Structural rigidity of first hydration spheres of Na^+ and Ca^{2+} in cluster models. Full geometry optimizations of $[M(H_2O)_6]^{n+}$, $[M(H_2O)_6 \cdots H_2O]^{n+}$ and $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$ (M = Na and Ca, $n = 1$ for Na and 2 for Ca) by density functional calculations

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Abstract

The intrinsic structural rigidity of hexaaqua complexes of Na^+ and Ca^{2+} has been examined on the basis of full geometry optimizations on cluster models of $[M(H_2O)_6]^{n+}$, $[M(H_2O)_6 \cdots H_2O]^{n+}$ and $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$ (M = Na and Ca, $n = 1$ for Na and 2 for Ca) by use of the *ab initio* density functional method with Gaussian-type basis sets. The optimized geometries of $[Na(H_2O)_6]^+$ and $[Ca(H_2O)_6]^{2+}$ were both a regular octahedron. In the optimization for adding a water molecule or a chloride anion to the $[Na(H_2O)_6]^+$ model, $[Na(H_2O)_6 \cdots H_2O]^+$ and $[Na(H_2O)_6 \cdots Cl]$, each octahedral $[Na(H_2O)_6]^+$ unit was kept within six-coordination, although both structures were strongly distorted. On the other hand, in the $[Ca(H_2O)_6 \cdots H_2O]^{2+}$ and $[Ca(H_2O)_6 \cdots Cl]^+$ system, the additional ligand, H_2O and Cl^-, was participated in the coordination to the Ca^{2+} ion and the coordination number of Ca^{2+} was changed from six to seven. The results were compared with those of the K^+ and Mg^{2+} complexes previously reported, and the differences in the intrinsic structural rigidity of the hexaaqua complexes of Na^+, K^+, Mg^{2+} and Ca^{2+} were explained in terms of the charges and ionic radii of the cations. The formation of an $M^{n+} - Cl^-$ ion-pair in aqueous solution was also discussed.

Introduction

Recently, we performed the full geometry optimizations for $[M_1(H_2O)_6]^{n+}$, $[M_1(H_2O)_6 \cdots H_2O]^{n+}$ and $[M_1(H_2O)_6 \cdots Cl]^{(n-1)+}$, ($M_1 = K$ and Mg, $n = 1$ for K and 2 for Mg) [1], and found a unique specificity of the coordination structure of the ions. The octahedral structure of the $[K(H_2O)_6]^+$ unit was easily broken by the addition of an external ligand such as H_2O and Cl^- through the optimization, whereas that of the $[Mg(H_2O)_6]^{2+}$ unit was almost kept. The difference between the structural rigidities of the octahedral K^+ and Mg^{2+} units are well understandable by taking into account the differences in the charges and ionic radii of the cations; K^+, a large univalent ion, is soft and Mg^{2+}, which is a small divalent ion, is hard. The result agrees with the fact that the K^+ and Mg^{2+} ions are

referred to as so-called 'structure-breaking' and 'structure-making' ions, respectively [2]. Also it is well known that smaller and/or higher charged cations than K^+, such as Na^+ and Ca^{2+}, have been regarded as structure-making ions [2]. Therefore, the octahedral $[Na(H_2O)_6]^+$ and $[Ca(H_2O)_6]^{2+}$ units would be expected to hold their structures through the geometry optimization. It is very interesting to perform the full geometry optimizations of the $[M(H_2O)_6 \cdots H_2O]^{n+}$ and $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$ systems (M = Na and Ca, $n = 1$ for Na and 2 for Ca) and compare them with those of the K^+ and Mg^{2+} complexes reported previously [1].

