Hydration of the Cations Al^{3+} and Cu^{2+}. A Theoretical Study

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Abstract: The hydration number and the hydration energy of the cations Al^{3+} and Cu^{2+} are discussed on the basis of LCAO-MO-SCF ab initio calculations. A simple model is proposed for the second hydration shell. The calculated binding energies account for the hydration number of six of the Al^{3+} and Cu^{2+} cations in solution and for the S_N1 mechanism proposed for the exchange of the water molecules between the hydration sphere of Al^{3+} and the bulk solvent.

Introduction

The hydration of metal cations is a key phenomenon for the understanding of the chemistry of aqueous solutions. Many theoretical studies have been devoted to the prediction of the structure of cation hydrates.[1-18] This is an attractive problem for a theoretical approach since (1) both the cation and the water molecule represent relatively small systems and (2) the hydration energies are relatively large; the theoretical values obtained at the SCF level of calculation are probably relatively accurate since the hydrated systems and the corresponding fragments are usually closed-shell systems for which the change in correlation energy along the energy hypersurface is probably small (see ref 12).

The hydration of metal cations may be studied for either its structural aspects or its kinetic implications. The structural aspect is related to the hydration number and the hydration energy. The dynamical aspect deals with the exchange mechanism of the water molecules between the bulk water and the first hydration shell. So far, the theoretical studies of cation hydration have been concerned only with the structural aspects. Most of these studies deal with the hydration of alkali and alkali-earth cations, and comparatively little work has been devoted to the hydration of cations either from the group 3A[16] or from the transition metal series.[2,5,6] Three different levels of approximation have been used for the theoretical studies of cation hydration.

(1) Semiempirical Methods (mostly EHT and CNDO).[1-8] These methods have been used for cation-water assemblies including up to eight water molecules, thus providing for a description of the first solvation shell and allowing a discussion of the preferential hydration number. However, the results obtained are probably not very accurate. Both hydration numbers of 4 and 6 have been reported for the Li^+ cation from CNDO studies.[4,7] On the basis of an EHT study,[5] a hydration number of 4 is found for the ions of the first transition series, a rather unexpected conclusion since it has been inferred that for all the di- and tripositive ions of the first transition series the aquo ions are octahedral $M(H_2O)_6{}^{m+}$ species.[19]

(2) Ab Initio Methods at the SCF Level. Most often, one or two water molecules at most are considered (however, a calculation has been reported with six molecules of water around the cation Li^+ [15]). The computed hydration energies appear rather accurate as one may judge from the comparison with the enthalpies of hydration in the gas phase.[18]

(3) Calculations Based on the Pairwise Additivity Approximation. Here the potential surfaces for mono- and dihydrates are used to generate the surfaces for polyhydrates.[15,16]

Most of the previous theoretical studies consider only the first hydration shell surrounding the metal cation. A general trend found in this type of calculation is a monotonic increase of the hydration energy with the hydration number (whereas one would expect a maximum binding energy for the "experimental" value of the hydration number, usually 4 for Li^+ or 6). In fact, there is no reason to believe that the interaction between the cation and the water molecules is limited to the first hydration shell. Kollman and Kuntz reported that in the most stable configuration of the cluster (Li^+,$5H_2O$) one water molecule prefers to be in the second coordination sphere.[17] Diercksen and Kraemer found an interaction energy of 16 kcal/mol between a water molecule bound to a Li^+ cation and a second water molecule, a value well above the hydrogen bond energy for the water dimer.[11]

We report here a systematic ab initio study of the hydration of the cations Al^{3+} and Cu^{2+} with up to eight water molecules. The cation Al^{3+} has been chosen on the basis of (i) the large charge which makes it a prototype structure maker; (ii) the wealth of experimental data regarding the mechanism of exchange of water with the bulk solvent.[20,21] The cation Cu^{2+} has been chosen as representative of the transition metal cations since the d^9 configuration makes the open-shell SCF treatment relatively easy.

