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Theoretical Study of Water-Exchange Reactions of Hexahydrated Divalent Cations in the First Transition Series: Relationship between Reaction Mechanism and Stability of Heptacoordinated Species

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We studied the characteristics of model intermediary species on reaction pathways using the ab initio molecular orbital method in order to explain a change in the mechanistic behavior of the water-exchange reaction of hexahydrated divalent cations when the central elements were changed in the first transition series. Calculations show that the hexacoordinated species binding to the entering water in the second shell, the dissociative pentacoordinated species of scandium(II) and copper(II) ions, and the associative heptacoordinated species of scandium(II) ion are at local minima, whereas the heptacoordinated species of copper(II) ion is at a second-order saddle point. We also considered calcium(II) and zinc(II) ions in order to examine the correlation between the intermediary species and the reaction mechanisms. All of the intermediary species for calcium(II) and zinc(II) ions resemble those of scandium(II) and copper(II) ions, respectively. The dissociative mechanism can operate for both the calcium(II) and zinc(II) ions. The associative mechanism, however, can operate only for the calcium(II) ion, and the zinc(II) ion has no meaningful stationary point on the reaction path. We also considered the effect of the electronic structures on the reaction mechanisms. We conclude as the following: The dissociative mechanism is operative for a water exchange of all members of the first transition series. An associative mechanism is expected for the water-exchange reaction of the earlier members, which have stable heptacoordinated species. The possibility of the operation of the associative mechanism depends on the existence of appropriate associative heptacoordinated species.

In coordination chemistry, the replacement of a coordinating ligand by an entering ligand, which is called a ligand substitution reaction, is one of the most important reactions. Nucleophilic substitution reactions, such as S_N1 and S_N2 reactions and transesterification, are a kind of ligand substitution reaction. Many investigations of organic substitution reactions from the viewpoint of kinetics and substituent effects have contributed to explaining the reactivities of organic compounds, and led to the establishment of physical organic theory. The pathway of the S_N2 reaction was identified, and the solvent effect on it has also been investigated theoretically.[1a—1c] For inorganic substitution reactions, systematic studies on the ligand substitution of inert cobalt(III) complexes showed that the operative mechanism of the reaction is dissociative.[2] Many studies from the viewpoint of activation parameters, especially activation volumes, clarified the reaction mechanisms of labile complexes.[3] Recently, the water-exchange reactions of tetrahydrated beryllium(II), palladium(II), and platinum(II) were also studied theoretically.[4]

The classification of the mechanisms of substitution reactions is based on the characteristics of their intermediates.[2b,5] In the dissociative (D) mechanism, an intermediate with a reduced coordination number is formed after the cleavage of the bond between the leaving ligand and the central metal ion. This is followed by the immediate entrance of the entering ligand. In the associative (A) mechanism, an intermediate with an expanded coordination number is formed with the coordination of the entering ligand. This is followed by the cleavage of the bond between the leaving ligand and the metal ion. The interchange mechanism has a transition state instead of an intermediate. The interchange mechanism is classified further according to the degree of the bond breaking at the transition state. In the transition state for the dissociative-interchange (I_d) mechanism, the degree of bond breaking between the leaving ligand and the metal ion is larger than that of bond making between the entering ligand and the metal ion, and vice versa for the associative-interchange (I_a) mechanism.

It is important to study the nature of stationary points on the reaction path, such as intermediates and transition states of the reaction, in order to understand any ligand substitution reaction process. The intermediate and the transition state are connected to each other by a reaction path. For example, the local minima, where the reactant or the product is bound to the entering or leaving group, are connected through a saddle point for a gas-phase simple S_N2 reaction, such as the reaction between a halide anion and methyl halide.[1a,1c] For another type of substitution reaction, such as the base-catalyzed hydrolysis of methyl formate, the possible reaction pathway passes through some intermediates and transition states.[1d)]

An ion in solution is solvated by solvent molecules, which are always replaced by free solvent molecules. This quite simple process, called a solvent-exchange reaction, is regarded as being one of the most fundamental reactions, because it becomes competitive with the formation of complexes in solution, and also, the reaction, itself, has a symmetrical nature. Many experimental studies on the solvent exchange reactions of the first transition series demonstrate that the activation mode of the water-exchange process of octahedral hexahydrated divalent cations varies from I_a for earlier members to I_d for later members.[6a)] Åkesson et al. investigated the correlation between the gas-phase water dissociation energies calculated by a constrained geometry optimization method and the rate constants for the water-exchange reaction.[7a,7b)] They concluded that the dissociative process (D or I_d) operates in the water exchange for all divalent cations in the first transition series. Powell et al. suggested that additional considerations of the change in the volume of bulk water improve Åkesson's theoretical activation volumes, and that their activation volumes confirm the operation of the associative (A or I_a) process.[6c)] From the viewpoint of the relation between the experimental $\Delta G^{\ddagger}$ or $\Delta H^{\ddagger}$ and the calculated electronic energies of the transition states, Rotzinger concluded that the I_a and D mechanisms are feasible for vanadium(II) ion, whereas for nickel(II) ion only the dissociative mechanism is possible.[8)] Katz et al. determined the structures and relative energies for many coordinating types of hydrated calcium(II) and zinc(II) ions.[9)]

We considered the possible intermediary species on the reaction paths and studied their characteristics to investigate the mechanistic behavior for the water-exchange reaction of hexahydrated divalent cations in the first transition series. In order to study the change in the mechanistic behavior as the central divalent cations are changed in the first transition series, we selected scandium(II) ion, the earliest member of the first transition series, and copper(II) ion, the latest one, as model species of the earlier and the later members. The considered model system consists of a central divalent cation and seven water molecules directly taking part in the water-exchange reaction (1):

$$[\mathrm{M(H_2O)_6}]^{2+} + \mathrm{H_2O^*} \rightarrow [\mathrm{M(H_2O)_5(H_2O^*)}]^{2+} + \mathrm{H_2O} \qquad (\mathrm{M = Ca, Sc, Cu, and\ Zn}) \qquad (1)$$

Here, H_2O^* means the entering water. The constituents of the coordination shells in which these water molecules are placed depend on the reaction mechanisms and the positions on the reaction pathways concerning the mechanisms. The conceivable initial or final state of the water-exchange reaction is denoted as *hexacoordination*, where six waters are placed in the first coordination shell and the entering water is placed in the second coordination shell ($[M(H_2O)_6]^{2+}\cdot H_2O$). A reasonable intermediary species on the path of the associative process is denoted as *heptacoordination*, where all seven waters are placed in the first coordination shell ($[M(H_2O)_7]^{2+}$). A reasonable intermediary species in the dissociative process is denoted as *pentacoordination*, where five waters are placed in the first coordination shell and two waters are placed in the second coordination shell ($[M(H_2O)_5]^{2+}\cdot 2H_2O$).

We also studied the associative and dissociative mechanisms for the water-exchange reaction of the hexaaqua ions of calcium(II) and zinc(II) in order to investigate the relationship between the *coordination* and the reaction mechanism and to confirm the availability of our modeling. It is expected that these closed-shell systems are similar to the target open-shell systems concerning the characteristics on the reaction pathways, because they neighbor scandium or copper in the periodic table. This similarity is also discussed in this paper. The above-mentioned relationship was applied to scandium(II) and copper(II) ions to consider the operative process for each metal(II) ion.

Computational Details

We used two basis sets (Basis I and Basis II). Detailed explanations of them are given in Appendix. We determined the structures of hexaaqua metal(II) ion ($[M(H_2O)_6]^{2+}$), *hexacoordinations*, *heptacoordinations*, and *pentacoordinations* (vide supra), and characterized them by frequency calculations. Åkesson et al. performed CASSCF calculations with all five 3d orbitals as the active space for hexahydrated titanium(II), cobalt(II), and iron(II) ions to examine the nondynamical correlation effect for this type of open-shell system. The hydration energies given by CASSCF and SCF were not significantly different. They concluded that the mixing of states was merely an atomic effect.[7e,7f)] Thus, we carried out structural calculations at the RHF level for closed-shell systems and at the UHF level for open-shell systems using Basis I and Basis II. All of the identified stationary points were subjected to MP2 calculations to assess the effects of electron correlation. The structures of the closed-shell systems were reoptimized at the MP2 level to compare with the results of SCF.

