J. Phys. Chem. A **2004,** *108,* 113−120

Modeling Small Aluminum Chlorohydrate Polymers

Vojislava Pophristic* and Michael L. Klein

Center for Molecular Modeling and Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Marian N. Holerca

Colgate-Palmolive Company, Piscataway, New Jersey 08855

Received: July 14, 2003; In Final Form: October 15, 2003

Despite many experimental studies, the structure of aluminum chlorohydrate system is not well understood due to its complexity. Using a combination of Car Parrinello molecular dynamics and ab initio methods, we conclusively determine the structures of aluminum chlorohydrate monomer, dimer, trimer, and hexamer species. Contrary to the common assumption that the Al coordination shell in these compounds consists of OH groups and H_2O molecules only, we find that Cl^- ion incorporation in the octahedral structure of aluminum chlorohydrate monomer, dimer, and trimer increases their stability in the gas phase. The hexamer gas-phase structure is predicted to be built from both penta- and hexacoordinated Al^{3+} ions. Gas-phase optimized dimer and hexamer complexes are found to exhibit stable behavior in water solutions in the course of 7−8 ps of a Car Parrinello molecular dynamics run.

I. Introduction

Aluminum chlorohydrate ($Al_2(OH)_5Cl{\cdot}2H_2O$, ACH) is a basic aluminum complex which is in widespread commercial use. Among other applications, it is the active ingredient of all antiperspirants currently on the market.[1] In aqueous solution it polymerizes, forming a number of polymer species, some of which play a crucial role in antiperspirant action.[2] To better understand the chemistry behind antiperspirant activity, atomic level structural information about the species involved is needed. In this article, we report and discuss the structures of small ($n = 1-6$, n representing the number of Al atoms in the polymer) ACH polymers.

The postulated mechanism of ACH transformation upon dilution and aging consists of several steps.[3] Octahedral monomers, $Al(H_2O)_6Cl_3$, which are formed in the following reaction in water solution:

$$3Al_2(OH)_5Cl{\cdot}2H_2O \rightarrow Al(H_2O)_6^{\ 3+} + 3Cl^- + 5Al(OH)_3 \qquad (1)$$

undergo deprotonation and then bind into dimers:

$$Al(H_2O)_6^{\ 3+} \rightarrow Al(OH)(H_2O)_5^{\ 2+} + H^+ \qquad (2)$$

$$2Al(OH)(H_2O)_5^{\ 2+} \rightarrow Al_2(OH)_2(H_2O)_8^{\ 4+} + 2H_2O \qquad (3)$$

Deprotonation of the dimer initiates further polymerization, resulting in the formation of larger polymers such as $Al_3(OH)_4(H_2O)_9^{\ 5+}$, $Al_6(OH)_{12}(H_2O)_{12}^{\ 6+}$, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{\ 7+}$, and Al_{14}–Al_{200} species. The composition of ACH solutions depends on many factors, including temperature, pH, and aging.[1] Due to the resulting complexity of aluminum chlorohydrate systems, it is difficult to obtain detailed structural data using experimental methods. Existence of the monomer, dimer, and Al_{13}-mer has been strongly supported by a number of experimental studies, including X-ray[4−6], NMR,[7] Raman,[8] and IR[5,9] spectroscopies. Other species (e.g., the trimer and the hexamer) have been proposed based primarily on potentiometry.[3,10]

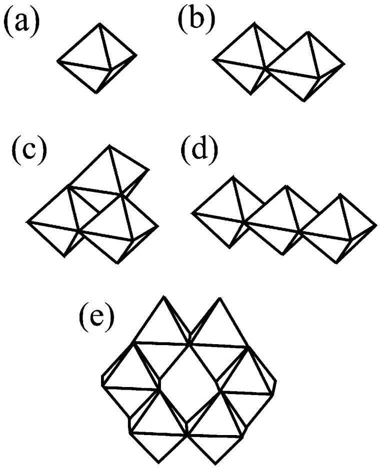

Figure 1. Suggested structures of the octahedral monomer (a), dimer (b), compact (c) and linear (d) trimer, and hexamer (e).

Despite the large number of studies[1] undertaken in the last three decades on various aspects of aluminum chlorohydrate chemistry, neither the structures nor the geometrical parameters are precisely known (an exception is the monomer, e.g., ref 11) due to the complex composition of the system. It is believed that all the above-mentioned polymers consist of octahedral units, with Al atoms in the center, surrounded by a combination of six H_2O molecules and OH groups (Figure 1).[12] The structural role of the Cl^- ion is not clear: although it is widely assumed that Cl^- is completely ionized and free in dilute solutions, there are indications that some of the Cl^- ions are bound to ACH polymer species.[3]

A computational study of the ACH system circumvents some of the difficulties encountered by experiments by investigating

10.1021/jp0360422 CCC: $27.50

constituent species individually, in the gas phase and in aqueous solution. We focus on the smaller polymers, namely, the monomer, the dimer, the trimer, and the hexamer, as well as $Al_2(OH)_5Cl{\cdot}2H_2O$. Additionally, provoked by the finding that one Cl^- ion spontaneously substitutes an axial H_2O molecule of the octahedral dimer structure (discussed in Section III.C), we examine the effect of the position of Cl^- ions on the stability of the ACH polymers. Our models, although by necessity simpler than the aluminum chlorohydrate solution, provide useful information for an understanding of ACH chemistry.

II. Methodology

Computational studies of the ACH system were performed by using ab initio (Car-Parrinello) molecular dynamics (CP-MD)[13] and static quantum mechanics, by CPMD[14] and Gaussian 98[15] programs. In CPMD simulations, we use an analytical local pseudopotential for hydrogen, a Goedecker-type pseudopotential for aluminum,[16] and nonlocal norm-conserving soft pseudopotentials of Troullier-Martins type[17] for all the other elements. Angular momentum components up to $l_{max} = 1$ have been included for Al, O, and Cl. For all elements, the pseudopotential has been transformed to a fully nonlocal form using the scheme proposed by Kleinmann and Bylander.[18] CPMD is based on density functional theory (DFT); we employed the BLYP exchange correlation functional.[19,20] The electronic wave functions were described by a plane wave basis with a 70 Ry cutoff. The use of a plane wave basis implies periodic boundary conditions. All simulations were performed in a periodically repeating cubic box, with the edge varying depending on the size of the system. The simulation cell edge was 14.8 Å for the case of the monomer, the dimer, and the compact trimer; for the linear trimer, it was 19.0 Å; for the hexamer, 17.0 Å. Minimum-energy geometries of gas-phase structures were obtained by simulated annealing, followed by geometry optimization. Simulated annealing runs were started from a temperature of 100 K and used scaling factors of 0.9998 and 0.9999 for ionic velocities. In all calculations, classical equations of motion have been integrated with a velocity Verlet algorithm with a time step of 0.1207 fs and a fictitious mass for the electronic degrees of freedom of $\mu = 800$ au.