The Calculations

LCAO-MO-SCF calculations were carried out with the system of programs Asterix[22] using Gaussian basis sets (11,7,5) for Cu,[23] (10,6) for Al,[24] (8,4) for O,[25] and (4) for H.[26] These Gaussian basis sets were contracted to [4,3,2/4,3/3,2/2], namely a minimal set for the inner shells and the Cu 4s and 4p shells together with a double-ζ set for the valence shells. The open-shell SCF calculations were carried out within the restricted Hartree-Fock formalism.[27]

The systems $M(H_2O)_n$ ($M = Al^{3+}$ or Cu^{2+}, $n = 1-8$) are represented in Figures 1-10. The n water molecules distributed around the metal cation represent the first coordination sphere. The experimental geometry of the water molecule (bond length of 0.957 Å and bond angle of 104.52°) was used.[28,29] The $M-H_2O$ unit is assumed planar with the metal atom along the bisector of the HOH angle ($\theta = 0°$, Figure 1).[30] In the highly symmetric clusters of Figures 1-10 the only parameter left is the metal-oxygen distance. For the clusters $Al(H_2O)_n{}^{3+}$ with $n \leq 6$, the aluminum-oxygen distance has been kept to the experimental value of 1.90 Å.[28,32] For $n = 7$ with a pentagonal bipyramidal structure, the axial bond length has been assumed equal to 1.90 Å and optimization of the equatorial Al-O distance yielded a value of 2.12 Å. For the monocapped trigonal prism corresponding to $n = 7$, a common value of 2.12 Å was assumed for the Al-O bond lengths.[33] For $n = 8$ with a square antiprism structure we have assumed an Al-O distance of 2.20 Å.

For the clusters $Cu(H_2O)_n{}^{2+}$ with $n = 1, 2,$ and 4 (square planar), the Cu-O bond length has been optimized. The optimized bond length of 1.948 Å for $n = 4$ (square planar) has been kept for $n = 4$ (tetrahedral), $n = 5$ (trigonal bipyramid

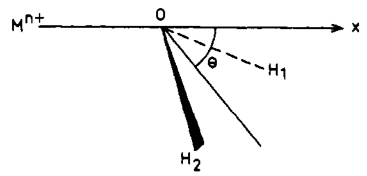


Figure 1. Geometry of the cluster $M(H_2O)^{m+}$.

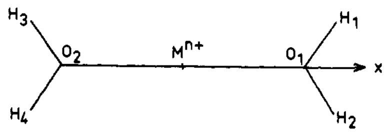


Figure 2. Geometry of the cluster $M(H_2O)_2{}^{m+}$.

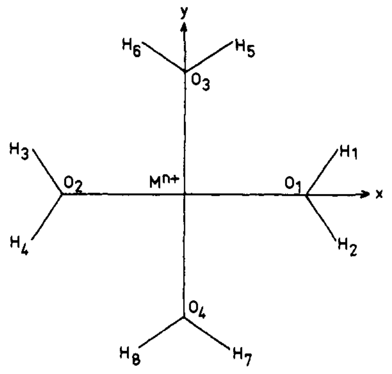


Figure 3. Geometry of the cluster $M(H_2O)_4{}^{m+}$ (square planar).

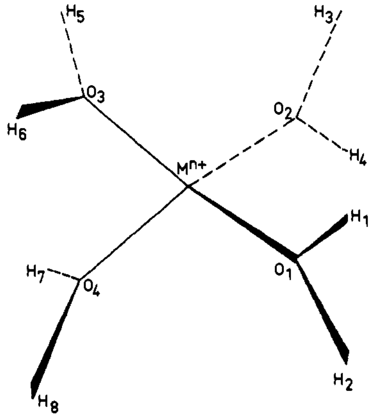


Figure 4. Geometry of the cluster $M(H_2O)_4{}^{m+}$ (tetrahedral).

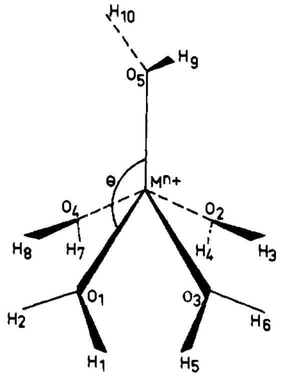


Figure 5. Geometry of the cluster $(M(H_2O)_5{}^{m+}$ (square pyramidal).

