
11. K. B. Wiberg, H. Castejon, and T. A. Keith, *J. Comput. Chem.* **17**, 185 (1996).
12. M. W. Schmidt *et al.*, *J. Comput. Chem.* **14**, 1347 (1993).
13. K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990).
14. M. J. Frisch *et al.*, "GAUSSIAN94, Rev. B.3," Gaussian, Inc., Pittsburgh, Pennsylvania (1994).
15. A. A. Rashin and B. Honig, *J. Phys. Chem.* **89**, 5588 (1985).
16. J. A. Tossell, *Geochim. Cosmochim. Acta* **61**, 1613 (1997).
17. A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
18. (a) J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, *J. Chem. Phys.* **102**, 5497 (1996); (b) L. Olsson and D. Cremer, *J. Phys. Chem.* **100**, 16881 (1996).
19. G. Johansson, *Acta Chem. Scand.* **16**, 403 (1962).
20. J. A. Tossell, *J. Noncryst. Solids* **120**, 13 (1990).
21. J. Mason (Ed.), "Multinuclear NMR," Plenum, New York (1987).