We also determined the associative and dissociative reaction pathways for calcium(II) and zinc(II) ions. Basis I was used to calculate these intrinsic reaction coordinates.

We used Gaussian92 program[10)] on IBM RS6000 for all ab initio molecular orbital calculations and MOLCAT program[11)] on Macintosh for visualizations of the molecular structures and vibrational modes. We discuss the energy in kcal mol^{-1} (1 kcal mol^{-1}= 4.1884 kJ mol^{-1}) and in atomic unit (a.u., 1 a.u.= 627.50959 kcal mol^{-1}) and bond length in Å (1 Å = 100 pm).

Results and Discussion

a. Hexahydrated Ions and Hexacoordinated Species in the Initial States: *Hexacoordinations*. Frequency calculations show that all of the optimized hexahydrated divalent cations are at local minima on the potential surface. Their energies and fundamental geometrical parameters are summarized in Table 1. The hexaaquacalcium(II) ion, $[Ca(H_2O)_6]^{2+}$, and the hexaaquazinc(II) ion, $[Zn(H_2O)_6]^{2+}$, are closed-shell systems with the d^0 and d^{10} configurations, respectively. Their T_h structures reflect the configurations. The coordination number and the Ca–O distance determined by X-ray diffraction are 6.0 and 2.44 Å, respectively.[13a)] The computed distance of 2.434 Å is in agreement with this experimental value. The coordination number and the Zn–O distance characterized by X-ray scattering are 6.2 and 2.15 Å, respectively.[13b)] The experimental value is in agreement with the computed distance of 2.136 Å. The Jahn–Teller effect makes open-shell systems subject to distortions from T_h symmetry. For the d^1 configuration of the hexaaquascandium(II) ion, $[Sc(H_2O)_6]^{2+}$, the six coordinating waters depart from a 3-fold axis of an octahedron to form almost a D_3 structure because of the expansion of the singly occupied d_{z^2}-orbital along the 3-fold axis (Fig. 1a). The resulting is similar to the all-vertical D_{3d} structure, named by Åkesson et al.[7f)] Because a stable D_{3d} structure similar to our structure was also found in the hexaaquatitanium(III) ion with a d^1 configuration,[12)] this geometry is specific to *hexacoordination* with a d^1 configuration. The D_{2h} structure for the hexaaquascandium(II) ion is higher in energy than the present structure, and is at a second-order saddle point which has vibrational modes related to the internal rotations of the coordinating waters. The structure of the hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$, with a d^9 configuration is D_{2h} symmetry. The singly occupied d-orbital is perpendicular to the z-axis, as shown in Fig. 1b. The double occupation of the d_{z^2}-orbital results in an elongation of the copper–oxygen bonds on the z-axis. The Cu–O distances for equatorial and axial oxygen atoms, characterized by the extended X-ray absorption fine structure (EXAFS) method, are 2.04±0.01 and 2.29±0.05 Å, respectively,[13c)] which are in agreement with the computed distances of 2.07 and 2.26 Å, respectively.

A hexaaqua metal(II) ion bound by a water in the second coordination shell, $[Sc(H_2O)_6]^{2+}\cdot H_2O$ or $[Cu(H_2O)_6]^{2+}\cdot H_2O$, is regarded as being the 'initial state' of the water-exchange reaction (Figs. 2b and 2e and Tables 2 and 3). There are the following three ways of interaction between

Table 1. Structural Parameters and Energies of Hexaaqua Metal(II) Ions[a)]

Metal(II) ion	Metal–Oxygen (Å)	O–H (Å)	∠HOH (degree)	Energy (a.u.)
Calcium(II)	2.434	0.950	106.0	−1132.808976
Scandium(II)	2.338	0.950	106.4	−1215.780016
Copper(II)[b)]	2.071, 2.067	0.950, 0.951	108.0, 108.3	−2094.752098
	2.264	0.950	106.6	
Zinc(II)	2.136	0.950	107.5	−2233.597091

a) All the calculations are performed using Basis II. The structural parameters and the energy of an optimized water molecule are as follows: O–H is 0.944 Å, ∠HOH is 106.7° and the total energy is −76.046801 a.u. b) Equatorial parameters are in the upper row and axial parameters are in the lower one.

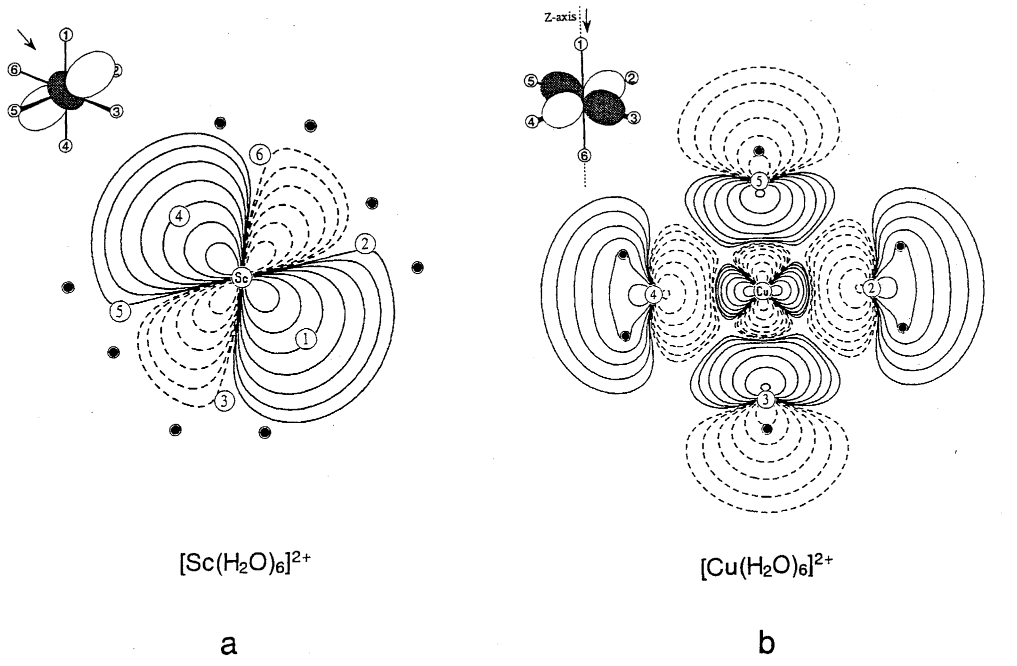
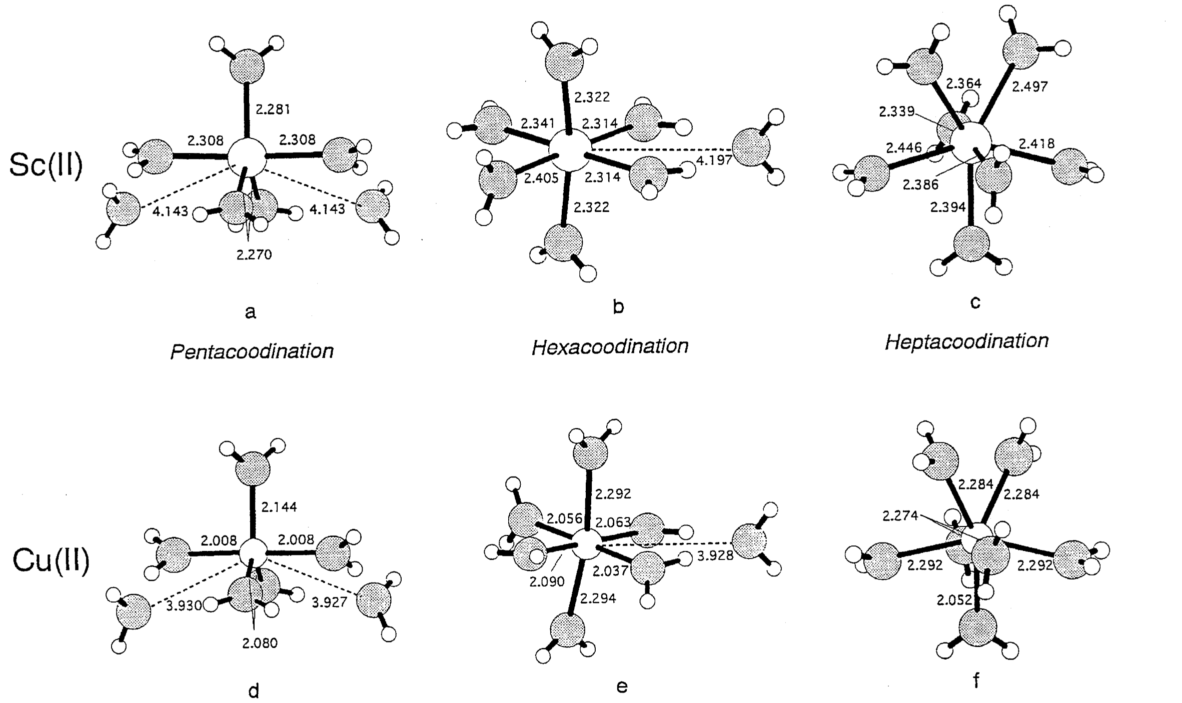