After the optimization by the CPMD code, structures of smaller polymers ($n = 1-3$) were refined by Hartree–Fock (HF) optimizations, with the basis sets ranging from 6-31G(d,p) to 6-311G(3df,2p). The monomer and dimer HF energies were corrected for the zero-point vibrational energy. Harmonic frequencies for the HF optimized monomer and dimer structures were calculated to ensure that the geometries correspond to local minima. The size of the polymers prevented higher level optimizations. Several studies on aqueous Al^{3+} complexes[11,21] have shown that bond lengths change only slightly upon going to the MP2 level optimization.

Optimized gas-phase structures were used as the starting geometries for the simulations in solution. Such computations were undertaken for the dimer (cubic box with a 12.0 Å edge and 37 H_2O molecules) and the hexamer (cubic box with a 14.0 Å edge and 47 H_2O molecules). Stabilities of these species in solution were determined by equilibrating the systems at 300 K using a Nose-Hoover thermostat[22-24] for 2–6 ps, depending on the polymer (see below).

As mentioned in the Introduction, the literature suggests that ACH polymers consist of octahedral units comprising an Al^{3+} ion and H_2O/OH coordination groups, whereas Cl^- ions are loosely bound to the surface of the polymer. We investigate other possibilities. The notation that we adopt for the octahedral compounds is the following: if a molecule contains only H_2O/OH groups in the coordination shell, its structure is termed structure **1**. In the case when one chloride ion is strongly bound to the Al^{3+}, i.e., is a part of the coordination shell, the structure is denoted structure **2**. Structure **3** refers to a case where two chloride ions are a part of the octahedral structure.

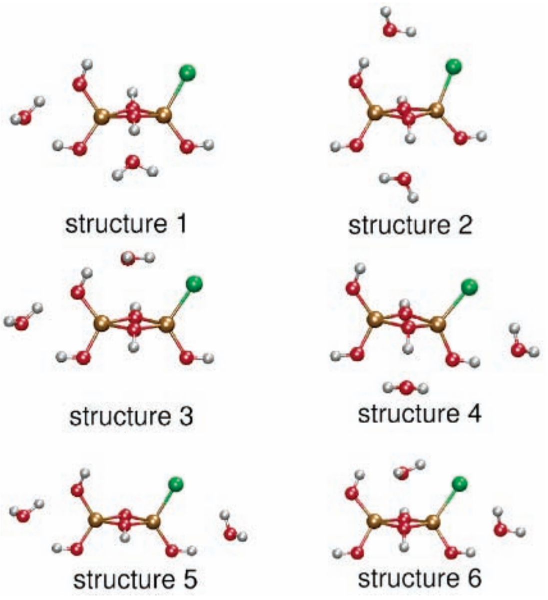

Figure 2. Structures of six tetrahedral dimer configurations, $Al_2(OH)_5Cl{\cdot}2H_2O$. Chloride ions, green; oxygen atoms, red; aluminum atoms, gold; hydrogen atoms, light gray.

TABLE 1: Energies (kcal/ mol) of Various Forms of $Al_2(OH)_5Cl{\cdot}2H_2O$, Relative to Structure 1[a]

structure[b]	HF 6-31G(d,p)	HF 6-31G(2d,p)	HF 6-311G(3df,2p)	BLYP[c] plane wave basis
2	1.3	0.5	0.6	2.5
3	1.4	1.5	1.3	2.7
4	5.5	5.1	3.9	6.2
5	6.8	6.2	5.2	7.5
6	7.5	6.7	5.5	9.6

[a] Rounded off to the nearest 0.1 kcal/mol. [b] For notation, refer to Figure 2. [c] All BLYP optimizations were carried out with the plane wave basis, as described in Section II.

III. Results

A. Tetrahedral Dimer, $Al_2(OH)_5Cl{\cdot}2H_2O$. $Al_2(OH)_5Cl{\cdot}2H_2O$ (eq 2, Section I) consists of two tetrahedral Al atoms, bonded by two OH bridges (Figure 2). Structures with a Cl bridge were ruled out based on the preliminary HF optimization of the $Al_2(OH)_5Cl$ unit. The configuration with the Cl bridge is ~20 kcal/mol higher in energy than the corresponding one with both bridges formed from OH groups.[25]

The positions of the H_2O molecules with respect to the $Al_2(OH)_5Cl$ unit were investigated by placing H_2O molecules in four locations predicted to provide the strongest interaction with the surrounding groups. Simulated annealing and consequent optimization resulted in six such conformations (Figure 2). The order of stability is preserved with all the methods/basis sets used (Table 1). Both the BLYP and HF studies show that the most stable structure (structure **1**) is the one with H_2O molecules furthest away from the Cl^- ion. The second and third most stable structures (structures **2** and **3**, respectively) differ negligibly in energy. They are similar: one H_2O molecule in both structures is positioned above the $Al_2(OH)_2$ plane, away

TABLE 2: Representative Geometrical Parameters of the Tetrahedral Dimer, $Al_2(OH)_5Cl{\cdot}2H_2O$[a]

structure[b]	1	2	3	4	5	6
Al−Al	2.755	2.755	2.752	2.789	2.788	2.789
	2.793	2.788	2.790	2.851	2.843	2.833
Al−Cl	2.117	2.132	2.125	2.133	2.132	2.148
	2.142	2.160	2.156	2.167	2.160	2.181
$\angle$Cl−Al−O_{H_2O}	117.9	116.8	117.3	116.5	116.9	115.6
	118.9	118.5	116.9	116.8	117.4	116.9

[a] Bond lengths and distances in Å, bond angles in degrees, rounded off to the nearest 0.001 Å and 0.1°, respectively. First row, HF/6-311G(3df,2p) values; second row, BLYP/plane wave basis values. [b] For notation, refer to Figure 2.

from the Cl^- ion; the other one is located in a groove adjacent to the Cl^- ion. A similar result is found with species **4** and **5**. The structure which has both H_2O molecules in the vicinity of the Cl^- ion (structure **6**) is ~7 kcal/mol higher in energy than the most stable structure.

