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## Calculation of the structural and NMR properties of the tridecameric $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ polycation

J. A. TOSSELL\*

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

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**Abstract**—The aluminum tridecameric polyoxocation,  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  is a major component in partially hydrolyzed  $\text{Al}^{+3}(\text{aq})$  solutions and has been extensively studied experimentally, mainly using NMR techniques. I have calculated the equilibrium geometry of this cation using the Hartree-Fock method and a polarized double-zeta effective core potential basis set, obtaining bond distances which agree well with X-ray crystallographic studies of selenate and sulfate salts of the polycation (Al[4]:  $4 \times 1.85 \text{ \AA}$  calc,  $4 \times 1.84 \text{ \AA}$  exp; Al[6]:  $4 \times 1.85$ ,  $2 \times 2.05 \text{ \AA}$  calc,  $2 \times 1.84$ ,  $2 \times 1.88$ , 1.91, 2.04  $\text{ \AA}$  exp [where the numbers in brackets indicate the coordination numbers]). I have also calculated electric field gradients and NMR shielding constants at all the atoms using the standard 6-31G\* basis set and Hartree-Fock and hybrid Hartree-Fock-density functional (B3LYP) techniques. Using the Hartree-Fock method, the central four-coordinate Al is calculated to be deshielded by  $\sim 56$  ppm, and the six-coordinate Al atoms by  $\sim 16$  ppm, vs. the  $\text{Al}(\text{OH})_2^{+3}$  reference, compared to experimental shifts of 63 and 12 ppm, respectively. The central Al[4] is thus shielded by  $\sim 20$  ppm with respect to the tetrahedral monomer  $\text{Al}(\text{OH})_4^{-1}$ . Al-NMR shifts obtained from the B3LYP calculations are very similar. The calculated O-NMR shifts, vs. free gas-phase  $\text{H}_2\text{O}$ , are 17 ppm for the  $\eta\text{-OH}_2$  groups, 30 ppm for the  $\mu\text{-OH}$  and  $\mu\text{OH}'$  groups, and 55 ppm for the  $\mu_4\text{-O}$  group, which match well with the experimentally assigned shifts of 20, 30, and 55 ppm, respectively (vs. liquid  $\text{H}_2\text{O}$ ). The B3LYP method yields O shifts, which are systematically about 40 to 50% larger. It is not clear whether the discrepancies in the calculated O shifts vs. liquid water are a result of deficiencies in the model (neglect of the aqueous environment) or in the method (lack of correlation in the Hartree-Fock method). Studies on the  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  cation with small numbers of explicit waters hydrogen-bonded to it indicate that O shifts can be perturbed strongly by the presence of solvent. The calculated  $^{17}\text{O}$  nuclear quadrupole coupling constants, NQCC (using the 6–31G\* Hartree-Fock calibration factor of Ludwig et al., 1996 to relate electric field gradients to NQCC values) are 1.7 MHz for  $\mu_4\text{-O}$ , 7.8 to 8.0 MHz for the  $\mu\text{OH}$  and  $\mu\text{OH}'$  groups and 10.7 MHz for the  $\eta\text{OH}_2$  group. The  $\mu\text{OH}$  values are substantially higher than experimental values of 5 to 6 MHz observed for  $\text{Al}_2\text{OH}$  groups in Al oxyhydroxides. B3LYP values are very similar. However, hydrogen bonding to water in simple model compounds like  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  reduces the  $-\text{OH}$  NQCC values to  $\sim 6$  MHz. Copyright © 2001 Elsevier Science Ltd

### 1. INTRODUCTION

The aqueous solution chemistry of Al(III) is an old topic within solution chemistry, but the nature of the chemical species involved is still unresolved and of considerable interest. The chemical behaviour of Al(III) as well as its toxicity are dependent on its chemical speciation, which is characterized generally by its tendency to form strong oligomeric hydroxo complexes (Bottero et al., 1980; Tossell, 1998). The most familiar aqueous oligomer of Al is the “ $\text{Al}_{13}$ ” polyoxocation,  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ , which bears a resemblance to the structure of Al (hydr)oxides (Furrer et al., 1992). This “ $\text{Al}_{13}$ ” cation is an example of an  $\epsilon$ -Keggin structure, comprised of a central  $\text{AlO}_4$  tetrahedron surrounded by 12 octahedrally coordinated Al sharing edges. Each Al octahedron contains one water molecule and six of these deprotonate above  $\text{pH} = 6$ , leading to agglomeration and precipitation (Furrer et al., 1992). Four different oxygens can be distinguished in  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ : a single internal  $\mu_4\text{-O}$ , the 12 terminal  $\eta\text{-OH}_2$ , and two different types of  $\mu_2\text{-OH}$  within the total of 24 (Johansson, 1960). Previous  $^{27}\text{Al}$ -NMR studies have easily