Fig. 1. The contour maps of singly occupied d orbitals of hexaaquascandium(II) ion (a) and hexaaquacopper(II) ion (b) viewed from the direction of the arrow in the upper picture. The planes of the maps contain the central cations. Dots mean hydrogen atoms and numbered circles mean oxygen atoms projected into the plane. The orbital energies of hexaaquascandium(II) and hexaaquacopper(II) ions are −0.564 and −0.899 a.u., respectively.

the entering water and first-shell waters (see Scheme 1): (1) The entering water placed on a 3-fold axis of an octahedron interacts with three first-shell waters. (2) The entering water interacts with two first-shell waters. (3) The entering water interacts with only one first-shell water without a rearrangement of the first-shell waters.

The small energy requirement to reorient the first-shell waters an the large stabilization in the formation of hydrogen bonds contribute to the determination of the path of interaction. Case (1) seems to be the most favorable for penetration into the first coordination shell, because the smallest steric hindrance is expected. However, this structure is unstable, and our calculation shows that the most stable structure is case (2) for the zinc(II) ion. A structure of type (1) for titanium(III) ion was shown as a transition state for approaching the central cation.[8)] A type (2) interaction was also shown in the initial state for the water-exchange reaction on the beryllium(II) ion.[4a)] A frequency calculations show that



a
Pentacoodination

b
Hexacoodination

c
Heptacoodination

d

e

f

Fig. 2. The structures of *pentacoordination*, *hexacoordination*, and *heptacoordination* of scandium(II) and copper(II) ions. The numbers in the figure represent interatomic distance in Å. In *pentacoordination*, the angles between the axial bonds of the trigonal bipyramid are 178° for scandium(II) and 179° for copper(II).

Table 2. Energies of Scandium(II) Species[a)]

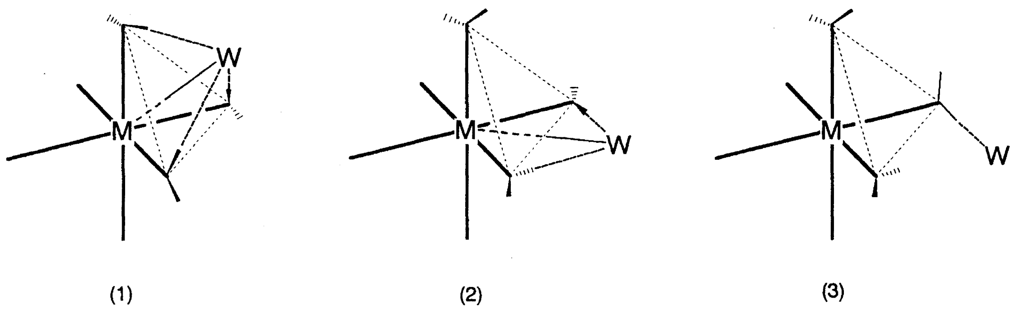
Species	Nature of stationary-point	UHF[b)]		MP2 for UHF structure	
		Total energy (a.u.)	Energy[c)]	Total energy (a.u.)	Energy[c)]
Pentacoordination	Local minimum	−1291.854366	3.5	−1293.662872	2.7
Hexacoordination	Local minimum	−1291.859915	0.0	−1293.667169	0.0
Heptacoordination	Local minimum	−1291.850794	5.7	−1293.656890	6.5
	Saddle point	−1291.850059	6.2	−1293.656054	7.0

a) All the calculations are performed using Basis II. b) UHF means UHF energies of UHF optimized structures. c) The relative energy in kcal mol^{-1} measured from *hexacoordination*.

Table 3. Energies of Copper(II) Species[a)]

Species	Nature of stationary-point	UHF[b)]		MP2 for UHF structure	
		Total energy (a.u.)	Energy[c)]	Total energy (a.u.)	Energy[c)]
Pentacoordination	Local minimum	−2170.836831	−2.7	−2172.886318	−5.0
Hexacoordination	Local minimum	−2170.832519	0.0	−2172.878273	0.0
Heptacoordination	Second-order saddle point	−2170.797844	21.8	−2172.840272	23.8

a) All the calculations are performed using Basis II. b) UHF means UHF energies of UHF optimized structures. c) The relative energy in kcal mol^{-1} measured from *hexacoordination*.

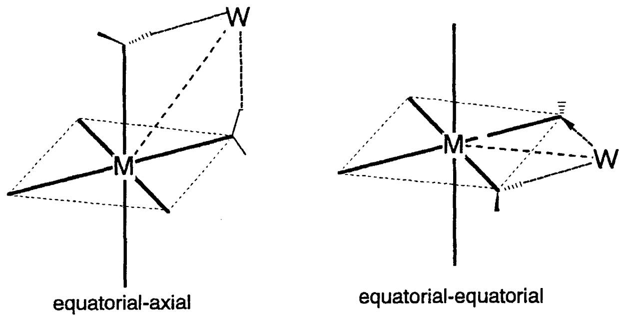


Scheme 1.

the hexacoordinated initial state of type (2) for scandium(II) and copper(II) ions are at local minima.

The nonbonding singly occupied d-orbital of the scandium(II) ion spreads onto the plane formed by the hydrogen-bonded waters (Fig. 3b). A complex with the d-orbital which is out of the plane is higher in energy by 1 kcal mol^{-1}. The rearrangement of the hydrogen-bonded first-shell water contributes to a reduction of the repulsive interaction between the d-electron and lone pairs of the waters.

There are two ways to bind the entering water in the hexacoordinated initial state of the copper(II) ion, because of the Jahn–Teller elongation of the axial bonds, as shown in Scheme 2. The singly occupied orbital is shown in Fig. 4b. The species with an equatorial–equatorial interaction is lower in energy than that with an equatorial–axial interaction, which is not a stationary point.



Scheme 2.

b. Associative Heptacoordinated Species: *Heptacoordinations.* In the activation process via the associative mechanism, the leaving water molecule is still bound to the central metal(II) ion retaining a reasonable short bond length when the entering one penetrates the first coordination shell. An associative reaction mechanism of the hexacoordinated metal(II) ions leads to *heptacoordination*, where seven water molecules attach to the metal ion in the first coordination