The $Al_2(OH)_2$ structural motif, important for studies of larger units, has geometrical parameters stable with respect to the method and basis set used for optimization and with respect to the different environments (Table 2, Figure 2). Upon repositioning the hydrogen-bonded H_2O molecules, the Al−O_{bridge}−Al angle varies from 96.9° to 100.6°, the Al−O_{bridge} bond length from 1.826 Å to 1.884 Å, and the Al−O_{H_2O} bond from 1.696 Å to 1.736 Å, closely agreeing with the published values of the related $Al_2(OH)_6$ species.[26] The Al−Cl bond is shortest in the most stable form, structure **1**, where neither of the H_2O molecules is adjacent to Cl. The lengths of hydrogen bonds depend on the orientation of the H_2O molecule relative to the $Al_2(OH)_5Cl$ unit (Figure 2). In the case of the most stable structure (structure **1**), there are four strong hydrogen bonds between the water molecules and the OH groups, two per each water molecule, ranging in length from 1.7 to 2.1 Å. Both the hydrogen bond number and its geometry vary across all six structures, illustrating a competition between the two. However, this appears to be an artifact of including only a few explicit H_2O molecules in the model, and such effects should not be relevant in dilute solutions.[21]

B. Monomer, $Al(H_2O)_6Cl_3$. The existing literature suggests that the monomer, $Al(H_2O)_6Cl_3$, consists of an Al^{3+} ion, coordinated by six H_2O molecules[27] in an octahedral arrangement, with Cl^- ions surrounding the octahedron (structure **1**, Figure 3).[1] However, our gas-phase studies of the position of the Cl^- ion indicate that the structure which incorporates one of the chloride anions as a part of the octahedron (structure **2**, Figure 3) is more stable than the one with six coordinating H_2O molecules (structure **1**). The energy difference between the gas-phase optimized structures with and without one strongly bound Cl^- ion converges to 10 kcal/mol (Table 3).

Bond lengths obtained by BLYP are larger than those obtained with HF, but both methods give similar overall trends (Table 4). These values are in general agreement with the previously published theoretical geometries of $Al(H_2O)_6{}^{3+}$.[11,26,28,29] The Al−O_{H_2O} bond distance in these forms and the Al−Cl_{bound} bond length in structure **2** are somewhat longer than the corresponding ones in the tetrahedral dimer, $Al_2(OH)_5Cl{\cdot}2H_2O$, to accommodate hexagonal coordination as opposed to the tetragonal one. The overall shape of both monomers is a distorted octahedron, due to the asymmetrical environment. Structure **1** is slightly more compact than structure **2**, as evident from its shorter bond lengths. This is consistent with a higher steric crowding when a chloride ion is a part of the octahedral structure. In structure **1**, three chloride ions are bonded to the octahedral water molecules by two hydrogen bonds each. In structure **2**, two "free" chloride ions are attached to the surface of the octahedron by three hydrogen bonds each; an H_2O molecule located on the outside of the octahedron makes one hydrogen bond with an H_2O molecule located within the octahedron.

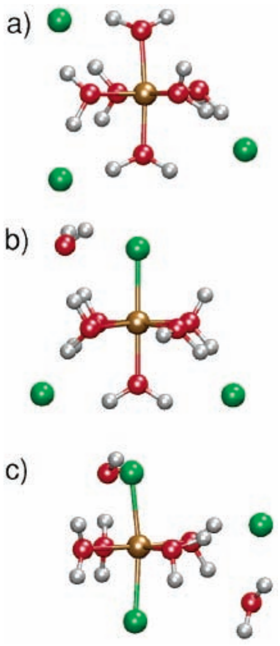

Figure 3. Aluminum chlorohydrate monomer configurations. Chloride ions, green; oxygen atoms, red; aluminum, gold; hydrogen, light gray. (a) Structure **1**, only H_2O molecules present in the coordination shell; (b) structure **2**, one Cl^- ion in the coordination shell; (c) structure **3**, two Cl^- ions in the coordination shell.

TABLE 3: Relative Energies (kcal/ mol) of the Three Forms of the Octahedral Monomer

	HF				
ΔE[a]	6-31G(d,p)	6-31G(2d,p)	6-311G(2d,p)	6-311G(3df,2p)	BLYP[b]
1	11.1	9.4	10.8	9.9	5.1
3	3.3	3.8	3.0	4.3	8.0

[a] $\Delta E = E_i - E_2$, where E_i corresponds to structures **1** or **3**, and E_2 to structure **2**, (Figure 3). Also, see footnote *a*, Table 1. [b] See footnote *c*, Table 1.

TABLE 4: Comparison of Monomer Geometries[a]

	HF/6-311G(3df,2p)	BLYP[d]
Al−O_{H_2O} (**1**)[b]	1.865−1.921	1.911−1.985
Al−O_{H_2O} (**2**)[b]	1.895−1.946	1.917−1.986
Al−O_{H_2O} (**3**)[b]	1.897−1.987	1.922−2.040
Al−Cl (**2**)	2.238	2.286
Al−Cl (**3**)	2.234/2.285	2.286/2.316
$\angle O_{H_2O}$−Al−O_{H_2O} (**1**)[c]	87.2−92.5/178.0	85.2−95.6/172.5−179.0
$\angle O_{H_2O}$−Al−Cl (**2**)[c]	91.9−93.4/179.4	92.1−93.5/179.3
$\angle$Cl−Al−Cl (**3**)[c]	172.2	170.7

[a] Bond lengths in Å, angles in degrees. For notation, see Figure 3. Also, see footnote *a*, Table 2. [b] Due to the C_1 symmetry, analogous bond lengths and angles are different, falling in the range given. [c] Two ranges correspond to two kinds of angles: those between bonds approximately in perpendicular positions and those that are parallel. [d] See footnote *c*, Table 1.

To further examine the effect of the location of chloride ions on the stability of the monomer, a structure containing two Cl^- ions strongly bound to the Al^{3+} ion (structure **3**, corresponding to $Al(H_2O)_4Cl_2{\cdot}(2H_2O,Cl)$, Figure 3) was optimized. Table 3 shows that such an arrangement is several kcal/mol less stable

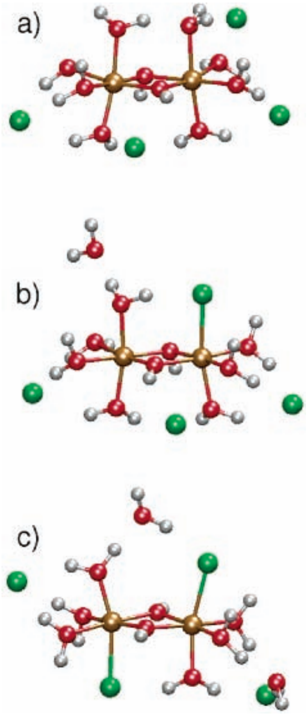

Figure 4. Octahedral dimer configurations. Chloride ions, green; oxygen atoms, red; aluminum, gold; hydrogen, light gray. (a) Structure **1**, only H_2O molecules present in the coordination shell; (b) structure **2**, one Cl^- ion in the coordination shell; (c) structure **3**, two Cl^- ions in the coordination shell.

than structure **2**, which incorporates only one chloride ion in the aluminum coordination shell. The energy effect of positioning Cl^- ions in the first coordination shell of aluminum is larger in the DFT case for structure **3** and in the HF case for structure **1**. Geometrical parameters of structure **3** follow those of structure **2**, except for somewhat longer bonds, due to the presence of two bulky substituents.