Another interesting aspect of the previous results for the optimization of $[M_1(H_2O)_6 \cdots Cl]^{(n-1)+}$ was on the formation of $M_1^{n+} - Cl^-$ ion-pairs [1]. For $[Mg(H_2O)_6 \cdots Cl]^+$ the octahedral $[Mg(H_2O)_6]^{2+}$ unit remained almost unchanged, and the additional Cl^- ion was not coordinated to Mg^{2+} but connected to

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hexahydrated Mg^{2+} ion by hydrogen bondings [1]. For $[K(H_2O)_6 \cdots Cl]$, on the other hand, the octahedral $[K(H_2O)_6]^+$ unit was completely destroyed and the Cl^- ion participated in coordination to the K^+ ion accompanied by dissociation of three water molecules from the K^+ ion. It is also interesting to examine if Na^+ and Ca^{2+} form any ion-pair type with Cl^- through the optimization of the $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$ system.

Here, in order to examine the structural rigidity of $[M(H_2O)_6]^{n+}$ and the possibility of the formation of the $M^{n+}-Cl^-$ contact ion-pair, we tried to carry out the full geometry optimizations of $[M(H_2O)_6]^{n+}$, $[M(H_2O)_6 \cdots H_2O]^{n+}$ and $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$ by using the density functional method. Also their dissociation energies were calculated and compared with the previous results for K^+ and Mg^{2+}.

Procedure

Computational details

Ab initio calculations were carried out according to the density functional scheme by the use of the DGauss program [3, 4]. The basis sets are Gaussian functions: (6321/411/1) for sodium, (63321/5211/1) for calcium, (6321/521/1) for chlorine, (621/41/1) for oxygen, and (41) for hydrogen [4]. Exchange-correlation energy was considered including in the non-local corrections developed by Becke [5] and Perdew [6] with about 42 000 grid points. The error in the calculation of the total energies is less than 5.0×10^{-7} a.u. No symmetrical restriction was used during the calculations. All calculations were performed by a CRAY Y-MP8I/8128 computer.

Initial geometries

Water molecules were placed at the apexes of a regular octahedron with T_h symmetry around the central metal atom. The initial M-O distances for both Na^+ and Ca^{2+} were assumed to be 240.0 pm which are equivalent to the sum of the radii of the M^{n+} cation ($Na^+ = 102$ pm, $Ca^{2+} = 100$ pm [7]) and a water molecule (141 pm [8]). The structure of the respective water molecule was assumed to have an O-H bond length of 95.0 pm and an H-O-H angle of 105.0°.

For optimization of $[M(H_2O)_6 \cdots H_2O]^{n+}$, the additional water oxygen atom, O(7), was placed at a distance of 240 pm along the axis from the center of gravity of the triangle defined by the three oxygen atoms, O(1), O(2) and O(5), to the central metal (see Fig. 2(a) and 3(a)). The orientation of the two hydrogen atoms of the water molecule, H(7A) and H(7B), was in parallel to the line of O(2) and O(5). In the case of $[M(H_2O)_6 \cdots Cl]^{(n-1)+}$, the Cl^- ion was placed at an M-Cl distance of 280.0 pm along the same axis (see

Fig. 2(b) and 3(b)), which corresponds to the sum of the ionic radii of M^{n+} and Cl^- (181 pm [7]).

Energy calculations

Dissociation energy was defined as the difference between the total energy of the optimized complex and the sum of the energies of the respective constituents, i.e. Na^+, Ca^{2+}, H_2O and/or Cl^-, being computed with the same basis set. The energy of -76.4424 a.u. was used for a water molecule, which is the total energy of H_2O optimized as an isolated molecule. The structure of the optimized water molecule has the O-H distance of 97.7 pm and the H-O-H angle of 105.7°.

Results and discussion

$[Na(H_2O)_6]^+$ and $[Ca(H_2O)_6]^{2+}$

The optimized geometries for the Na^+ and Ca^{2+} hexaaqua complexes were both a regular octahedron with O-M-O angles of 90.0° or 180.0° within $\pm 0.1°$ as shown in Fig. 1. The orientations of the water molecules were almost all maintained, which was the same as those for K^+ and Mg^{2+} hexaaqua complexes [1]. The optimized M-O bond lengths were 226.8 and 239.1 pm for Na^+ and Ca^{2+} within ± 0.1 pm, respectively. Generally, the Na-O bond length optimized theoretically has been determined to be shorter than that of Ca-O (as shown in Table 2), although the ionic radii of Na^+ (102 pm) and Ca^{2+} (100 pm) determined experimentally by Shannon [7] are nearly equal. This may be due to the difference of environment in experiment and calculation; the former is in a crystalline state and the latter is assumed to be in a gaseous condition.