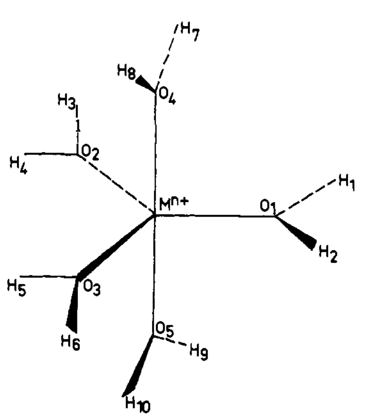


Figure 6. Geometry of the cluster $M(H_2O)_5{}^{m+}$ (trigonal bipyramidal).

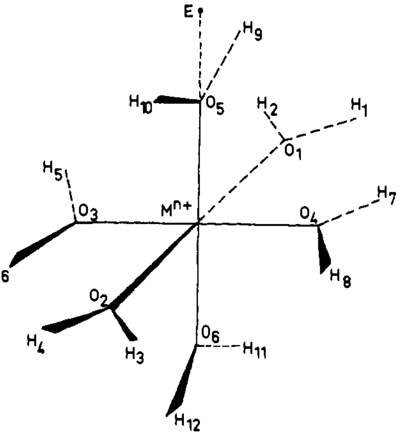


Figure 7. Geometry of the cluster $M(H_2O)_6{}^{m+}$.

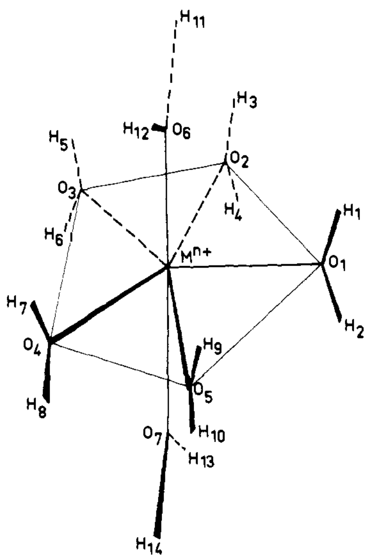


Figure 8. Geometry of the cluster $M(H_2O)_7{}^{m+}$ (pentagonal bipyramidal).

and square pyramid[34]), and $n = 6$ (for the equatorial bond lengths). When the Cu^{2+} ion is hexacoordinated, the octahedron is usually distorted with an elongation along one fourfold axis, so that there is a planar array of four short Cu–L bonds and two trans long ones.[35] Optimization of the two axial bond lengths in $Cu(H_2O)_6{}^{2+}$ yielded longer axial bonds of 2.06 Å. For $n = 7$ only the pentagonal bipyramid structure has been considered with an optimized value of 2.27 Å for the Cu–O_{eq} bond length and an assumed value of 1.94 Å for the Cu–O_{axial}

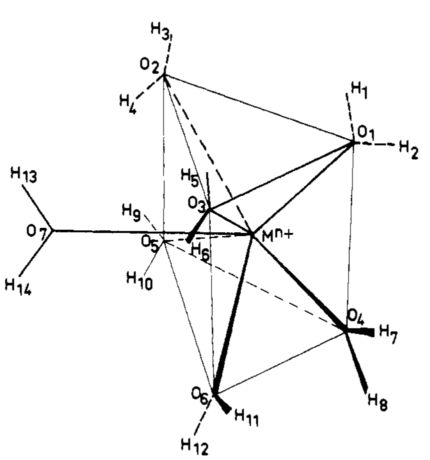
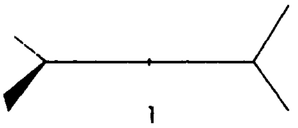


Figure 9. Geometry of the cluster $M(H_2O)_7{}^{m+}$ (monocapped trigonal prism).

bond length.[36] For $n = 8$ the square antiprism structure has been considered with the same metal–oxygen distance of 2.20 Å used for the Al^{3+} cluster.