C. Dimer, $Al_2(OH)_2(H_2O)_8Cl_4$. The dimer, $Al_2(OH)_2(H_2O)_8Cl_4$, consists of two octahedra, connected by two OH bridges (Figure 4a). This species is regarded as having only H_2O and OH moieties in the coordinating positions (e.g., ref 9; structure **1**, Figure 4a). However, in the course of our CPMD relaxation of such a starting geometry, one of the chloride ions spontaneously replaced a water molecule initially located in the axial location of the octahedron (structure **2**, Figure 4b). This arrangement remained stable throughout the simulated annealing procedure and was subsequently optimized by both BLYP and HF methods. To compare the previously postulated structure with the one thus obtained, we performed another computation, starting with the optimized dimer in which an H_2O molecule was placed in the position of the strongly bound Cl^- ion. After a simulated annealing run which captured the H_2O molecule in question in the vicinity of its starting location (using initially a scaling factor for ionic velocities of 0.9995), the structure with Al ions coordinated only by H_2O molecules was optimized (structure **1**, Figure 4a).

Relative stability of the gas-phase structures of the two dimer forms was investigated by geometry optimization at various computational levels. Table 5 demonstrates that structure **2** is ~10 kcal/mol more stable than structure **1**, regardless of the method/basis set used (in accord with the monomer's structure **1**, BLYP values are consistently lower than the HF ones). At the HF level, additional stability introduced by incorporation of a Cl^- ion in the octahedral structure is similar to the monomer case (Tables 3 and 5), indicating that the Cl^- ion plays an important structural role in both small forms of ACH.

TABLE 5: Relative Energies (kcal/mol) of the Three Forms of the Octahedral Dimer

	HF				
ΔE^a	6-31G(d,p)	6-31G(2d,p)	6-311G(2d,p)	6-311G(3df,2p)	BLYP^b
1	23.0	20.1	22.6	21.2	13.3
2	11.7	9.3	11.3	10.0	8.1

[a] $\Delta E = E_i - E_3$, where E_i corresponds to structures **1** or **2**, and E_3 to structure **3** (Figure 4). See footnote *a*, Table 1. [b] See footnote *c*, Table 1.

Geometries obtained by HF and BLYP optimizations agree in general (Table 6). Several conclusions can be drawn from the comparison with the monomer and tetrahedral dimer HF geometries. Dimer structure **1** is somewhat more compact than structure **2**. The Al−Cl bond is stretched more in the dimer structure **2** than in the corresponding monomer structure, due to the larger size of the dimer. Also, there is an increasing trend in the Al−Cl bond length when going from the tetrahedral dimer to monomer to octahedral dimer. Due to the presence of the neighboring octahedron, the Al−Cl bond is tilted by ~10° away from the $Al-O_{H_2O(axial)}$ direction, which is not the case in the monomer. The Al−Al distance is longer than in the tetrahedral dimer, and the related angles change accordingly, making the $Al_2(OH)_2$ motif more elongated (i.e., diamond shaped). In both structures **1** and **2**, three "free" chloride ions form three hydrogen bonds each. In structure **1**, the additional Cl^- ion is hydrogen bonded to two H_2O molecules.

Similarly to the monomer case, an examination of a third possible form of $Al_2(OH)_2(H_2O)_8Cl_4$ was undertaken. The $Al-O_{H_2O}$ axial bond, positioned trans to the Al−Cl bond of structure **2**, was substituted by an Al−Cl bond, thus leaving two H_2O molecules and two Cl^- ions loosely bound to the octahedral structure (structure **3**, Figure 4c). The gas-phase optimization resulted in a structure which is ~10 kcal/ mol more stable than structure **2** and ~20 kcal/mol more stable than structure **1** (Table 5). Thus, the form with two axially bound Cl^- ions in the trans arrangement turned out to be the most stable one. The geometry of structure **3** is characterized by a longer Al−Al distance than in structures **1** and **2** and distorted octahedral units (axial bonds deviate from the ideal 180° angle by 5−6°, Table 6).

A careful comparison between the monomer and the dimer studies points to the conclusion that the introduction of one chloride ion per monomer unit increases the stability by ~10 kcal/mol. The effect is seen for both the monomer and the dimer, as long as only one chloride ion is placed in each of the monomer units. Taking into account the apparent quantitative transferability of the stabilization effect from the monomer to the dimer in the case of the 1-fold substitution (one Cl^- ion substituting one H_2O molecule; $\Delta E_{\mathrm{stabilization}} \sim 10$ kcal/mol), one can expect that a double substitution within one monomer unit of a dimer would lead to a destabilization of the complex. Such a destabilizing effect of two chloride ions in a monomer unit is probably due to the steric crowding of one too many bulky substituents, and this reasoning should be valid for the dimer as well.

To explore the dimer structure in aqueous solution, optimized structure **2** was placed in a box of 37 H_2O molecules. After a 6 ps equilibration at 300 K using a Nose-Hoover thermostat, the system was allowed to evolve for 2 ps. During this time, the structure remained stable, preserving the anticipated octahedral geometry, as can be seen from Figure 5a. Both Al−O radial distribution functions (for the two Al^{3+} ions) have peaks

TABLE 6: Comparison of the Octahedral Dimer Structures 1, 2, and 3[a]

	Al−Al	Al−O_{OH}	Al−O_{H_2O}	Al−Cl	$\angle O_{H_2O(axial)}$/ Cl−Al−$O_{H_2O(axial)}$/Cl[b]
			Structure **1**		
HF/6-311G(3df,2p)	2.827	1.814−1.856	1.870−2.009		169.2/171.9
BLYP[c]	2.899	1.861−1.907	1.900−2.037		170.8/173.7
			Structure **2**		
HF/6-311G(3df,2p)	2.849	1.829−1.866	1.914−1.963	2.329	168.6/169.8
BLYP[c]	2.900	1.856−1.900	1.939−2.007	2.390	169.4/168.7
			Structure **3**		
HF/6-311G(3df,2p)	2.896	1.838−1.861	1.912−1.956	2.308/2.337	166.6/166.3
BLYP[c]	2.961	1.867−1.895	1.916−1.989	2.386/2.438	163.7/165.4

[a] Structures **2** and **3** incorporate one and two Cl^- ions as parts of the octahedral arrangement, respectively, whereas structure **1** has all H_2O molecules in coordinating positions. Bond lengths in Å, angles in degrees. See footnote *a*, Table 2. [b] This is the angle between the axial bonds originating in the same Al^{3+} ion. Depending on the dimer form, this angle is either $\angle O_{H_2O(axial)}$−Al−$O_{H_2O(axial)}$, $\angle O_{H_2O(axial)-}$Al−Cl, or ∠Cl−Al−Cl (Figure 4). [c] See footnote *c*, Table 1.