The dissociation energy calculated for $[Na(H_2O)_6]^+$ is very close to the enthalpy determined experimentally, as shown in Table 1. The agreement between the calculated and experimental values, which has been also found in the case of the $[K(H_2O)_6]^+$ complex [1], may be somewhat accidental, because the calculations do not include the effect of the outer sphere and neglect the presence of some other possible aqua complexes
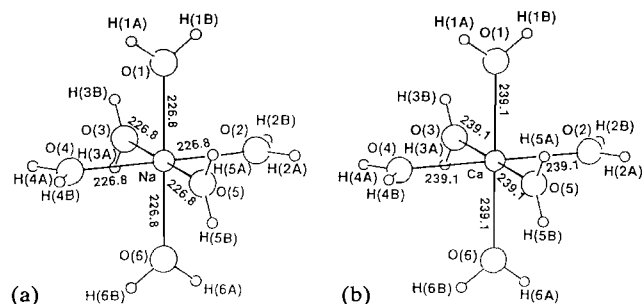

Fig. 1. Optimized geometries of $[Na(H_2O)_6]^+$ (a) and $[Ca(H_2O)_6]^{2+}$ (b) complexes.

TABLE 1. Dissociation energies (kJ/mol) of optimized complexes[a]

	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}
[M(H$_2$O)$_6$]$^{n+}$	-398.9	-314.4	-1340.2	-991.4
	(-407)	(-324)	(-1931)	(-1584)
[M(H$_2$O)$_6$$\cdots$(H$_2$O)]$^{n+}$	-482.7	-427.6	-1437.2	-1046.3
[M(H$_2$O)$_6$$\cdots$Cl]$^{(n-1)+}$	-911.4	-852.9	-2175.8	-1811.5

[a]Values for K$^+$ and Mg^{2+} were taken from ref. 1. Experimental enthalpies of hydration in parentheses are from ref. 10.

such as [Na(H$_2$O)$_4$]$^+$, [Na(H$_2$O)$_5$]$^+$, [Na(H$_2$O)$_7$]$^+$ and [Na(H$_2$O)$_8$]$^+$ which have been previously determined to have an experimental hydration number of 4–8 [9].

Such agreement not only in K$^+$ but also in Na$^+$, however, may imply that the experimentally determined hydration energies in univalent cations are affected importantly by the formation energies of the first hexahydration spheres and that the interactive effect of the outer sphere and the presence of the other types of aqua complexes are not so important in considering the hydration of the cations in an aqueous solution.

On the other hand, the dissociation energy calculated for Ca^{2+} is about 60% of the experimentally determined value (see Table 1). Such a large difference may be partially due to the existence of other aqua complexes such as [Ca(H$_2$O)$_5$]$^{2+}$, [Ca(H$_2$O)$_7$]$^{2+}$, [Ca(H$_2$O)$_8$]$^{2+}$, [Ca(H$_2$O)$_9$]$^{2+}$ and [Ca(H$_2$O)$_{10}$]$^{2+}$, which have been previously reported with hydration numbers of 5.5–9.2 [9]. A similar large discrepancy has also been found for Mg^{2+} (70%), which has been interpreted to be only the effect of the hydration of the outer sphere, because the [Mg(H$_2$O)$_6$]$^{2+}$ complex can be regarded as a unique aqua complex in aqueous solution [9]. Therefore, the effect of the outer sphere around the Ca^{2+} ion may be one of the major reasons for the large discrepancy.

The above results may imply that the effect of hydration of the outer sphere is more important for divalent cations such as Mg^{2+} and Ca^{2+} than for univalent ones such as Na$^+$ and K$^+$, although the exact comparison between the calculated and experimental hydration energies cannot be performed from the present results.