The water molecules were not allowed to rotate freely about the metal–oxygen axis. To reduce the amount of computation, a geometry with the highest possible symmetry and the maximum number of water molecules in the same plane was usually assumed (for instance, in the cases $n = 4$ and $n = 6$ of Figures 3 and 7, the four water molecules lie in the same plane). The corresponding error in the calculated binding energies is probably small, of the order of a few kcal/mol. For the system $Cu(H_2O)_2{}^{2+}$, the configuration **1** of symmetry D_{2d} is found more stable than **2** (symmetry D_{2h}) by 1.7 kcal/mol.[31] If the



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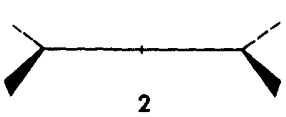

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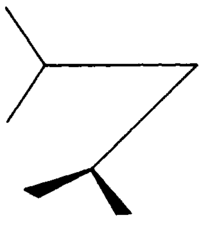
two water molecules are no longer on the same axis but along perpendicular axis, structure **3** is found more stable than **4** by 2.5 kcal/mol.[31] We do not attach too much significance to these small energy differences, but rather to the fact that they are much smaller, by about two orders of magnitude, than the calculated binding energies.



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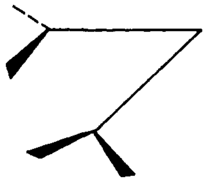

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The electronic ground states and the corresponding energy values are reported in Tables I and II. The optimized bond lengths in the clusters $Cu(H_2O)_n{}^{2+}$ with $n = 1, 2, 4$ are also given in Table II.

Discussion

Binding Energies for the First Solvation Shell. We discuss first the results for the symmetrical clusters corresponding to the progressive building of the first coordination sphere. The optimized Cu–O bond length of 1.948 Å for $n = 4$ is in good agreement with the experimental value of 1.93 ± 0.03 Å for the Cu–O equatorial bond lengths in aqueous copper chloride solutions.[38]

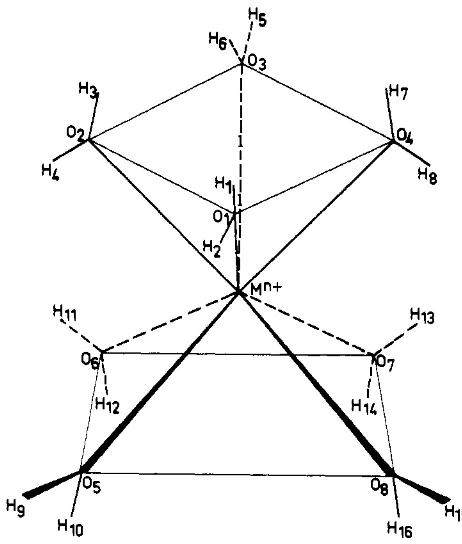


Figure 10. Geometry of the cluster $M(H_2O)_8{}^{m+}$.

The binding energies given in Tables I and II for each value of n are defined as

$$\Delta E(n) = -E[M(H_2O)_n{}^{m+}] + E(M^{m+}) + nE(H_2O)$$

the energy values for the cation and the water molecule being computed with the same basis set.[39] The computed binding energy of 191 kcal/mol for the cluster $Al(H_2O)^{3+}$ is very close to the value of 180 kcal/mol reported in the literature.[16] For the clusters $Cu(H_2O)^{2+}$ and $Cu(H_2O)_2{}^{2+}$, improvement of the basis set by inclusion of polarization functions at the level of the oxygen and hydrogen atoms decreases only slightly the computed binding energies: 108 kcal/mol for $n = 1$ instead of 115 kcal/mol, and 205 kcal/mol for $n = 2$ instead of 220 kcal/mol.[31] This indicates that the computed binding energies of Tables I–III are probably not too sensitive to the basis set superposition effect.[40] The computed binding energies of Tables I and II increase in a monotonic way when the number of water molecules in the first hydration shell increases (up to eight). A similar behavior may be noted for the enthalpies of hydration in the gas phase of the monovalent strontium, lead, and bismuth ions.[41-43] Our results do not support the conclusions of Zhogolev et al.,[5] based on extended Hückel calculations, that the hydration number of 4 is energetically the most favorable one for the transition metal ions. The binding energy computed for $n = 6$ does not correspond to a maximum, although a value of 6 has been reported for the hydration number of the cations Al^{3+} [44] and Cu^{2+}.[45] However, one finds that the binding energy $\Delta E_{n-1,n}$ corresponding to the successive addition of water molecules decreases sharply beyond $n = 6$,