TABLE 7: Optimized Bond Lengths and Angles of the Compact and Linear Trimer Structures[a]

	compact trimer		linear trimer	
	HF/ 6-311G(3df,2p)	BLYP[b]	HF/6-311G(3df,2p)	BLYP[b]
Al−Al	2.906−2.959	2.986−3.008	2.906−2.959	2.882/2.908
Al−$O_{OH(equatorial)}$	1.809−2.012	1.850−2.042	1.830−1.894	1.870−1.931
Al−$O_{OH(axial)}$	1.821−1.973	1.859−2.036		
Al−$O_{H_2O(equatorial)}$	1.899−1.960	1.931−2.015	1.898−1.955	1.946−2.003
Al−$O_{H_2O(axial)}$	1.878−1.934	1.904−2.001	1.890−1.994	1.918−2.128
$\angle O_{H_2O}$−Al−$O_{OH(axial)}$	165.9−173.1	171.7−174.5	168.3−176.4	169.0−178.3
∠Al−Al−Al	59.1−60.9	59.7−60.5	176.7	173.22

[a] Bond lengths in Å, angles in degrees. See footnote *a*, Table 2. [b] See footnote *c*, Table 1.

at ∼2 Å, whereas the corresponding running coordination numbers show plateaus at 5 and 6, for Al^{3+} ions with and without strongly bound Cl^- ion, respectively. Figure 5b demonstrates that the Cl^- ion does not exhibit a tendency to diffuse out of its octahedral position in the course of 8 ps, remaining ∼2.4 Å from the closest Al^{3+} ion. The Al−Al distance is also similar to the gas-phase value, oscillating just below 3.0 Å, with no drift (Figure 5c).

D. Trimer, $Al_3(OH)_4(H_2O)_{9-10}Cl_5$. With an increasing number of Al atoms, possibilities for different arrangements of octahedral monomer units increase rapidly. Although more Al_3 configurations are conceivable, we focus on the two described by Brinker and Scherer.[12,30] The linear structure ($Al_3(OH)_4(H_2O)_{10}Cl_5$) consists of three octahedral units bridged by OH groups (Figure 6b); the more compact structure ($Al_3(OH)_4(H_2O)_9Cl_5$) consists of a dimer with the third octahedron bound to the dimer by three bridges (through two axial OH groups and one dimer bridging OH group; Figure 6a). It is believed that the structure shown in Figure 6a is more stable due to its more compact geometry (this structure will be referred to as the "compact trimer"). Gas-phase stabilities of the linear and compact trimers are not directly comparable, due to the different molecular formulas. Therefore, we first focus on their geometrical features.

BLYP and HF methods give comparable geometries for both structures, with HF values lower, as found throughout our studies (Table 7). The optimized geometries correspond to the suggested ones, i.e., the octahedrally built structure is preserved. The Al−Al−Al angle in the linear trimer is several degrees less than the ideal angle of 180°, indicating a bent main molecular axis. This is probably a consequence of the asymmetrical environment produced by five chloride ions. The Al−Al−Al angles in the compact trimer are very close to their ideal value of 60°. The Al−Al distance in the compact trimer is ∼0.1 Å longer than in the linear one, due to a greater number of steric contacts in the former. The equatorial bond lengths (Al−O_{H_2O} and Al−O_{OH}) are more evenly distributed in the linear than in the compact trimer. The trend of increasing Al−Al distances as octahedral units are added to the dimer is preserved. As in the other cases, the chloride ions in both the compact and linear structures are bound to the surface of the trimer by two to three hydrogen bonds each.

TABLE 8: Relative Energies (kcal/mol) of the Two Forms of the Compact and Linear Trimers

	HF		
Δ*E*[a]	6-31G(d,p)	6-31G(2d,p)	BLYP[b]
compact	14.4	13.0	3.8
linear	3.8	1.9	2.1

[a] $\Delta E = E_1 - E_2$, where E_1 and E_2 correspond to energies of trimer structures **1** (only H_2O molecules in the coordination shells of Al^{3+} ions) and **2** (Cl^- incorporated into octahedral structure) (Figure 6). See footnote *a*, Table 1. [b] See footnote *c*, Table 1.

To investigate the role of Cl^- position in the stability of the trimer, the axial Al−O_{H_2O} bonds in both the compact and the linear trimers were substituted by Al−Cl bonds. Figure 6a shows the substitution in the compact trimer (structure **2**). In the case of the linear trimer, the bond of the terminal monomer unit was used for this structural change (Figure 6b, structure **2**). Optimization of such compact and linear trimers yields support for the conclusions of the monomer and the dimer analyses: the presence of one Cl^- ion in the coordination shell increases the stability of the polymer, although only slightly for the linear trimer (Table 8). It should be noted, however, that, in the case of the linear substituted trimer, the movements of the terminal units relative to the central one are so strong that the final form is no longer linear (∠Al−Al−Al = 148.9°, as opposed to the linear structure discussed in the previous paragraph, where the corresponding angle is close to 180°).

Quantitatively, the stabilization effect of the chloride ion substitution in the compact trimer shows a similar trend to the two smaller molecules (Table 8). The BLYP optimization