distinguished the Al[4] and Al[6], although the NMR feature corresponding to Al[6] is quite broad (Kunwar et al., 1984). Similarly,  $^{17}\text{O}$ -NMR studies have distinguished the  $\eta\text{-OH}_2$ ,  $\mu_2\text{-OH}$ , and  $\mu_4\text{-O}$  signals (Thompson et al., 1987; Phillips et al., 2000). Recently, the rate of exchange with  $^{17}\text{O}$ -labeled  $\text{H}_2\text{O}$  has been determined for the different O sites. The fastest exchanging site is the  $\eta\text{-OH}_2$ , while the two different  $\mu_2\text{-OH}$  sites show significantly different water exchange rates and the  $\mu_4\text{-O}$  does not seem to exchange (Phillips et al., 2000). There has also been some study of both the mechanism of formation of the related  $\text{Ga}_{13}$  polyoxocation from simpler species (Michot et al., 2000) and of the agglomeration of the  $\text{Al}_{13}$  species (Vogels et al., 1995). There have also been efforts to prepare “substituted”  $\text{Al}_{13}$  species (Parker et al., 1997). Analogies have also been drawn between  $\text{Al}_{13}$  and the surfaces of various Al(hydr)oxides (Phillips et al., 2000).

I therefore felt that it would be useful to calculate some of the properties of this polycation at a reasonable quantum mechanical level. Although the molecular ion considered is certainly very large, it represents a feasible target for quantum mechanical methods of moderate rigour. I anticipated that such methods would be able to semiquantitatively match the experimental NMR data if the atomistic models proposed for this

\*(tossell@chem.umd.edu).

species were qualitatively correct. Such calculations would also provide a foundation for later work on the acid-base and other surface properties of the material and its interaction with the aqueous environment.

## 2. COMPUTATIONAL METHODS

I use the techniques of Hartree-Fock theory, Hartree-Fock perturbation theory, and density functional theory. The theoretical foundations and capabilities of these techniques are discussed in Hehre et al. (1986) and Jensen (1999). The basis sets used for the calculation of the equilibrium geometry were of the relativistic effective core potential type, as implemented by Stevens et al. (1992) (which I designate SBK), with polarization functions added on the non-H atoms. These basis sets neglect core electrons but properly describe their effects upon the valence electrons, with relativistic effects incorporated.

Geometry optimizations and calculations of electric field gradients at the nuclei and NMR shieldings were carried out using the quantum chemistry software packages GAMESS and GAUSSIAN 94 (Schmidt et al., 1993; Frisch et al., 1994). For calculation of the electric field gradients, EFGs ( $q$ ) at the nuclei, and the NMR shieldings ( $\sigma$ ), I use the all-electron 6-31G\* basis set (Hehre et al., 1986) and both the Hartree-Fock method and a hybrid Hartree-Fock density functional method known as B3LYP (Becke, 1992). This method has yielded good results for EFGs in a number of different systems (Bailey et al., 2000). In most cases the B3LYP values of  $q$  are only a few percent smaller than the HF values. NMR shieldings were calculated at the Hartree-Fock or B3LYP level using a 6-31G\* basis set and the GIAO method as implemented in GAUSSIAN 94 (Wolinski et al., 1992). The accuracy of the B3LYP approach to NMR shieldings is presently under debate. Although some researchers have obtained good results with B3LYP (e.g., Cheeseman et al., 1996; Casanovas et al., 1999), a comprehensive study of numerous gas-phase molecules using large basis sets has concluded that DFT shieldings are not as accurate as those obtained using correlated methods like MP2 and do not even offer a significant improvement over HF results (Wilson et al., 1999).  $^{17}\text{O}$ -NMR shifts ( $\delta$ ) were calculated relative to the calculated shielding for a single  $\text{H}_2\text{O}$  molecule optimized in the gas-phase using the same methodology, ignoring the gas-liquid shift of  $\sim 36$  ppm. Our rationale for using this gas-phase reference is discussed more fully in the "Results" section.  $^{27}\text{Al}$ -NMR shifts were calculated with respect to  $\text{Al}(\text{OH})_6^{+3}$ , as in our earlier work (Tossell, 1998). EFGs expressed in atomic units (au), were converted to NQCC values using nuclear quadrupole moments from Ludwig et al. (1996) for O and Kello et al. (1999) for Al. The molecular plots were drawn using the program, MacMolplt (Bode and Gordon, 1998).