Table I. SCF Energies and Computed Binding Energies for the Clusters $Al(H_2O)_n{}^{3+}$

n	Structure	E, au	Binding energy, kcal/mol	$\Delta E_{n-1,n}$, kcal/mol
1		−315.8730	191	191
2	Linear	−392.0501	363	172
3	Trigonal planar	−468.1808	507	144
4	Tetrahedral	−544.2745	626	119
	Square planar	−544.2341	601	94
5	Trigonal bipyramid	−620.2919	698	72
	Square pyramid	−620.2948	700	74
6	Octahedral	−696.3005	765	65
7	Pentagonal bipyramid	−772.2038	765	0
	Capped trigonal prism	−772.1593	737	(−28)
8	Square antiprism	−848.1302	781	16

Table II. SCF Energies and Computed Binding Energies for the Clusters $Cu(H_2O)_n{}^{2+}$

n	Structure	Electronic ground state	E, au	Binding energy, kcal/mol	$\Delta E_{n-1,n}$, kcal/mol	Optimized Cu-O bond length, Å
1		$^2A_1$	−1710.7122	115	115	1.839
2	Linear	^2A_g	−1786.7822	220	105	1.862
4	Square planar	$^2B_{1g}$	−1938.7860	345		1.948
	Tetrahedral	$^2B_2$	−1938.7752	338		
5	Square pyramid	$^2A_1$	−2014.7471	381	36	
	Trigonal bipyramid	$^2A_1$	−2014.7466	381	36	
6	Octahedron	^2A_g	−2090.6952	410	29	
7	Pentagonal bipyramid	$^2A_1$	−2166.6002	411	1	
8	Square antiprism	$^2E_2$	−2242.6614	415	5	

probably as a consequence of the strong steric interactions between different water ligands (we have mentioned that for $n = 7$ and 8 some oxygen-oxygen distances are less than the sum of the van der Waals radii). Experimentally the solvation number of the Al^{3+} cation may be decreased from 6 to 4 by increasing the steric requirements of the ligands.[46] Conversely, coordination numbers of 7 or 8 have been reported for alkali and alkali-earth cations coordinated by multidentate ligands, with large metal-ligand distances imposed by the stereochemistry of the ligands.[47-50] Coordination numbers of 8 have also been reported for aqueous lanthanum(III) chloride and gadolinium(III) chloride solutions, with lanthanide-oxygen distances of 2.4-2.5 Å.[51,52]

Not only do the results of Tables I and II not account for the experimental hydration number, but the computed binding energies of about 780 kcal/mol for Al^{3+} and 415 kcal/mol for Cu^{2+} are well below the experimentally reported hydration enthalpies, respectively 1116 and 503 kcal/mol.[53] The discrepancy is certainly too large to be traced to the various approximations of the theoretical treatment: limitation of the basis set expansion, neglect of the zero-point energy, and neglect of the contribution of the correlation energy to the binding energy.[54] We believe that the main reason for this discrepancy is the neglect of the hydration shells beyond the first hydration shell. To check this point, we have used a relatively simple model of the second coordination sphere.