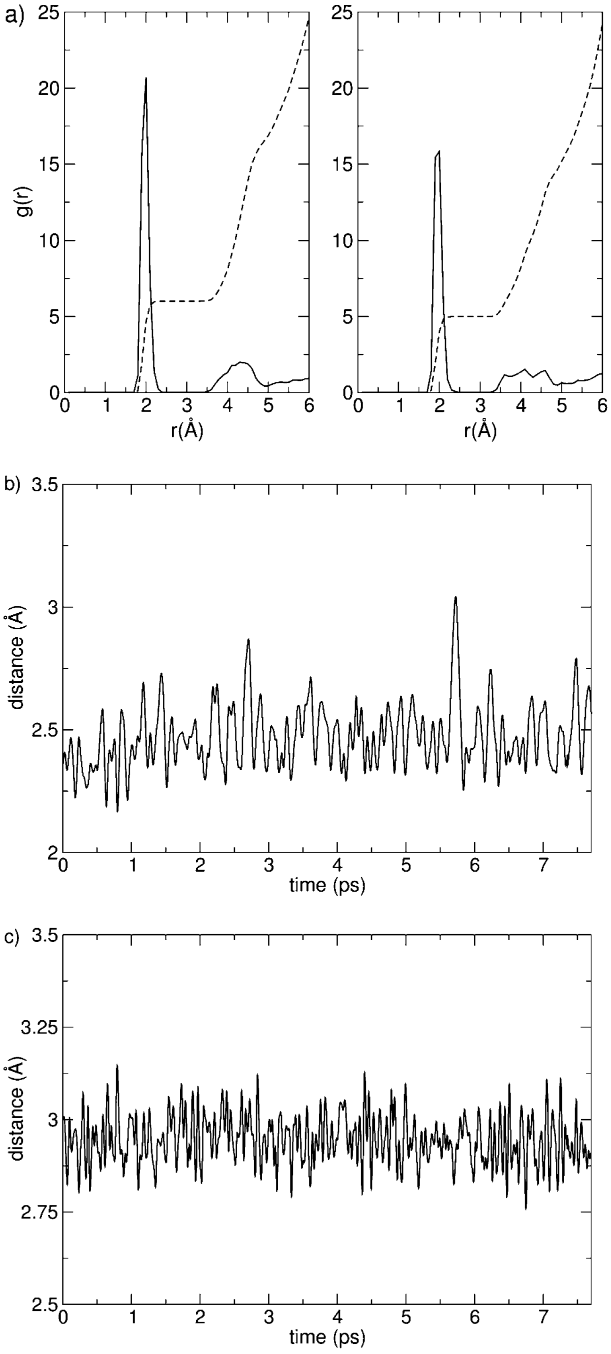

Figure 5. Octahedral dimer (structure **2**) stability in aqueous solution. (a) The Al−O radial distribution functions and corresponding running coordination number integrals for the two Al^{3+} ions. (b) Structure **2** Al−Cl distance as a function of time. (c) Structure **2** Al−Al distance as a function of time.

underestimate of this effect is even more pronounced than in the other two cases, whereas the HF value of ~15 kcal/mol follows in general the value obtained for the monomer and the dimer.

E. Hexamer, $Al_6(OH)_{12}(H_2O)_{12}Cl_6$. Potentiometric experiments indicate that a polymer form containing six Al ions exists in solution.[10] Such a hexamer is believed to consist of six octahedral units bound into a ring structure (Figure 1).[1] The hexamer, besides occurring as a free $Al_6(OH)_{12}(H_2O)_{12}Cl_6$ molecule, is the building block of aluminum hydroxide gel.[31]

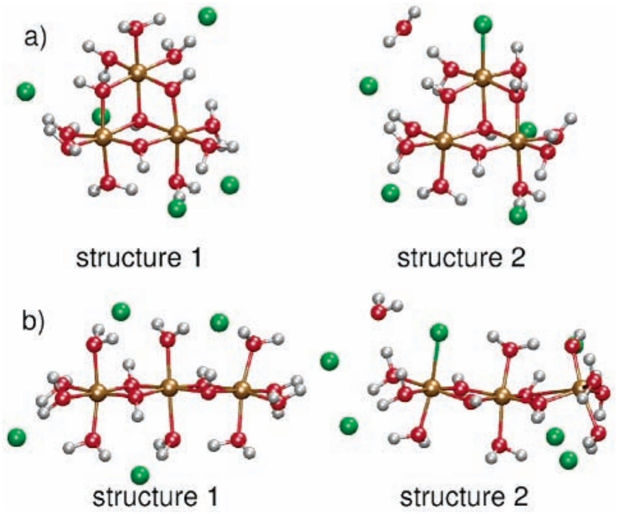

Figure 6. Optimized compact (a) and linear (b) trimer structures. Chloride ions, green; oxygen atoms, red; aluminum, gold; hydrogen, light gray. Structure **1**, only H_2O molecules present in the coordination shell; Structure **2**, one Cl^- ion in the coordination shell.

TABLE 9: Optimized Hexamer Bond Lengths (Å) and Angles (deg)

	BLYP[a]
Al−Al	2.865−2.954
Al−O_{OH}	1.804−1.950
Al−O_{H_2O}	1.944−2.030
∠Al−Al−Al	112.8−114.6/131.5; 132.4[b]

[a] See footnote *c*, Table 1 and footnote *a*, Table 2. [b] See Section III.E.

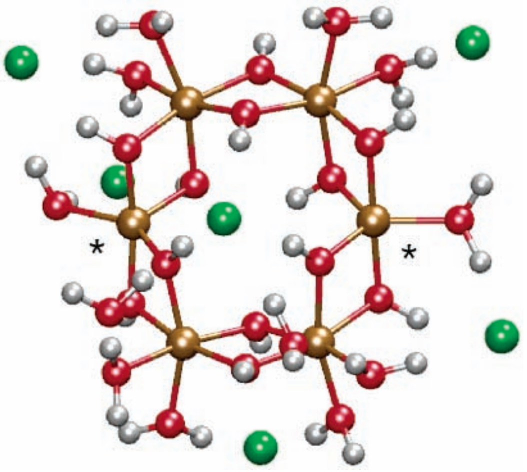

Figure 7. Optimized hexamer structure. Star signs indicate the cavities formed by H_2O molecules leaving the octahedral part of the structure. Chloride ions, green; oxygen atoms, red; aluminum, gold; hydrogen, light gray.

Our starting geometry makes use of the optimized dimer structures. After initial relaxation at 100 K, the hexamer structure is subjected to simulated annealing, followed by a BLYP/plane wave optimization. Due to the size of the $Al_6(OH)_{12}(H_2O)_{12}Cl_6$ polymer, an HF optimization was not attempted. The minimal energy structure closely resembles the suggested six-membered ring (Table 9). The Al−Al distances differ at most by 0.1 Å from each other. The Al−O_{H_2O} bond lengths do not deviate much either. The ring structure distortion is evident mainly through two Al−Al−Al angles which are ~20° more open than the others (listed separately in Table 9). The reason for this is the clustering of the Cl^- ions in the vicinity of the central Al atoms of these two angles (Figure 7). Because these chloride ions are strongly bound to the H_2O molecules of the hexamer, they pull the structure into a less symmetric form. Al−Al and

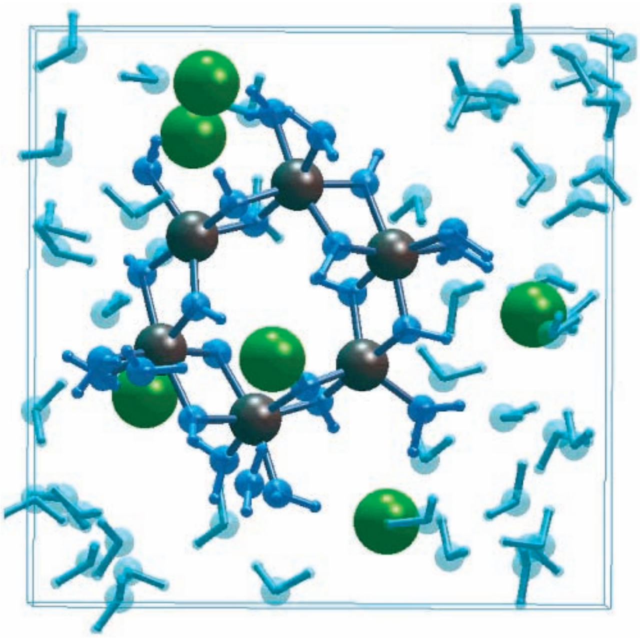

Figure 8. Snapshot of $Al_6(OH)_{12}(H_2O)_{12}Cl_6$ in a box with 47 H_2O molecules, after a 2-ps CPMD run. Chloride ions, green; aluminum, gray; octahedrally bound water molecules and OH groups (including two water molecules that left the hexamer structure), blue; water molecules (bulk), translucent blue.