[Na(H$_2$O)$_6$$\cdots$H$_2$O]$^+$ and [Na(H$_2$O)$_6$$\cdots$Cl]

In order to examine the effect of the additional water molecule or Cl$^-$ ion to [Na(H$_2$O)$_6$]$^+$, the full geometry optimizations of [Na(H$_2$O)$_6$$\cdots$H$_2$O]$^+$ and [Na(H$_2$O)$_6$$\cdots$Cl] were carried out. Figure 2 summarizes their initial and optimized structures.

In the calculation of [Na(H$_2$O)$_6$$\cdots$H$_2$O]$^+$, the octahedral [Na(H$_2$O)$_6$]$^+$ unit was kept in six-coordination, although the structure was greatly distorted by addition of the water molecule, O(7), as shown in Fig. 2(a). The additional water molecule was repelled from the first hydration shell to be connected to the [Na(H$_2$O)$_6$]$^+$
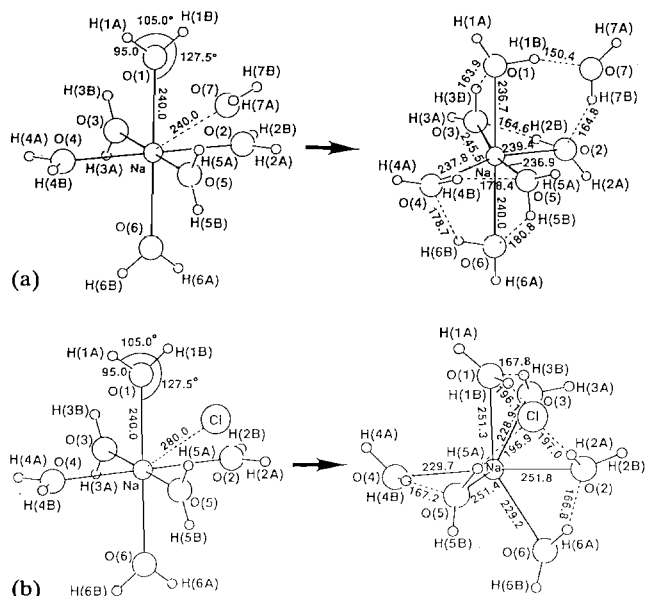

Fig. 2. Initial (left) and optimized (right) geometries of [Na(H$_2$O)$_6$$\cdots$(H$_2$O)]$^+$ (a) and [Na(H$_2$O)$_6$$\cdots$Cl] (b) complexes.

octahedron by hydrogen bonding. This is significantly different from the result of the optimization previously performed for [K(H$_2$O)$_6$$\cdots$H$_2$O]$^+$ [1], in which the octahedral [K(H$_2$O)$_6$]$^+$ unit was completely broken. The rather rigid octahedral structure in [Na(H$_2$O)$_6$]$^+$ as compared with [K(H$_2$O)$_6$]$^+$ must be due to the smaller ionic radius in Na$^+$ than in K$^+$. The present result also coincides with the fact that Na$^+$ and K$^+$ are generally referred as structure-making and structure-breaking ions, respectively [2].

The optimized structure of [Na(H$_2$O)$_6$$\cdots$Cl] is given in Fig. 2(b) together with the initial structure. Since the binding energies between Na$^+$ and Cl$^-$ ions are calculated to be much larger than those between Na$^+$ and the water molecule (Tables 2 and 3), the formation of an Na$^+$–Cl$^-$ ion-pair was expected to be energetically favorable through the optimization of [Na(H$_2$O)$_6$$\cdots$Cl]. The Cl$^-$ ion, however, could not participate in coordination to Na$^+$ and was connected to the hydrated water molecules by hydrogen bonds with an Na$\cdots$Cl distance of 409.2 pm (Fig. 2(b)), although the initial octahedron of [Na(H$_2$O)$_6$]$^+$ was greatly distorted within six-coordination. In the case of the [K(H$_2$O)$_6$$\cdots$Cl]

TABLE 2. The optimized metal–water oxygen distances, R (pm), and the dissociation energies, ΔE (kJ/mol)