Model for the Second Hydration Shell. For the sake of economy, the study of the second hydration shell was limited to the case of the Al^{3+} ion. The model systems considered explicitly include one or at most two water molecules in the second hydration shell; namely, they correspond to the interaction between a cluster $Al(H_2O)_n{}^{3+}$, $n = 5$, 6, or 7 (with n water molecules in the first hydration shell and the same structures as above), and one (or two) additional molecule(s) of water in the second hydration shell. A first series of calculations was carried out for $n = 6$, with two different locations of the additional water molecule: (i) the additional water molecule is located along the (1,1,1) axis of the octahedron (Figure 7), the corresponding Al-O(7) distance being set to 3.3 Å on the basis of a steric criterion (namely a distance of 2.69 Å between the oxygen atom O(7) and the three nearby oxygen atoms from the first solvation shell, close to the sum of the van der Waals radii for the oxygen atoms), the corresponding interaction being of the type charge-dipole and dipole-dipole interactions;[55] (ii) the additional water molecule forms a hydrogen bond with a water molecule from the first hydration shell, as shown in Figure 11 (the distance between the two oxygen atoms being set to 2.68 Å[11]). The corresponding SCF energies are reported in Table III. For both locations of the additional water molecule in the second coordination sphere, the interaction is energetically favorable, but the binding energy is larger, 39 kcal/mol instead of 26 kcal/mol (see Table III), when the water molecules of the first and second hydration shells are hydrogen bonded. In what follows we have assumed that each water molecule of the first hydration shell is hydrogen bonded to two water molecules of the second hydration shell (Figure 12). That the interactions between the two hydration shells are approximately additive was checked by carrying out one calculation where two water molecules in the second hydration shell form hydrogen bonds to the same water molecule of the first shell; the binding energy for the first and second hydrogen bonds are found respectively equal to 39 and 35 kcal/mol (Table III).

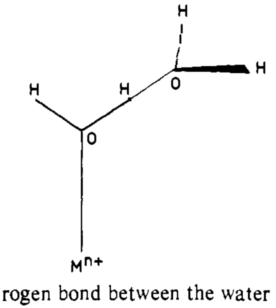


Figure 11. The hydrogen bond between the water molecules of the first and second hydration shells.

The total energies and the binding energies for the clusters with six, seven, or eight molecules of water and different distributions of these water molecules between the two hydration shells are reported in Table III. The cluster with six water molecules prefers to have all six molecules in the first hydration shell; the clusters with seven or eight molecules of water prefer to have six molecules in the first hydration shell and the one

Table III. Total Energies and Binding Energies for the Clusters $Al(H_2O)_n{}^{3+}$ with n_1 Molecules of Water in the First Hydration Shell, n_2 Molecules of Water in the Second Hydration Shell, and n_∞ Molecules of Water at Infinity

n	n_1	$n_2{}^a$	n_∞	E, au	Relative energy, kcal/mol
6	5^b		1	−696.1969	0
	5^b	1		−696.2660	43
	5^b	1^c		−696.2433	29
	6			−696.3004	65
7	6		1	−772.2027	0
	6	1		−772.2651	39
	6	1^c		−772.2446	26
	7			−772.2038	0
8	6		2	−848.1050	0
	6	1	1	−848.1677	39
	6	2		−848.2241	75
	7		1	−848.1064	0
	7	1		−848.1763	45
	8			−848.1302	16

[a] Unless otherwise stated, a water molecule in the second hydration shell is hydrogen bonded to a water molecule in the first hydration shell. [b] With the square pyramid structure. [c] No hydrogen bonding; see text.

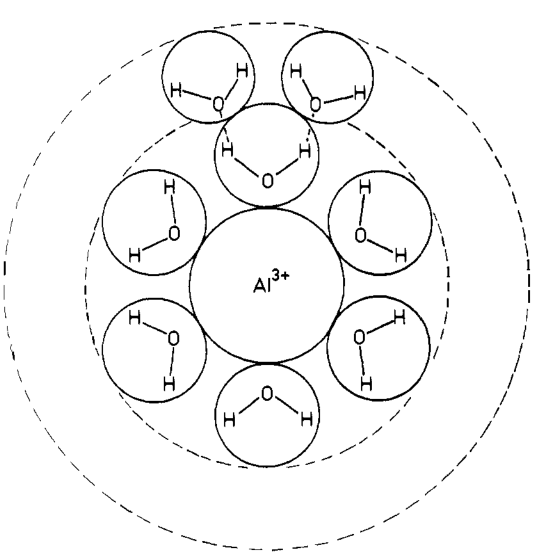


Figure 12. A schematic representation of the first and second hydration shells around the cation Al^{3+}.