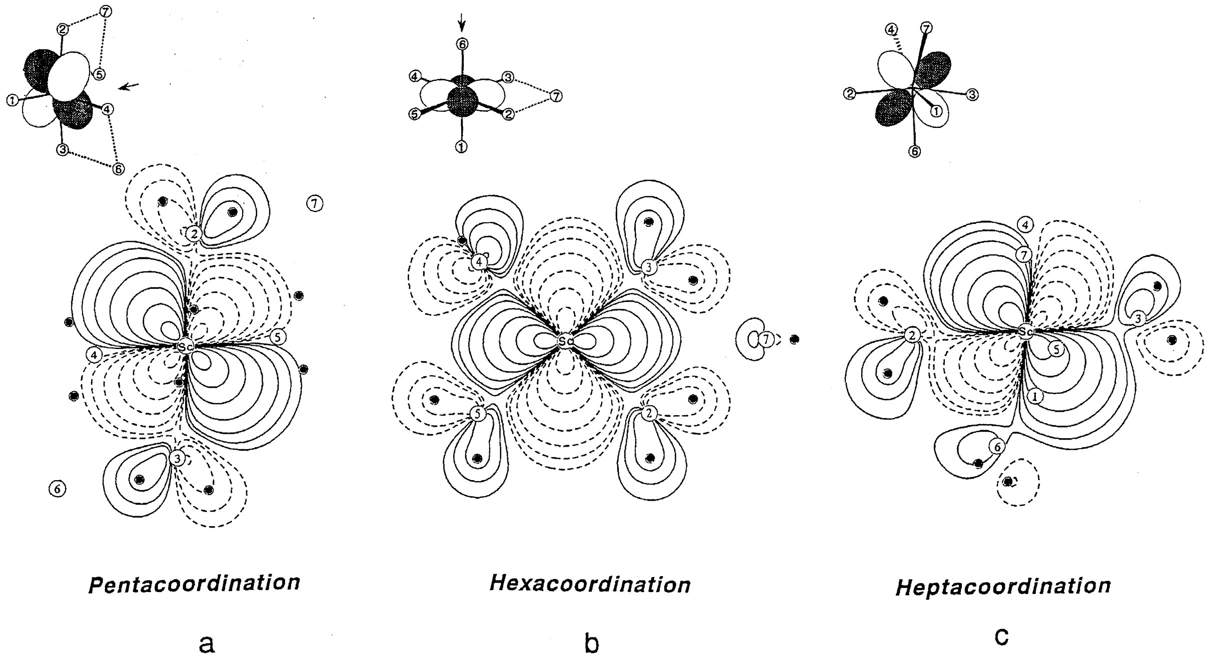
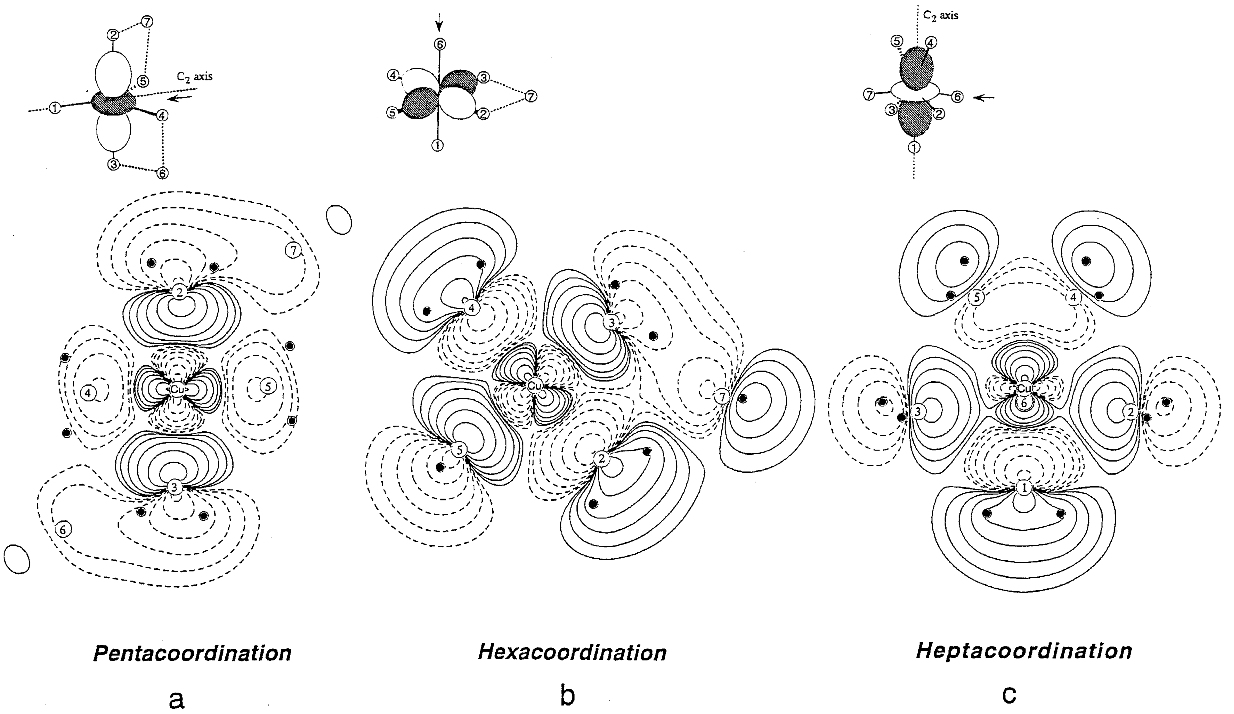


Fig. 3. The contour maps of singly occupied d orbitals of *pentacoordination* (a), *hexacoordination* (b), and *heptacoordination* (c) of scandium(II) ion viewed from the direction of the arrow in the upper picture. They are the highest occupied α-orbitals. The planes of the maps contain Sc^{2+}. In the case of *heptacoordination*, the plane of the map is the same plane as the paper. Dots mean the positions of hydrogen atoms and numbered circles mean oxygen atoms projected into the plane. The orbital energies of the *pentacoordination*, *hexacoordination*, and *heptacoordination* are −0.559, −0.545, and −0.542 a.u., respectively.



Pentacoordination
a

Hexacoordination
b

Heptacoordination
c

Fig. 4. The contour maps of singly occupied d orbitals of *pentacoordination* (a), *hexacoordination* (b), and *heptacoordination* (c) of copper(II) ion viewed in the direction of the arrow in the upper picture. The planes of the maps contain Cu^{2+}. Dots mean hydrogen atoms and numbered circles mean oxygen atoms projected into the plane. The orbital energies of the *pentacoordination*, *hexacoordination*, and *heptacoordination* are −0.910, −0.881, and −0.882 a.u., respectively.

shell. The optimized structures of *heptacoordinations* of the scandium(II) ion ($[Sc(H_2O)_7]^{2+}$) and copper(II) ion ($[Cu(H_2O)_7]^{2+}$) are shown in Figs. 2c and 2f, and their energies are given in Tables 2 and 3, respectively.

The *heptacoordination* of scandium(II) ion is at a local minimum. The structure is pentagonal bipyramidal with a distorted equatorial plane. The nonbonding singly occupied d-orbital of the scandium(II) ion spreads out of the equatorial plane (see Fig. 3c). This intermediate is obtained by a distortion from a C_2 symmetry species having one imaginary frequency.

The *heptacoordination* of copper(II) ion is neither at local minimum nor at a transition state, but at a second-order saddle point with C_2 symmetry along the shortest Cu–O bond. The shortest bond results from the singly occupied d_{z^2}-orbital extended on the C_2 axis (see Fig. 4c). In spite of a geometry optimization without symmetry constraints, no local minima nor saddle points were found in the neighborhood of this second-order saddle point. The imaginary mode with the frequency $158.1i$ cm^{-1} describes the concerted motion of the approaching of water molecule 4 to the Cu and the leaving water molecule 5 (the numbering shown in Fig. 4c), and corresponds to the motion leading to the *hexacoordination.* The other, with a frequency $189.7i$ cm^{-1}, describes the simultaneous leaving of water molecules 2 and 3 from the Cu, and corresponds to the motion leading to the *pentacoordination.*

The differences in the characteristics and energetics of heptacoordinated species may be attributed to the difference in the lengths of their metal–oxygen bonds. The shorter bonds for copper(II) (2.06—2.29 Å) than those for scandium(II) (2.34—2.49 Å) cause an increased repulsive interaction between the coordinating water molecules.

c. Dissociative Pentacoordinated Species: *Pentacoordinations.* In operating the dissociative mechanism, the bond between the leaving water molecule and the central metal ion is cleaved before the penetration of the entering water into the first coordination shell. A dissociative reaction of the hexacoordinated metal(II) ions leads to *pentacoordination*, in which five water molecules attach to the centeral metal(II) ion in the first coordination shell and the other water molecules are placed in the second coordination shell. The *pentacoordination* for both scandium(II) ion ($[Sc(H_2O)_5]^{2+}\cdot 2(H_2O)$) and copper(II) ion ($[Cu(H_2O)_5]^{2+}\cdot 2(H_2O)$) is at local minima. The optimized structures are depicted in Figs. 2a and 2d, and the energies are tabulated in Tables 2 and 3. The essential first-shell structures of both model molecules are trigonal bipyramidal.