	Method	R	$-\Delta E$
Na$^+$	DGauss	216.9	107.2
	STO-3G[a]	200	126
	4-31G[b]	220	138
	Extended[c]	220	113
	MINI-1[d]	212	117
	Exp.[e]		100.4
	Exp.[f]		87.9
Ca^{2+}	DGauss	232.1	218.6
	STO-3G[a]	220	197
	4-31G[b]	230	267
	Extended[c]	240	222
	MINI-1[d]	227	214

[a]Ref. 11. [b]4-31G basis set for water and special basis sets for cations; ref. 11. [c]Ref. 12. [d]Ref. 13. [e]Ref. 14. [f]Ref. 15.

TABLE 3. Equilibrium distances, R (pm), and dissociation energies ΔE (kJ/mol), for MCl$^{(n-1)+}$

	Method	R	$-\Delta E$
Na$^+$	DGauss	234.2	565.2
	Exp.[a]	235.9	
	Exp.[a]	238.8	
Ca^{2+}	DGauss	250.3	1123.0

[a]Ref. 16.

system, the K$^+$ ion was coordinated with the additional Cl$^-$ ion [1], as expected from the difference between K–Cl and K–H$_2$O binding energies. From the above results, it is clear that the structure of the octahedral hexaaqua complex of Na$^+$ is more rigid than that of K$^+$.

Considering the rigidity of the first hydration sphere of Na$^+$, the present result may indicate that the solvent-shared ion-pair could also be formed between [Na(H$_2$O)$_6$]$^+$ and Cl$^-$ in aqueous solution under certain conditions, although the binding energy of Na$^+$–Cl$^-$ suggests the possibility of the formation of an Na$^+$–Cl$^-$ contact ion-pair.

The contact between Na$^+$ and Cl$^-$ has been detected in nearly saturated aqueous solutions by the X-ray diffraction method, in which the molar ratio of H$_2$O to NaCl is 8.98 [17]. The optimization tried here, however, did not demonstrate the formation of an Na$^+$–Cl$^-$ contact ion-pair in spite of the ratio of 6 which is a higher concentration than in the experimental conditions. The apparent contradiction may be due to the difference of the respective conditions; the X-ray experiment was carried out on the bulk solution at 25 °C, in which the hydration water molecules are included not only for Na$^+$ but also for Cl$^-$, whereas the present geometry optimization was performed on only the hex-

ahydrated Na$^+$ and the Cl$^-$ ion without hydration water molecules.

$[Ca(H_2O)_6 \cdots H_2O]^{2+}$ and $[Ca(H_2O)_6 \cdots Cl]^+$

The optimized geometries of $[Ca(H_2O)_6 \cdots H_2O]^{2+}$ and $[Ca(H_2O)_6 \cdots Cl]^+$ are shown in Fig. 3 together with their initial geometries. In the optimization of the respective system, the additional water molecule or Cl$^-$ ion was taken up in coordination to Ca^{2+} and then the coordination number of the Ca$^+$ ion was varied from six to seven as shown in Fig. 3(a).