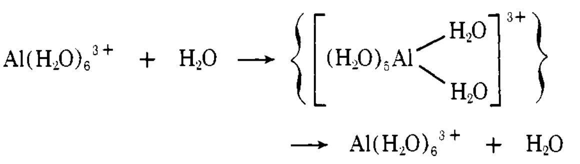
or two molecules left in the second hydration shell. The data of Table III are thus in agreement with the coordination number of 6 assigned to the Al^{3+} ion. A simple rationale may be given by pointing out that the binding energy $\Delta E_{n-1,n}$ corresponding to the successive addition of water is larger than the hydrogen bond energy up to $n = 6$, but becomes smaller for n greater than 6. When the hydration number exceeds 6, it is energetically more favorable for the additional water molecule to form a second hydration shell than to insert in the first shell. A similar analysis has been given by Kollman and Kuntz in their discussion of the hydration number of Li^+.[17]

The total hydration energy of the Al^{3+} cation may be estimated by summing up the binding energy for the six water molecules of the first hydration shell together with the energy of the twelve hydrogen bonds connecting the two coordination spheres, namely

$$E(\text{hydration}) = 765 + 12 \times 37 - 24 \times 7 = 1041 \text{ kcal/mol}$$

by using an average hydrogen bond energy of 37 kcal/mol and taking into account that one has to break down 24 hydrogen bonds in the bulk water (the binding energy for the water dimer being computed as 7 kcal/mol with the same basis set). This computed hydration energy of 1041 kcal/mol may be compared with the experimental hydration enthalpy of 1116 kcal/mol; the agreement may be considered as good given the simple model used. The effects of temperature and of added aprotic solvents on the proton magnetic resonance spectra of Al^{3+} aqueous solutions has been interpreted in terms of strong secondary solvation.[58] Hydrogen-bonded interactions between the water molecules of the first hydration shell and chloride anions in the second coordination sphere have been postulated to interpret the x-ray diffraction data for aqueous lanthanum(III) chloride and gadolinium(III) chloride solutions.[51,52]

Exchange Reaction between Water Molecules Coordinated to Al^{3+} and the Solvent. The exchange reaction of the water molecules between the aquo complex $Al(H_2O)_6{}^{3+}$ and the noncoordinated water molecules has been studied by NMR.[20,21] An S_N1 mechanism was inferred, mostly on the basis of the entropy of activation, and the enthalpy of activation was estimated as 27 kcal/mol. However, on the same basis, an S_N2 mechanism was proposed for the exchange reaction of $Ga(H_2O)_6{}^{3+}$.[21] It is generally considered that the transition state for an S_N2 mechanism (eq 1) may resemble a seven-coordinated system, whereas the transition state for an S_N1 mechanism (eq 2) should be similar to the five-coordinated intermediate.[59,60]



$$Al(H_2O)_6{}^{3+} + H_2O \rightarrow \left\{ \left[(H_2O)_5Al \begin{matrix} \nearrow H_2O \\ \searrow H_2O \end{matrix} \right]^{3+} \right\} \rightarrow Al(H_2O)_6{}^{3+} + H_2O \qquad (1)$$

$$Al(H_2O)_6{}^{3+} \rightarrow H_2O + \underset{\substack{\text{five-coordinated} \\ \text{intermediate}}}{Al(H_2O)_5{}^{3+}} \xrightarrow{H_2O} Al(H_2O)_6{}^{3+} \qquad (2)$$