In the *pentacoordination* of the scandium(II) ion, the axial bonds are slightly longer than the equatorial ones. The singly occupied d-orbital of scandium(II) ion is perpendicular to the non-hydrogen-bonded equatorial bond, as shown in Fig. 3a. The symmetry of the *pentacoordination* of copper(II) is C_2. The singly occupied d-orbital is perpendicular to the C_2 axis (Fig. 4a). The doubly occupied d_{z^2} orbital causes an elongation of the bond of the non-hydrogen-bonded equatorial water molecule (Fig. 2d). The most stable structure of the pentaaquacopper(II) ion without a second shell is square pyramidal. The dominant lobe of the fully occupied d_{z^2} type orbital projects along the apex bond. The trigonal bipyramidal structure of the copper(II) ion is slightly unstable in accordance with a calculation by Åkesson et al., who stated the energy difference to be 3.3 kJ mol^{-1}.[7a] The energy difference may not be large enough to prevent isomerization. Thus, in the presence of second-shell water molecules, basal water molecules in the square pyramidal structure reorient to form a hydrogen bond with them. This structure is unstable, and the repulsive interaction between a nonbonding d-orbital and an occupied orbital of hydrogen of the basal water molecules changes the geometry of the first coordination shell from square pyramidal to trigonal bipyramidal. The *pentacoordination* for copper(II) has a lower energy than the *hexacoordination* because of the stability of the *pentacoodination*, itself, and strong hydrogen bonds.[14]

d. Stability of *Pentacoordination* and *Heptacoordination* and Reaction Pathways for Calcium(II) and Zinc(II) Ions. We studied the water-exchange reaction of calcium(II) and zinc(II) ions in order to examine the relationship between the reaction mechanisms and the corresponding coordinations. The optimized structures and energies of *hexacoordination*, *heptacoordination*, and *pentacoordination* of calcium(II) and zinc(II) ions are given in Tables 4, 5, and 6. The numbering of the oxygen atoms is shown in Fig. 5. Their bond lengths between the central cation and first-shell waters are isotropic, in contrast to the anisotropy observed in the open-shell systems, because these divalent cations have no partially filled d-orbitals. All of the intermediary species for calcium(II) and zinc(II) ions are located at local minima, except for the *heptacoordination* of zinc(II) ion located at a second-order saddle point. The imaginary modes of 126.8i cm^{-1} and 86.9i cm^{-1} correspond to the motions leading to the *hexacoordination* and *pentacoordination*, respectively. The trend in the relative energies of the calcium(II) and zinc(II) ions is similar to those of the scandium(II) and copper(II) ions, respectively.

In the operation of the associative mechanism for the calcium(II) ion, the entering water penetrates the first coordination shell by pushing the hydrogen-bonded water molecules (see Scheme 3). In the transition state, the entering water is at a distance of 3.059 and 3.150 Å for MP2 and RHF, respectively, from the calcium cation, and is placed in the equatorial plane (Fig. 6a). The transition state is higher than the initial state by 5.4 kcal mol^{-1} and 4.6 kcal mol^{-1}

Table 4. Energies of Intermediates and Transition States on the Dissociative and Associative Reaction Pathways for Water-Exchange Reaction of Calcium(II) Ion

State[b]	CN[c]	Nature of	RHF[a]		MP2 for RHF structure		MP2[a]	
		stationary-point	Total energy (a.u.)	Energy[d]	Total energy (a.u.)	Energy[d]	Total energy (a.u.)	Energy[d]
D. IM	5	Local minimum	−1208.802771	3.6	−1210.504456	2.6	−1210.512887	2.3
			−1208.881785[e]	3.7	−1210.661356[e]	2.9		
D. TS	(6)	Saddle point	−1208.796803	7.3	−1210.496622	7.5	−1210.505860	6.7
GR	6	Local minimum	−1208.808438	0.0	−1210.508629	0.0	−1210.516542	0.0
			−1208.887697[e]	0.0	−1210.666013[e]	0.0		
A. TS	(7)	Saddle point	−1208.801143	4.6	−1210.499987	5.4	−1210.507937	5.4
A. IM	7	Local minimum	−1208.804518	2.5	−1210.503219	3.4	−1210.510836	3.6
			−1208.883791[e]	2.5	−1210.661491[e]	2.8		

a) RHF means RHF energies of RHF optimized structures. MP2 means MP2 energies of MP2 optimized structures. b) D, A, IM and TS are abbreviations of dissociative, associative, intermediate, and transition state, respectively. GR means the initial state of the water-exchange reaction. D. IM, GR, and A. IM are *pentacoordination*, *hexacoordination*, and *heptacoordination*, respectively. c) Coordination number. The number of water molecules placed in the first coordination shell. Parentheses mean including the entering or leaving water molecule in the number. d) The relative energy in kcal mol^{-1} measured from *hexacoordination*. e) Energy calculated using Basis II.

Table 5. Energies of Intermediates and Transition States on the Dissociative and Associative Reaction Pathways for Water-Exchange Reaction of Zinc(II) Ion

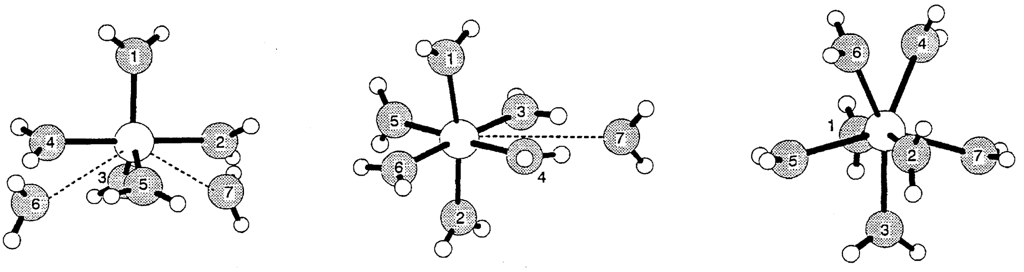
State[b]	CN[c]	Nature of	RHF[a]		MP2 for RHF structure		MP2[a]	
		stationary-point	Total energy (a.u.)	Energy[d]	Total energy (a.u.)	Energy[d]	Total energy (a.u.)	Energy[d]
D. IM	5	Local minimum	−2309.594369	−1.6	−2311.618992	−2.8	−2311.627010	−2.9
			−2309.679693[e]	−1.9	−2311.790829[e]	−3.8		
D. TS	(6)	Saddle point	−2309.581215	6.7	−2311.603781	6.8	−2311.612297	6.3
GR	6	Local minimum	−2309.591886	0.0	−2311.614539	0.0	−2311.622363	0.0
			−2309.676596[e]	0.0	−2311.784764[e]	0.0		
A. TS2	7	Second-order	−2309.565471	16.6	−2311.587875	16.7	−2311.595687	16.7
		Saddle-point	−2309.648693[e]	17.5	−2311.756690[e]	17.6		

a) RHF means RHF energies of RHF optimized structures. MP2 means MP2 energies of MP2 optimized structures. b) D, A, IM, and TS are abbreviations of dissociative, associative, intermediate, and transition state, respectively. GR means the initial state of the water-exchange reaction. D. IM, GR, and A. TS2 are *pentacoordination*, *hexacoordination*, and *heptacoordination*, respectively. c) Coordination number. The number of water molecules placed in the first coordination shell. Parentheses mean including the entering or leaving water molecule in the number. d) The relative energy in kcal mol^{-1} measured from *hexacoordination*. e) Energy calculated using Basis II.