Both polarized SBK and 6-31G\* basis sets are relatively small by contemporary quantum chemical standards, but for the  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  polycation they are the largest presently feasible. Using the 6-31G\* basis set, the calculation on  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  utilized 943 basis functions. Certainly such a highly charged cation would be strongly hydrated in aqueous solution, but for the present, we consider only the free gas-phase cation. However, we have studied the effect of hydration upon some of the calculated properties for the much smaller  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$  molecule, a dimeric model for the  $-\text{OH}$  and the  $-\text{OH}_2$  groups and the Al[6] of the tridecameric cation. In general, it is found that  $^{17}\text{O}$ -NMR shieldings and NQCC values are sensitive to solvent effects, particularly if the solvent is H-bonding. Recently, such solvent effects have been treated using supermolecule or microsolvation techniques with small numbers of explicit water molecules. For example, the recent results of Kowalewski et al. (2001) show large changes in the  $^{17}\text{O}$  shifts for the O atoms of methyl formate when a small number of explicit water molecules are included in the calculation.

## 3. RESULTS

Calculated and experimental geometries are compared in Table 1. The experimental distances are taken from a fairly old X-ray crystallographic study on the selenate salt of  $\text{Al}_{13}$  (Johansson, 1960). The calculated and experimental distances compare well, but there is some discrepancy for the Al[6] bond

Table 1. Calculated and experimental bond distances (in Å) in  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ .

Site	$R(\text{Al-O})_{\text{calc.}}$	$R(\text{Al-O})_{\text{exp.}}^a$
Al[4]	$4 \times 1.85$	$4 \times 1.84$
Al[6]	$4 \times 1.85$ $2 \times 2.05$	$2 \times 1.84, 2 \times 1.88$ 1.91, 2.04

<sup>a</sup> From Johansson, 1960.

distances to  $-\text{OH}_2$ . These bonds are weak and are on the periphery of the cluster, so they could be more strongly influenced by hydration or crystal packing forces. A plot of the molecular geometry of the  $\text{Al}_{13}$  polyoxocation is given in Figure 1, with the different Al and O sites labeled. Calculated values of Al-NMR shielding and shift, EFG, and NQCC are given for the Al[4] and Al[6] sites in Table 2, along with experimental values of the shifts (Kunwar et al., 1984). Agreement is reasonably good but it appears that the shift is slightly overestimated for Al[6] and somewhat underestimated for Al[4]. If the error were mainly in the theoretical method, we might expect the shifts of both sites to be either under- or overestimated. Different errors for the two sites may suggest that hydration effects are the main source of error. The central Al[4] is also calculated and observed to be strongly shielded with respect to monomeric Al[4], e.g.,  $\text{Al}(\text{OH})_4^{-1}$ , whose experimentally observed shift is  $\sim 80$  ppm. In a previous study (Tossell, 1998), using the HF GIAO method with a 6-31G\* basis set, we calculated a shift of between 89 and 84 ppm for  $\text{Al}(\text{OH})_4^{-1}$  compared to  $\text{Al}(\text{OH}_2)_6^{+3}$ , depending on whether we corrected the calculated bond distances for Born hydration energy effects. Increased shielding of the central Al[4] in the  $\text{Al}_{13}$  tridecamer cation is expected since it is highly polymerized, that is, each O is shared with three other Al cations. The calculated values for the NQCC at Al are also consistent with experiment, that is, the Al[4] signal is an extremely narrow line with NQCC  $\sim 0.8$  MHz while for Al[6], the NQCC is estimated as  $\sim 10.2$  MHz, based on results for basic Al sulfate and selenate (Kumar et al., 1984).