More precisely, it is assumed that the relative energies of the five- and seven-coordinated species represent a lower limit to the energy of the transition states corresponding respectively to the S_N1 and S_N2 mechanisms. On the basis of the hydration energies of Table I, the energy needed to increase the hydration number from 6 to 7 should be close to 0, whereas the abstraction of one water molecule from the six molecules in the first hydration shell should require about 65 kcal/mol. The S_N2 mechanism would appear as energetically much more favorable than the S_N1 mechanism. However, this conclusion is probably in error, because, in the reaction considered, the exchanged molecules of water are either taken from infinity or removed to infinity. A more realistic scheme would consider the exchange of a water molecule between the first and the second hydration shells according to

$$Al(H_2O)_6{}^{3+} \xrightarrow{S_N1} Al(H_2O)_5(H_2O^{2S})^{3+} \qquad (3)$$

$$Al(H_2O)_6(H_2O^{2S})^{3+} \xrightarrow{S_N2} Al(H_2O)_7{}^{3+} \qquad (4)$$

where H_2O^{2S} denotes a molecule in the second hydration shell. The idea that the exchange reaction involves a water molecule from the second hydration shell may be found in ref 61. The SCF energies for the corresponding clusters with six or seven water molecules are given in Table III. The activation energies are now respectively 21 and 38 kcal/mol for the S_N1 and S_N2 mechanisms, written as eq 3 and 4. The S_N1 mechanism is the most favorable energetically, the lower limit of 21 kcal/mol computed for the activation energy being in satisfactory agreement with the experimental enthalpy of activation of 27 kcal/mol.[21]

Conclusion

We have found that a model of the hydrated cations Al^{3+} and Cu^{2+} which is limited to the first hydration shell does not account for the experimental value of 6 reported for the coordination number. Furthermore, the computed hydration energies are well below the experimental enthalpies of hydration. To improve the description of the hydrated cation, we have used a simple model where each water molecule of the first hydration shell is hydrogen-bonded to two water molecules in the second hydration shell. This model accounts for the hydration number of 6 for the Al^{3+} cation in solution, since additional water molecules prefer to fill the second hydration shell and form hydrogen bonds to the water molecules of the first shell rather than to coordinate to the Al^{3+} cation. This model with six water molecules in the first hydration shell and twelve water molecules in the second shell yields a computed hydration energy which is close to the experimental enthalpy of hydration. The same model accounts for the S_N1 mechanism proposed for the exchange of the water molecules between the hydration sphere and the bulk solvent, provided that the exchange is considered to take place between the first and the second hydration shells. Although detailed calculations have been carried out only for the hydration of the Al^{3+} cation, the model can probably be extended to other divalent and trivalent cations (the interaction between the first and the second hydration spheres is probably stronger for the trivalent cations).

To check this point, a calculation was carried out for the system $Cu(H_2O)_7{}^{2+}$ with six water molecules in the first hydration shell and a seventh molecule in the second hydration shell (hydrogen bonded to one equatorial ligand of the first shell) and yielding a binding energy of 434 kcal/mol with a hydrogen bond energy of 24 kcal/mol. This result, when compared to the ones of Table II, indicates that the cluster with seven or more molecules of water around a Cu^{2+} ion prefers to have six water molecules in the first hydration shell and the additional molecules in the second hydration shell. A simple, additive calculation, similar to the one presented above for the Al^{3+} ion, yields a total hydration energy of 530 kcal/mol in good agreement with the experimental hydration enthalpy of 503 kcal/mol. The results of Table II invalidate the conclusions of Zhogolev et al,[5] based on extended Hückel calculations, that the hydration number of 4 is energetically the most favorable one for the transition metal cations (although tetrahedral coordination has been proposed for nonaqueous solutions of cobalt(II), in aqueous solutions cobalt(II) exists essentially as $[Co(H_2O)_6]^{2+}$).[62] We have not considered the interaction between the metal cation and the water molecules beyond the second hydration shell, which is probably relatively unimportant (according to the population analysis, the water molecules of the second hydration shell are comparatively less polarized than the molecules of the first hydration shell[31]).

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(33) Then the O(7)-O(2) distance of Figure 9 is equal to 2.35 Å, somewhat shorter than the sum of the van der Waals radii for two oxygen atoms, but comparable to the O_{eq}–O_{eq} distance of 2.47 Å for the pentagonal bipyramid structure.
(34) Optimization of the Cu-O_{apical} bond length for the square pyramid structure yielded a value of 2.07 Å.
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