Table 6. Structural Parameters of Calcium(II) and Zinc(II) Species[a)]

	Calcium(II)			Zinc(II)		
Bonds	*Pentacoordination*	*Hexacoordination*	*Heptacoordination*	*Pentacoordination*	*Hexacoordination*	*Heptacoordination*
M–O1	2.404	2.444	2.454	2.073	2.153	2.152
M–O2	2.396	2.444	2.454	2.106	2.151	2.152
M–O3	2.375	2.408	2.487	2.045	2.113	2.260
M–O4	2.396	2.413	2.498	2.106	2.111	2.306
M–O5	2.375	2.436	2.511	2.045	2.144	2.261
M–O6	4.211	2.450	2.498	3.947	2.154	2.306
M–O7	4.211	4.259	2.511	3.947	3.999	2.261
2M–O7[b)]	1.953	1.960		1.939	1.945	
3M–O7[b)]	1.951	1.964		1.905	1.949	

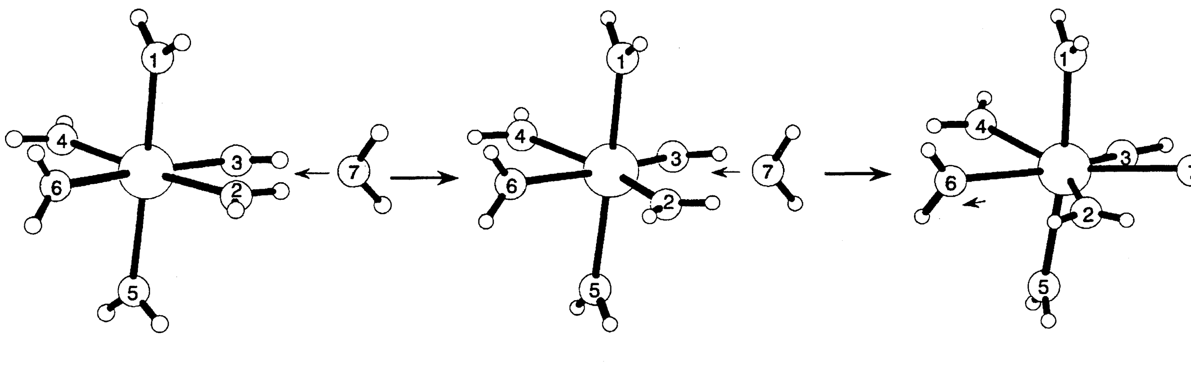
a) The unit is in Å. All the calculations are performed using Basis II. M means the central cations, calcium(II) and zinc(II). The numbering of oxygen atoms is show in Fig. 5. b) The distance of a hydrogen bond. 2H means the H connected to O2 and 3H means the H connected to O3.



Pentacoordination *Hexacoordination* *Heptacoordination*

a b c

Fig. 5. The numbering of oxygen atoms of zinc(II) species. a, b, and c represent *pentacoordination*, *hexacoordination*, and *heptacoordination* of zinc(II), respectively.



Initial State **Associative Transition State** **Associative Intermediate**

Scheme 3.

for MP2 and RHF, respectively. As the distance decreases further, the two water molecules on the equatorial plane are forced out of the plane due to an increase in the repulsive interaction between the water molecules. The intermediate has C_2 symmetry along one of the Ca–O bonds on the equatorial plane. This corresponds to the *heptacoordination* described in the previous section(**b**). The entering water molecule in the *heptacoordination* of calcium(II) is at a distance of 2.474 and 2.508 Å for MP2 and RHF, respectively. The trans-attack is favorable in the associative mechanism if it is assumed that the reaction pathway is symmetrical concerning the intermediate. On the other hand, for zinc(II) no local minima nor saddle points was found in the neighborhood of this second-order saddle point in spite of geometry optimization without symmetry constraints. There is no transition state for the associative mechanism of the zinc(II) ion.

The associative reaction pathways for the calcium(II) and zinc(II) ions differ intrinsically in the nature of the present stationary points. For the calcium(II) ion, the intermediate and transition states exist on the associative reaction path, whereas for the zinc(II) ion, none of them exists. The *heptacoordination* of the calcium(II) ion is the intermediate of the associative reaction mechanism. The *heptacoordination* of the zinc(II) ion is at a second-order saddle point, which re-

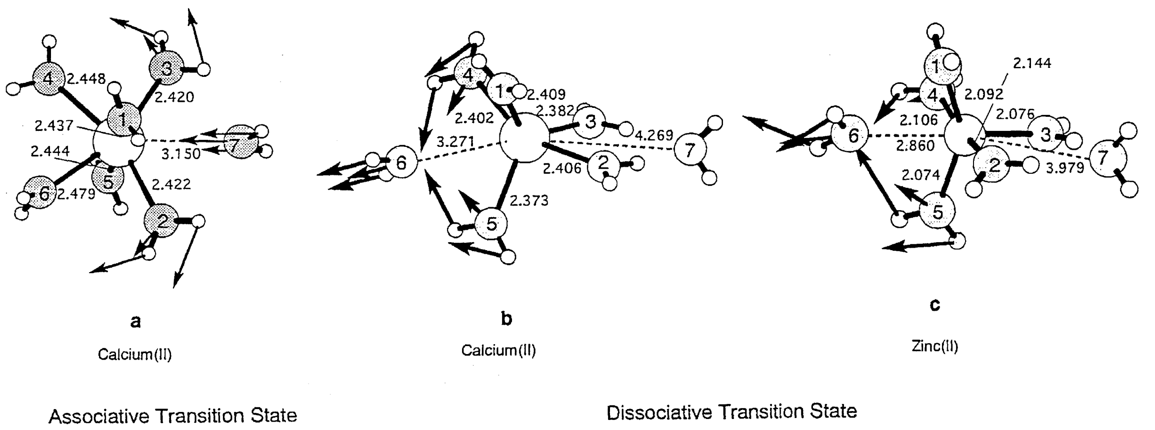


Fig. 6. RHF structures with transition vectors: (a) the associative transition state for calcium(II) ion, (b) the dissociative transition state for calcium(II) ion, (c) the dissociative transition state for zinc(II) ion.

flects the absence of available associative reaction pathways.

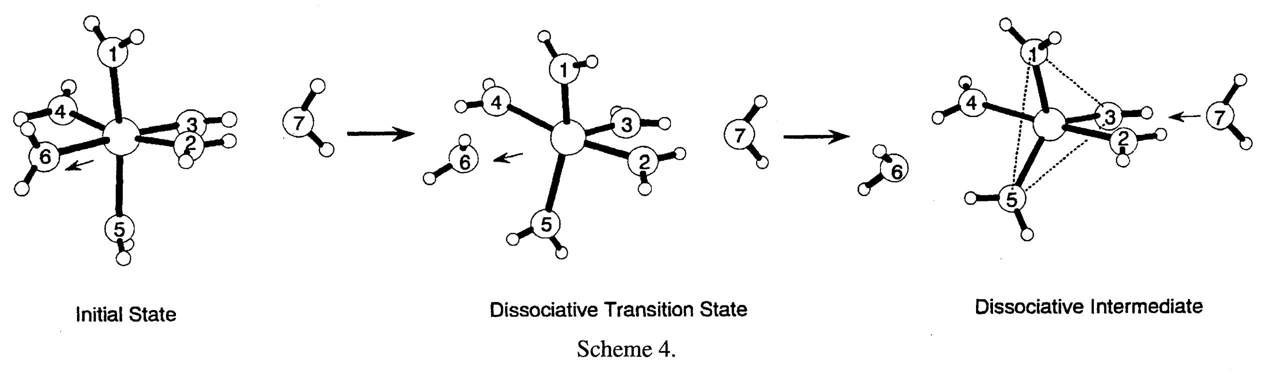
In the activation process via the dissociative mechanism, a water molecule at first leaves from the opposite side of the entering water, because of the persistence of hydrogen bonds linked to the entering water (see Scheme 4). Neighboring water molecules of the leaving water pursue it to fill the space occupied by the leaving water along the transition vector (Figs. 6b and 6c). This mechanism leads to *pentacoordination.*

There is no significant difference between the calcium(II) and zinc(II) ions in the characteristics of the reaction pathways of the dissociative mechanism. They have stable intermediates and saddle points on the reaction paths. These intermediates are similar to the *pentacoordinations.*

Figure 7 shows an energy diagram of the associative and dissociative mechanisms for the calcium(II) and zinc(II) ions on the intrinsic reaction coordinates. Figure 8 also shows changes in the distances between the oxygen atom of the entering water and the central cation (R1) and between the oxygen atom of the leaving water and the central cation (R2) along the intrinsic reaction coordinates for calcium(II) and zinc(II) ions. As is apparent from both Figs. 7 and 8, there are both an associative reaction pathway and a dissociative one for the water-exchange reaction of calcium(II) ion. On the other hand, for the zinc(II) ion there is only a dissociative water-exchange reaction pathway. In the water-exchange reaction, calcium(II) ion behaves as the limit of earlier members, and the zinc(II) ion behaves as the limit of later members in the first transition series.

e. Relation between the Reaction Pathways and Penta- and Heptacoordinated Species. A substitution reaction requires an intermediate or a transition state with an expanded coordination number in the operation of the associative mechanism, and requires those with a reduced coordination number in the operation of the dissociative mechanism. The dissociative mechanism can operate in the water-exchange reaction of both the calcium(II) and zinc(II) ions because of the presence of their *pentacoordinations* at local minima. On the other hand, the associative mechanism can operate for the calcium(II) ion, but never operates for the zinc(II) ion, because although the *heptacoordination* of the calcium(II) ion is stable, that of zinc(II) ion is neither an intermediate nor an associative transition state. The energetic relationship between these species is shown in Fig. 9.