Al−O distances and the internal structure of the octahedral units agree with the ones obtained for the octahedral dimer and trimer (Tables 6 and 7).

An interesting feature of the simulated annealing of the hexamer is that in the course of the annealing two water molecules leave their outer octahedral positions and move to hydrate Cl^- ions which are located in the exterior of the six-membered ring (Figure 7). On the other hand, chloride anions do not show any tendency of moving toward these unoccupied locations within the octahedra. This can be associated with their diminished mobility due to a higher level of solvation than in the case of the smaller polymers, in which the chloride ions are exposed to fewer peripheral H_2O molecules and possible hydrogen-bonding contacts. The outcome is an incomplete octahedral structure of the hexamer in the gas phase.

To investigate how probable this structure is in solution, the optimized $Al_6(OH)_{12}(H_2O)_{12}Cl_6$ unit was placed in a box with 47 water molecules and equilibrated for 2 ps at 300 K using a Nose-Hoover thermostat (Figure 8). After that, the system was allowed to evolve for nearly 7 ps. Figure 9a shows representative Al−O radial distribution functions and corresponding number integrals for hexa- (left) and pentacoordinated (right) Al^{3+} ions. Four Al^{3+} ions are octahedral, with OH/H_2O groups at ∼2 Å distance. Two monomer units remain incomplete even after 9 ps, with no tendency observed for bulk solution molecules to diffuse into the vacancies (note the number integral plateau at the value of 5 on the right, as opposed to the value of 6 on the left). The structure is otherwise stable in solution, with Al−Al distances oscillating around their gas-phase values (Figure 9b) and with the six-membered aluminum ring planar and highly symmetrical.

IV. Discussion

Our simulations conclusively demonstrate that the monomer, dimer, both trimer, and hexamer structures exist as stable polymers built from (in general) octahedral Al^{3+} units. The geometry of the monomer unit is slightly changed as the ACH polymer becomes larger, to accommodate more steric crowding, but its essential characteristics are preserved for all ACH polymers studied. The overall geometry of the dimer and hexamer in H_2O solution is maintained throughout ∼10 ps of CPMD runs.

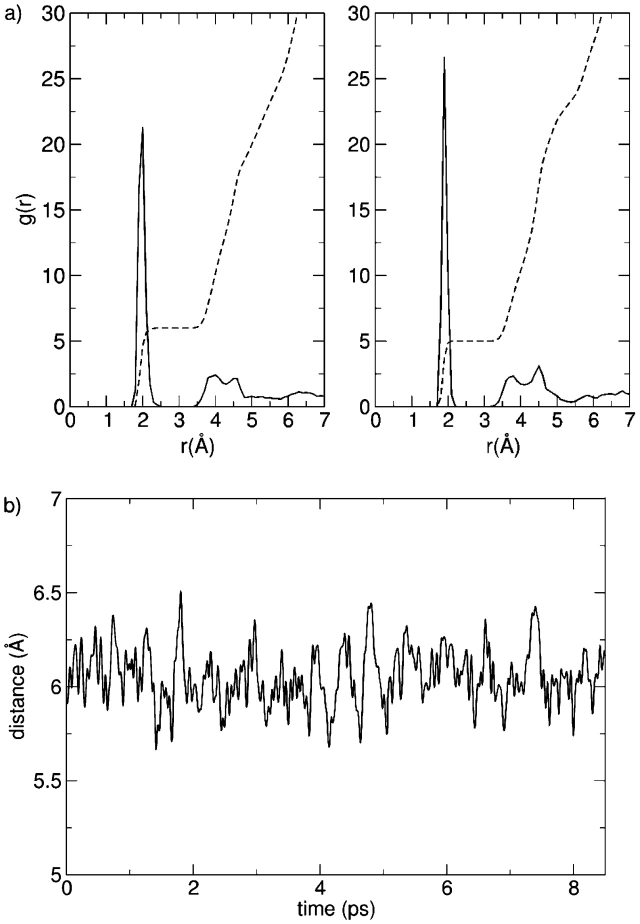

Figure 9. Structure and stability of the hexamer in solution. (a) Representative Al−O radial distribution functions and the corresponding running coordination number integrals for an octahedrally coordinated aluminum (left) and the incomplete monomer unit (right). (b) Time dependence of a representative Al−Al distance.

An interesting outcome of our gas-phase structural analysis of the ACH system is that in the smaller ACH species one of the chloride ions prefers to be a part of the octahedral structure surrounding aluminum atoms as opposed to occupying an outer, loosely bound position. For the dimer, in which the interchange of an H_2O molecule and a Cl^- ion is observed to occur spontaneously in gas phase, this position can be characterized as axial. The monomer, the dimer, and the trimer show an increased stability of ≥10 kcal/mol upon the inclusion of one chloride ion into the octahedral structure. Additionally, incorporation of two Cl^- ions into the dimer structure, one into each monomer unit, doubles the stabilization effect, leading to a 20 kcal/mol decrease in energy. A 2-fold substitution within one monomer unit, however, leads to a decreased stability, as can be seen from the monomer study. Assuming transferability of the effect from the monomer to the larger polymers based on 1-fold substitution, we predict that a 2-fold substitution of strongly bound H_2O molecules by Cl^- ions within one monomer unit in larger ACH polymers would lead to destabilization. Thus, the optimal structure of the small ACH polymers seems to incorporate one Cl^- ion per monomer unit into the octahedral structure, though in larger polymers, steric crowding might mitigate this effect.

The gas-phase CPMD study of the hexamer revealed that some H_2O molecules vacate the outer, axial octahedral positions and move to surround chloride ions which are peripheral to the polymer. Similar behavior is observed for the Al_{13}-mer.[6] As opposed to the dimer, no chloride ions diffuse into the unoccupied locations, due to more energetically favorable contacts with peripheral H_2O molecules at the surface of the larger polymer. Additionally, chloride ions, if embedded in the larger polymers, might exert too much steric strain due to their size and the bulkiness of the rest of the polymer.