Calculated values of O-NMR shielding and shift, EFG, and NQCC are given for the different O sites in Table 3, along with experimental values for the shifts (Thompson et al., 1987; Phillips et al., 2000) and measured NQCC values for related materials (Thompson et al., 1987; Walter and Oldfield, 1989). Calculated values are given for both HF and B3LYP methods. As is generally observed (e.g., Wilson et al., 1999; Xue and Kanzaki, 2000), the B3LYP values are systematically deshielded compared to the HF. However, both methods give the same trend, although the differences in shift are considerably larger using B3LYP. While the calculated relative shifts for the four different O sites in the  $\text{Al}_{13}$  tridecamer cation agree well with experiment (using the assignment of Phillips et al., 2000), the shifts with respect to the water reference match experiment only if we adopt free gas-phase  $\text{H}_2\text{O}$  as the reference.  $^{17}\text{O}$  in liquid water is deshielded compared to that in gas-phase water by  $\sim 36$  ppm. Such use of a gas-phase water reference would be correct only if the deshielding of the various O atoms in the  $\text{Al}_{13}$  cation by the aqueous environment was of similar magnitude to the deshielding of water in the bulk liquid. I find that when six water molecules are allowed to

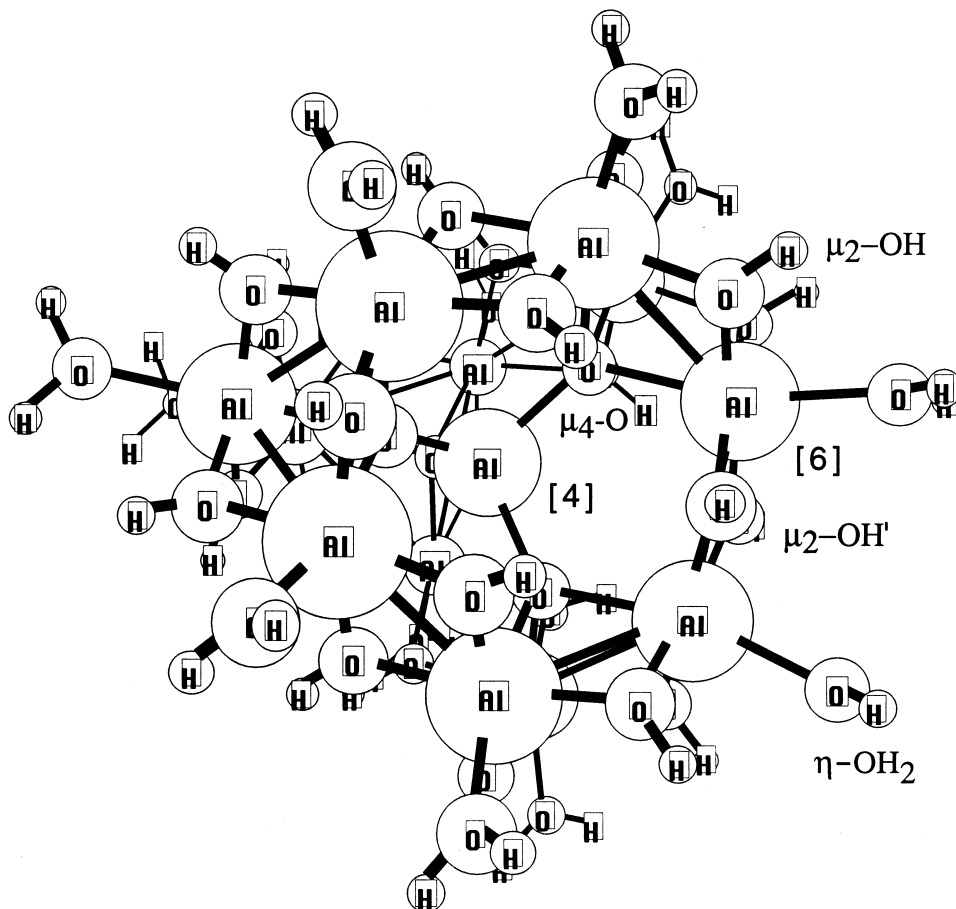


Fig. 1. Plot of the geometry of  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  optimized at the Hartree-Fock level using a polarized SBK basis. No symmetry was assumed, but the X-ray crystal structure of the selenate salt was used as the starting geometry. Examples of the various Al and O atom types are labeled on the right hand side of the figure.

interact with the simpler model molecule  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$ , some of the  $-\text{OH}_2$  groups are deshielded by as much as 23 ppm. Clearly, additional studies of hydration effects upon the  $^{17}\text{O}$  shieldings of the  $\text{Al}_{13}$  tridecameric cation are needed to establish the sensitivity to hydration effects of the different types of O atoms.