The relation between the reaction pathways and intermediary species (*pentacoordination* and *heptacoordination*) is applied to metal(II) ions in the first transition series. Only a dissociative mechanism can operate for the water-exchange reaction of copper(II) ion, because its *heptacoordination* is neither at a local minimum nor a saddle point, and its *pentacoordination* is at a local minimum. It should be noted that this is in agreement with the experimental result based on a positive activation volume of 2.0 $cm^3 mol^{-1}$ for water exchange on the copper(II) ion.[6c] Associative and dissociative mechanisms are operative for the water-exchange reaction of scandium(II) ion because both its *pentacoordination* and its *heptacoordination* are at local minima. Because it is expected that the pentacoordinated states of all the divalent aqua



Scheme 4.

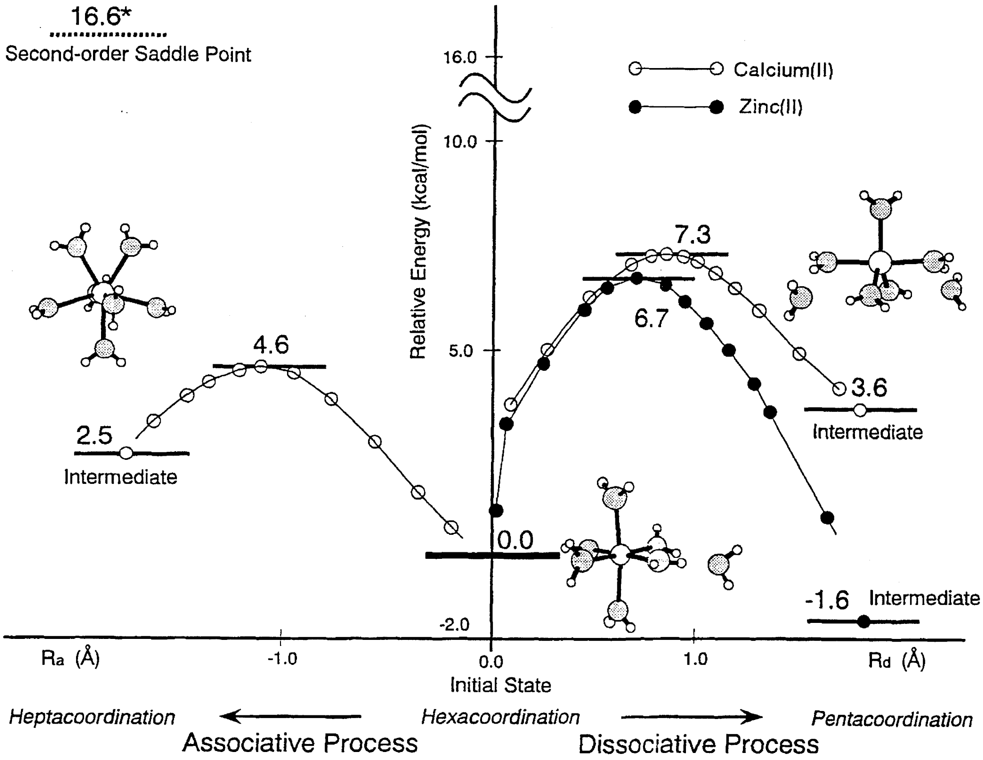
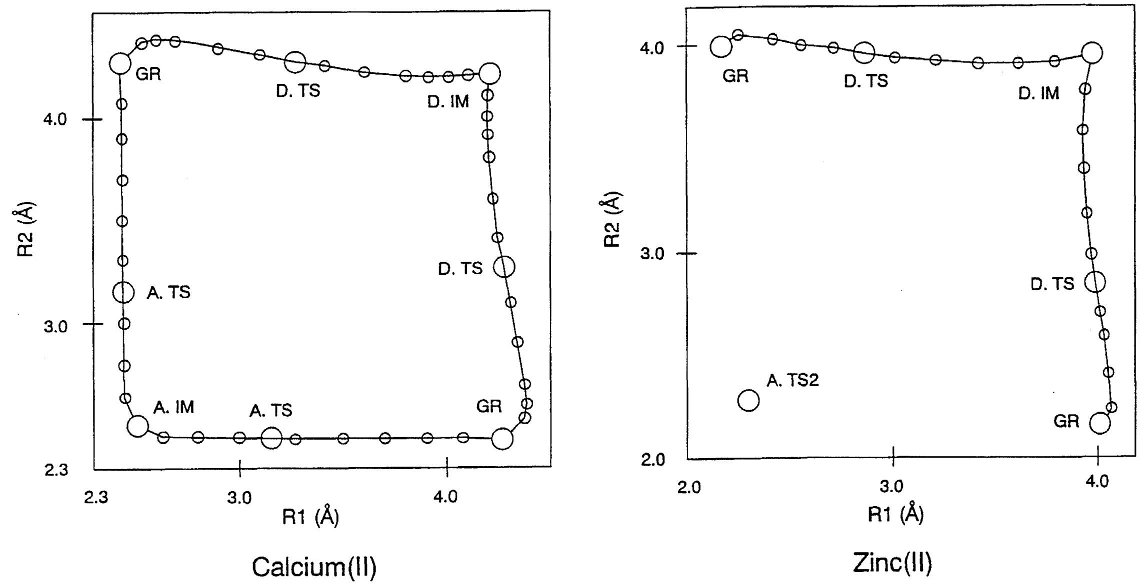


Fig. 7. The relative energy diagram of associative and dissociative mechanisms for calcium(II) and zinc(II) ions in kcal mol^{-1}. R_a is the difference in distance between the oxygen atom of the entering water and the central cation from that in the initial state. R_d is the difference in distance between the oxygen atom of the leaving water and the central cation from that in the initial state.



Calcium(II)

Zinc(II)

Fig. 8. The changes in the distance between the oxygen atom of the entering water and the central cation (*R*1) and between the oxygen atom of the leaving water and the central cation (*R*2) along the intrinsic reaction coordinate for calcium(II) and zinc(II) ions. D and A are abbreviations for dissociative and associative, respectively. GR, IM, TS, and TS2 mean the initial state of the water-exchange reaction, intermediate, transition state, and second-order saddle point, respectively.

ions in the first transition series are intermediates of the reaction, dissociative process can operate for a water exchange on divalent cations for all members of the first transition series, as suggested by Åkesson et. al.[7a,7b)] Therefore, although the heptacoordinated species for earlier members are stable intermediates, those of later members are not intermediates. The possibility of the operation of the associative mechanism depends on the existence of appropriate associative heptacoordinated species.

Chart 1 shows the nature of the heptacoordinated species on the potential surface. Although the heptacoordinated species of the calcium(II) ion is at a local minimum, but

Divalent cation	Ca(II)[a]	Sc(II)[a]	Ti(II)	V(II)[b]	Cr(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)[b]	Cu(II)[a]	Zn(II)[a]
local minimum	√	√	?		?						
transition state		√		√							
second-order transition state				√					√	√	√

Chart 1. The nature of associative structures of heptahydrated divalent cations of the first transition series on the potential surface. Present stationary points up to the second-order transition state are marked by "√" and the regions marked "?"are not yet elucidated.

a) This work. b) Ref. 8.