The structure of the $[Ca(H_2O)_6]^{2+}$ complex is much more stable than $[Na(H_2O)_6]^+$ judging from the dissociation energies of $[Ca(H_2O)_6]^{2+}$ and $[Na(H_2O)_6]^+$ (Table 1). This stability may originate from the difference of the charges not the ionic radii, because the radii of Na$^+$ and Ca^{2+} are nearly equal. The hexa-coordination structure of $[Ca(H_2O)_6]^{2+}$ was changed to hepta-coordination by the geometry optimizations of $[Ca(H_2O)_6 \cdots H_2O]^{2+}$ and $[Ca(H_2O)_6 \cdots Cl]^+$, whereas the hexahydration structure of $[Na(H_2O)_6]^+$ was maintained by the calculations. The stronger electrostatic interaction between the Ca^{2+} ion and the additional H$_2$O molecule makes possible the change of the co-ordination structure against the stability of the hexahydrated complex. In the case of the Mg^{2+} system, the hexahydration structure was also kept. The discrepancy between the Ca^{2+} and Mg^{2+} complexes, on the other hand, should be mainly due to the difference of their ionic radii because both cations have the same charge, i.e. the $[Ca(H_2O)_6]^{2+}$ complex involving a large cation has enough space to accommodate the additional water molecule into the hydration sphere, whereas the
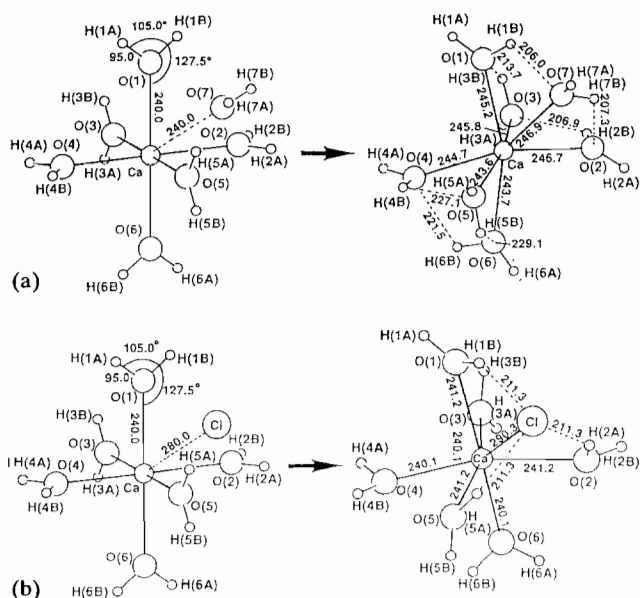

Fig. 3. Initial (left) and optimized (right) geometries of $[Ca(H_2O)_6 \cdots (H_2O)]^{2+}$ (a) and $[Ca(H_2O)_6 \cdots Cl]^+$ (b) complexes.

octahedral polyhedron of $[Mg(H_2O)_6]^{2+}$, containing a smaller cation than Ca^{2+}, is too compact and too rigid for the additional H_2O to break into.

Although a value of 5.5 has been reported for the hydration number of the Ca^{2+} ion in the solution state by the neutron diffraction method [18], the present result suggests that the Ca^{2+} ion prefers a heptahydration structure to a hexahydration one and that a hydration number lower than 6 is too small for that of Ca^{2+}.

The optimized structure of $[Ca(H_2O)_6 \cdots Cl]^+$ is drawn in Fig. 3(b). The additional Cl^- ion was co-ordinated to the Ca^{2+} ion and the coordination number of Ca^{2+} was also changed to seven. In the cases of the geometry optimizations of $[Na(H_2O)_6 \cdots Cl]$ and $[Mg(H_2O)_6 \cdots Cl]^+$ [1], the octahedral hexahydration unit was kept almost unchanged and the additional Cl^- ion was connected to the unit by hydrogen bondings. The discrepancies between the optimized structures of the Na^+ and Ca^{2+} complexes and between those of Mg^{2+} and Ca^{2+} should be also mainly due to the difference of the charges and their ionic radii, respectively, as described above.

The solution X-ray diffraction of an $MgCl_2$–$CaCl_2$–H_2O ternary system ($Mg:Ca:Cl:H_2O = 1:1:4:24$) reported by Caminiti et al. [19] has shown that all three ions are octahedrally coordinated with six water molecules and that neither an Mg^{2+}–Cl^- nor Ca^{2+}–Cl^- contact ion-pair forms. On the other hand, the double salt crystal of $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$, precipitated from the ternary solution at some concentration and temperature ranges, formed the octahedral $[CaCl_6]^{4-}$ and $[Mg(H_2O)_6]^{2+}$ units [20, 21]. The previous and present results for $[Mg(H_2O)_6]$ and $[Ca(H_2O)_6]^{2+}$ [1], respectively, suggest the easy formation of a Ca^{2+}–Cl^- ion-pair and the structural rigidity of $[Mg(H_2O)_6]^{2+}$, which should play an important role in the formation mechanism of the double salt crystal.

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