The presence of one chloride ion in the octahedral structure of the dimer appears stable in solution, where, during 8 ps of a CPMD run, the Cl^- ion does not show any tendency to leave its embedded position. Similarly, the optimized gas-phase structure of the hexamer is maintained in the solution, where we find no evidence of bulk H_2O molecules or chloride ions moving to occupy octahedral axial vacancies in the course of nearly 10 ps. We conclude therefore that the existence of incomplete octahedral ACH polymers, as well as polymers which have strongly bound chloride ions, is probable in ACH solutions.

Our results of the chloride ion behavior seem to support the conclusions of Tobias,[32] who showed that chloride ions prefer to occupy a surface location on the $Cl(H_2O)_{1-4}$ cluster, due to a favorable polarization of the chloride anion. Following this reasoning, the chloride ion doubly benefits from the position at the interface between the cluster and bulk water: due to an induced dipole in the Cl^- ion by the Al^{3+} ions and an asymmetrical environment, it experiences stabilizing interactions, along with hydrogen bonding interactions with bulk water molecules.

V. Summary

Aluminum chlorohydrate salts have been widely used by the cosmetic and water purification industries for almost 100 years. However, the structure and molecular dynamics of the species involved is yet to be elucidated and the current knowledge on the ACH salts lacks predictive power with regard to properties. Current analytical techniques offer limited information in that regard, and thus the details of the structure−property relationships are mostly unknown. This prompted our modeling investigation in an attempt to finally confirm some of the models proposed in the literature and to introduce novel information on the structure of the ACH salts.

While our results conclusively demonstrate the general octahedral structure of the monomer, dimer, trimer, and hexamer, we find that chloride ions play an important, unanticipated role in ACH polymer structure. Investigated polymers with $n = 2-6$ are shown to be built from octahedral units connected via OH bridges, with H_2O molecules coordinating Al^{3+} ions at peripheral positions. In small species, i.e., the monomer and the dimer, the Cl^- ion is found to be a part of the octahedral structure, assuming an axial peripheral location in the dimer. This explains findings of several groups,[3] whose experiments indicated that not all of chloride ions are in the free ionized form. The gas-phase structure of the hexamer is predicted to be built from incomplete octahedral units. This structure persists in solution, and there is no evidence that the Cl^- ions either occupy the vacancies or replace H_2O molecules in the hexamer within 9 ps of CPMD dynamics. Our models indicate that the described dimer and hexamer structures are stable in solutions.

Acknowledgment. The simulation work at the University of Pennsylvania was supported by a grant from the Colgate-Palmolive Co. V.P. thanks Dr. S. Nielsen and Dr. B. Chen for their help.

References and Notes

(1) Fitzgerald, J. J.; Rosenberg, A. H. Chemistry of Aluminum Chlorohydrate and Activated Aluminum Chlorohydrates. In *Antiperspirants and Deodorants*; Laden, K., Ed.; Marcel Dekker: New York, 1999; Vol. 20.

(2) Teagarden, D. L.; Hem, S. L. *J. Soc. Cosmet. Chem.* **1982**, *33*, 281.

(3) Fitzgerald, J. J. Chemistry of Basic Commercial Aluminum Hydrolysis Complexes. In *Antiperspirants Deodorants*; Laden, K., Felger, C. B., Eds.; Marcel Dekker: New York and Basel, 1988; Vol. 7, p 119.

(4) Johansson, G. *Acta Chem. Scand.* **1960**, *14*, 771.

(5) Teagarden, D. L.; Kozlowski, J. F.; White, J. L.; Hem, S. L. *J. Pharm. Sci.* **1981**, *70*, 758.

(6) Pophristic, V.; Balagurusamy, V. S. K.; Klein, M. L. *Phys. Chem. Chem. Phys.*, accepted for publication, 2004.

(7) Bottero, J. Y.; Cases, J. M.; Flessinger, F.; Poirier, J. E. *J. Phys. Chem.* **1980**, *84*, 2933.

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

(9) Riesgraf, D. A.; May, M. L. *Appl. Spectrosc.* **1978**, *32*, 362.

(10) Brosset, C.; Biedermann, G.; Sillen, L. G. *Acta Chem. Scand.* **1954**, *8*, 1917.

(11) Kubicki, J. D.; Sykes, D.; Apitz, S. E. *J. Phys. Chem. A* **1999**, *103*, 903.

(12) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: San Diego, 1990.

(13) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(14) Hutter, J.; Alavi, A.; Deutch, T.; Bernasconi, M.; Goedecker, S.; Marx, D.; Tuckerman, M.; Parrinello, M. *CPMD* MPI fur Festkorperforschung and IBM Zurich Research Laboratory, 1995−1999.

(15) Frisch, M. L.; et al. *Gaussian98*; Gaussian Inc.: Pittsburgh, 1998.

(16) Goedecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703.

(17) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.

(18) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425.

(19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(21) Sillanpaa, A. J.; Paivarinta, J. T.; Hotokka, M. J.; Rosenholm, J. B.; Laasonen, K. E. *J. Phys. Chem. A* **2001**, *105*, 10111.

(22) Nose, S. *J. Chem Phys.* **1984**, *81*, 511.

(23) Nose, S. *Mol. Phys.* **1984**, *52*, 255.

(24) Hoover, W. G. *Phys. Rev. A* **1985**, *31*, 1695.

(25) Optimizations of the $Al_2(OH)_5Cl$ unit with and without the Cl bridge were performed at the following levels: HF (basis sets 6-31G(d,p), 6-31G(2d,p), 6-311G(3df,2p)) and MP2/6-31G(d,p). The difference in energy converges to 19 kcal/mol.

(26) Gale, J. D.; Rohl, A. L.; Watling, H. R.; Parkinson, G. M. *J. Phys. Chem. B* **1998**, *102*, 10372.

(27) Depending on the pH, concentration and other conditions, it is believed that structures corresponding to $Al(H_2O)_n(OH)_m$, $n + m = 6$, exist for combinations of n and m involving $n = 3$, 4, 5, and 6 (ref 1). We investigate only the $Al(H_2O)_6^{3+}$ species.

(28) Bakker, A.; Hermansson, K.; Lindgren, J.; Probst, M. M.; Bopp, P. A. *Int. J. Quantum Chem.* **1999**, *75*, 659.

(29) Ruiz, J. M.; McAdon, M. H.; Garces, J. M. *J. Phys. Chem. B* **1997**, *101*, 1733.

(30) Evans, H. T. *Inorg. Chem.* **1966**, *5*, 967.

(31) Neil, S. L.; White, J. L.; Hem, S. L. *J. Pharm. Sci.* **1976**, *65*, 1188.

(32) Tobias, D.; Jungwirth, P.; Parrinello, M. *J. Chem Phys.* **2001**, *114*, 7036.