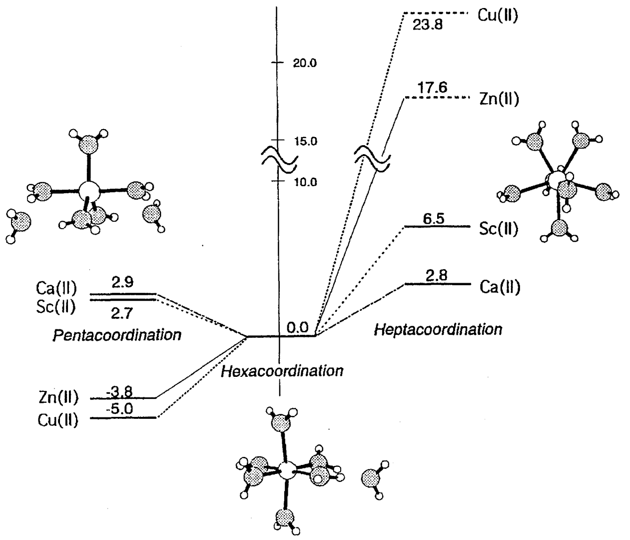


Fig. 9. Relative energies calculated at the MP2 level for the HF structures of *pentacoordinations*, *hexacoordinations*, and *heptacoordinations* of calcium(II), scandium(II), cooper(II), and zinc(II) ions treated in this work. The numbers mean relative energies in kcal mol^{-1}.

that of the vanadium(II) ion[8] is not at a local minimum. Nickel(II),[8] cooper(II), and zinc(II) ions have no associative transition state. Divalent cations of earlier members have large ionic radii, and can thus place seven water molecules in the first shell; however, those of later members cannot place the seven water molecules due to their small ionic radii. Moreover, there are electrostatic attractive interactions between the central metal(II) ions and water molecules as ligands, although the repulsive interaction is invoked when the coordinating water molecules are close to each other. The balance between those two opposite interactions influences the trend of the reaction mechanism. Furthermore, the electronic structure of the d electrons affects the stability of the *heptacoordinations*. The *heptacoordinations* of the earlier members are approximately pentagonal bipyramidal, as mentioned in the previous Sections (**b** and **d**) for the calcium(II) and scandium(II) ions. In the pentagonal bipyramidal structure, five 3d orbitals of the cation interact with the coordinating water molecules and split into two nonbonding orbitals (e_1'') and three antibonding ones (e_2', a_1'). These orbitals of the calcium(II) ion are unoccupied. For the scandium(II) ion with d^1 configuration and the titanium(II) ion with the d^2 configuration, the nonbonding orbitals are occupied. It is not expected that the *heptacoordinations* of the calcium(II), scandium(II), and titanium(II) ions become less stable in view of the electronic structure of the d orbital. For the high-spin vanadium(II) ion having a d^3 configuration, an antibonding orbital is also occupied. Therefore, the *heptacoordinations* of the vanadium(II) ion will become less stable. The nature of the pentagonal bipyramidal structures of the first transition series, i.e., local minimum, saddle point, or higher-order saddle point, should depend on the change in the electronic structure of the d orbitals, together with a difference in the Coulombic interaction induced by the change in the ionic radii. We anticipate examining the existence of local minima for the associative heptacoordinated species of titanium(II) ion and the existence of saddle points for the heptacoordinated species of chromium(II) and manganese(II) ions in order to fulfill the unelucidated region in Chart 1. In following papers we shall report on the relationship between the electronic structure and the structural stability of ionic heptacoordinated species of earlier members in the first transition series.

Conclusions

1. We studied the characteristics of model intermediary species on the reaction pathways in order to explain the change in the mechanistic behavior of the water-exchange reaction of hexahydrated divalent cations as the central elements are changed in the first transition series. The calculations show that the *hexacoordinations* and *pentacoordinations* of the scandium(II) and copper(II) ions and the *heptacoordination* of the scandium(II) ion are at local minima, whereas the *heptacoordination* of the copper(II) ion is at a second-order saddle point.

2. We considered the calcium(II) and zinc(II) ions in order to examine the relation between the intermediate species and the reaction mechanisms. All of the intermediary species for the calcium(II) and zinc(II) ions resemble those for the scandium(II) and copper(II) ions, respectively. The structures of the associative and dissociative intermediates of the calcium(II) and zinc(II) ions are similar to the intermediary species of the calcium(II) and zinc(II) ions, except for the

zinc(II) ion via the associative mechanism. There is neither a saddle point nor an intermediate related to the associative mechanism for the zinc(II) ion. The dissociative mechanism can operate for both the calcium(II) and zinc(II) ions. The associative mechanism can operate only for the calcium(II) ion.

3. The dissociative mechanism is operative for the water exchange of all members in the first transition series. The possibility of the operation of the associative mechanism depends on the existence of associative heptacoordinated species at local minima or saddle points. The associative mechanism is expected for water-exchange reactions on the earlier members having appropriate heptacoordinated species.

Appendix: Basis Set Used in Calculations

All of the calculations in this study were carried out using double-zeta plus polarizations basis set. For central cations, we used the [8s4p3d] segmented contraction of the (14s9p5d) primitive sets of Wachters.[15] The s and p spaces were contracted using contraction number 1, while the d space is contracted to (311). For calcium, we used d functions with exponents chosen in a geometric progression[16] ($\alpha_{Ca}=1.378$, 0.446, 0.144).[17] We used the basis set of Huzinaga–Dunning of the form [4s2p]/(9s5p) for oxygen and [2s]/(4s) for hydrogen.[17b,18] The basis set of hydrogen was scaled by a factor of 1.2. A d polarization function was added to the basis set of oxygen ($\alpha_O=0.85$). The two types of basis sets which we used were as follows:

Basis I : One 4p polarization function was added to a basis set of a central cation ($\alpha_{Ca}=0.059$, $\alpha_{Sc}=0.067$, $\alpha_{Cu}=0.117$, $\alpha_{Zn}=0.123$).[17a]

Basis II : Two 4p polarization functions of Wachters scaled by a factor of 1.5 were added to the basis set of a central cations,[15] and one p polarization function was added to the one of hydrogen ($\alpha_H=1.0$).

The influence of the basis sets on the structures is about 0.01 Å in the distance between metal cations and oxygen atoms of first-shell water molecules and less than 1° in the angle between the bonds.

We also examined the electron correlation effect on structures around the central cation for calcium(II) and zinc(II) by geometry optimization calculations using Basis I. The distance between the metal(II) ion and the oxygen atoms of first-shell water molecules in these structures are shorter by 0.03 Å for calcium(II) and by 0.01—0.02 Å for zinc(II). The change in the bond angles between the metal–oxygen bonds is 1—2°. The electron correlation effect on energies is slightly larger in dissociative species. These results show that the electron correlation is not as significantly effective for these species. The MP2 relative energies on the RHF optimized structures, which are in agreement with those on the MP2 optimized structures within about ten percent, are sufficient for estimating the electron correlation effects of these species.

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14) The energies of the reaction $[M(H_2O)_5]^{2+}+H_2O\rightarrow[M(H_2O)_6]^{2+}$; M=Ca, Sc, Cu, and Zn are −28.9, −28.8, −24.8, and −27.0 kcal mol^{-1}, respectively, at the HF/Basis II level. The relative stabilities of the *pentacoordination* to the *hexacoordination* for copper(II) and zinc(II) are by 2—4 kcal mol^{-1} larger than those for calcium(II) and scandium(II). Furthermore, there are the strong attractive interactions between the first and second coordination shells in the *pentacoordinations* of copper(II) and zinc(II) because of larger polarization of the water molecules in the first coordination shell, resulting from the shorter distance between coordinating water molecules and copper(II) or zinc(II). It is supported by the fact that Mulliken charges on hydrogen atoms of water molecules in the first coordination shell are larger in the *pentacoordinations*

of copper(II) and zinc(II). The energies for the formation of the second coordination shell, $[M(H_2O)_5]^{2+}+2H_2O\rightarrow[M(H_2O)_5]^{2+}\cdot 2H_2O$; M=Ca, Sc, Cu, and Zn, are −45.2, −46.1, −48.6, and −49.5 kcal mol^{-1}, respectively, at the HF/Basis II level. These effects contribute to the greater stabilization of the *pentacoordinations* of copper(II) and zinc(II).

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