Note that such problems in calculating  $^{17}\text{O}$ -NMR shifts are not at all unusual. In their study of NMR shieldings in  $\text{SiO}_2$  polymorphs, Xue and Kanzaki (2000) also adopted gas-phase water as the reference molecule for their computations of  $^{17}\text{O}$  shifts but found fairly good agreement with experiment shifts,

which were actually referenced to liquid  $\text{H}_2\text{O}$ . For electronegative atoms, nonlocal deshielding effects from distant atoms appear to be generally large as previously shown for N shieldings (Tossell, 1997) and O shieldings (Tossell, 1999). Others have shown that calculated  $^{17}\text{O}$  shieldings consistently converge more slowly with increasing cluster size than do  $^{29}\text{Si}$  shieldings (e.g., Bull et al., 2000; Xue and Kanzaki, 2000), confirming the importance of such nonlocal effects.

NQCC values are not available for the O atoms of the  $\text{Al}_{13}$  cluster, but the calculated values are in fair agreement with experimental results (Walter and Oldfield, 1989) for other Al

Table 2. Calculated and experimental  $^{27}\text{Al}$  NMR properties (shieldings and shifts<sup>a</sup> in ppm, EFGs in atomic units, nuclear quadrupole coupling constants in MHz).

Site	$\sigma$		$\delta$			$q^{\text{Al}}$		NQCC	
	HF	B3LYP	HF	B3LYP	exp.	HF	B3LYP	HF	B3LYP
Al[4]	580.6	554.6	55.8	55.8	63	0	0	0	
Al[6]	620.0	591.7	16.4	18.7	≈12	0.369	0.356	11.3	10.9

<sup>a</sup> The shift reference is  $\text{Al}(\text{OH})_6^{+3}$ , with a calculated shielding of 636.4 ppm for HF and 610.6 ppm for B3LYP, using the polarized SBK optimized geometry, the 6-31G\* basis and the GIAO method.

Table 3. Calculated and experimental  $^{17}\text{O}$ -NMR properties (as in Table 2). Shifts are calculated with respect to free gas-phase  $\text{H}_2\text{O}$ . Experimental shifts are given in parentheses. Experimental values of NQCC given are for  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  - selenate and Al oxyhydroxides.

Site	$\sigma$		$\delta^a$			$q^o$		NQCC <sup>b,c</sup>	
	HF	B3LYP	HF	B3LYP	exp.	HF	B3LYP	HF	exp.
$\eta$ - $\text{OH}_2$	310–312 av. 311	av. 299	17	23.5	20	1.83	1.73	10.7	
$\mu$ - OH	291–293 av. 292	av. 271	36	51	$\approx 30$	1.34	1.28	7.8	5–6
$\mu$ - $\text{OH}^+$	290–294 av. 292	av. 271	36	51	$\approx 30$	1.35–1.39 av. 1.37	av. 1.33	8.0	5–6
$\mu_4$ - O	273	235	55	87.3	55	0.29	0.28	1.2–2.2	

<sup>a</sup> Shift reference is free gas-phase water, with  $^{17}\text{O}$  shieldings of 328.0 ppm for HF and 322.2 ppm for B3LYP, using the polarized SBK optimized geometry, the 6-31G\* basis, and the GIAO method.

<sup>b</sup> Using the 6-31G\* calibration factor of Ludwig, et al. (1996) to relate  $q^o$  to NQCC.

<sup>c</sup> Experimental values from Thompson, et al. (1987) and Walter and Oldfield (1989).

(hydrox)oxides in the case of the  $\mu_4$ -O site and are somewhat larger than experiment for the  $\mu_2$ -OH sites. I have found that for  $\mu_2$ -OH sites in the simpler system  $\text{Al}_2(\text{OH})_2(\text{OH}_2)_8^{+4}$ , that by H-bonding single waters to these sites, the O-H bond is lengthened, reducing the NQCC value (calculated at the Hartree-Fock 6–31G\* level) from  $\sim 7.0$  to 5.7 MHz, thus giving considerably better agreement with experiment.

#### 4. CONCLUSIONS

It is clear that the  $\text{Al}_{13}$  polyoxocation can be treated fairly reliably by presently available quantum mechanical methods if sufficient computer resources are allocated (the geometry optimizations and NMR shielding required  $\sim 9$  d of CPU time on a Compaq DEC XP1000). Al-NMR shieldings can be obtained fairly accurately, but O-NMR shieldings show the same problems of nonlocal contributions recently observed for calculations on silicates (Bull et al., 2000; Xue and Kanzaki, 2000; Tossell, 1999). Nonetheless, the relative shifts of the different types of O are given fairly accurately at the HF level. O NQCC values can also be obtained fairly accurately, particularly if the effects of H-bonding to water are taken into account using simpler model systems.

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