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The Stability of Seven-Coordinate Species of Earlier Members in the First Transition Series: Heptahydrated Ti(II), V(II), Cr(II), and Mn(II) Ions Relevant to Intermediate and Transition State in Water-Exchange Reaction

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The structure and stability of heptahydrated divalent cations of earlier members in the first transition series ($[M(H_2O)_7]^{2+}$: M = Ti, V, Cr, and Mn) have been studied by ab initio molecular-orbital methods, because the heptahydrated cations are relevant to intermediates and transition states in their water-exchange reactions. The structure is pentagonal bipyramidal with a distorted equatorial plane. The heptahydrated divalent cations with d^0, d^1, d^2, and d^5 configurations are at the local minima, and those with d^3 and d^4 are at the saddle points, though there is an increase in hydration energy across the row of the periodic table from calcium to zinc. The trend of stability in a series of heptahydrated divalent cations strongly depends on the d-electron configuration, and differs significantly in the case of the penta- or hexahydrated cations that are at the local minima. It is concluded that an associative mechanism is possible for the water-exchange reaction on hexahydrated divalent cations of the earlier members in an aqueous solution.

The coordination number of complexes of transition elements varies with the coordinating ligands. The most commonly observed coordination structure of ions in the first transition series is six-coordinate octahedral. In an aqueous solution, divalent cations in the first transition series are hexahydrated.[1)] Heptacoordination, which is less familiar for compounds of the first transition series, is possible for an intermediary species of subsitution reactions occurring at six-coordinate metal ions. If the intermediary species is an intermediate, the type of reactions is classified as an associative (A) mechanism. If the intermediary species is a transition state, the type is regarded as being an associative-interchange (I_a) mechanism. On the other hand, if a substitution reaction occurs by way of a five-coordinate intermediate or a five-coordinate transition state, the reaction mechanism is dissociative (D) or dissociative-interchange (I_d), respectively.[2)] For solvent-exchange reactions of the first transition series, many experimental studies have suggested that the activation mode of the water-exchange process of octahedrally hexahydrated divalent cations varies from I_a for earlier members to I_d for later members.[3)]

Previously, we studied the water-exchange reaction on calcium(II) and scandium(II) as model species of the earlier members, and copper(II) and zinc(II), as model species of the later, in order to clarify the trend in the reaction mechanisms of the hexahydrated divalent cations in the first transition series.[4)] Considering the possible intermediary species on the reaction paths, we indicated the relationship between their characteristics concerning the location of the species on the potential surface, i.e., whether they are at local minimum, the saddle point, or the higher-order saddle point, and the possible reaction pathways. No suitable reaction pathway exists when the intermediary species are located at the higher-order saddle points. Two types of reasonable intermediary species for the associative and the dissociative processes were shown, i.e., an intermediary species with seven water molecules in the first coordination shell ($[M(H_2O)_7]^{2+}$) and the other with five water molecules in the first coordination shell and two water molecules in the second coordination shell ($[M(H_2O)_5]^{2+}\cdot 2H_2O$), respectively. The associative intermediary species for calcium(II) and scandium(II) were at the local minima and those for copper(II) and zinc(II) were at the second-order saddle points, though all of the dissociative intermediary species could be at the local minima. Their characteristics on the potential surface are remarkably dependent on the central ions of the heptahydrated species. We have concluded that the associative mechanism is expected for the water exchange of the earlier members, while the dissociative mechanism can be operative for the water exchange of all members in the first transition series. We have explained the dependency of the occupancy of σ-antibonding d-orbitals upon the characteristics and predicted the tendency of the characteristics of earlier members in the first transition series.[4)]

In this work, we especially paid attention to the seven-coordinate species, because the possibility of the operation of the associative mechanism depends on the characterisic of the seven-coordinate species, whether at the local minimum or at the saddle point, or at the second-order saddle point on the potential surface.[4] We examined such characteristics on the potential surface, i.e., the structural stability of heptahydrated divalent cations of the earlier members of the first transition series: titanium(II), vanadium(II), chromium(II), and manganese(II). Furthermore, we confirmed the relationship between the structural stability and the occupancy of σ-anti-bonding d-orbitals described in the previous paper.[4]

Computational Details

We determined the structures of heptahydrated divalent cations ($[M(H_2O)_7]^{2+}$: M = Ti, V, Cr, and Mn) and characterized their structural stability on the potential surface by frequency calculations. We also calculated the hydration energy for reaction (1) and compared it with the structural stability.

$$M^{2+} + 7H_2O \rightarrow [M(H_2O)_7]^{2+}$$
$$(M = \mathrm{Ca, Sc, Ti, V, Cr, Mn, Cu, and\ Zn}) \qquad (1)$$

All of the calculations were carried out using a double-zeta plus polarization basis set. For the central cations, we used the [8s4p3d] segmented contraction of the (14s9p5d) primitive sets of Wachters.[5] The s and p spaces are contracted using the contraction number (1), while the d space is contracted to [311]. We used the Huzinaga–Dunning [4s2p]/(9s5p) basis set for oxygen and [2s]/(4s) for hydrogen.[6] The basis set of hydrogen is scaled by the factor of 1.2. Two 4p functions of Wachters scaled by a factor of 1.5 are added to the basis set of a central cation,[5] one d polarization function is added to the basis set of oxygen (α_O=0.85), and one p polarization function is added to the basis set of hydrogen (α_H=1.0).

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 in order to examine the non-dynamical correlation effect for this type of open-shell system.[7] They showed that the hydration energies, given by CASSCF and SCF, were not significantly different, and that the mixing of states was merely an atomic effect. The MP2 optimized structures were not significantly different from the SCF structures for heptahydrated calcium(II) and zinc(II) ions.[4,8] Thus, we carried out structural calculations at the UHF level. The basis-set superposition errors (BSSE) involved in the hydration energies were estimated by the Boys-Bernardii counterpoise method.[9]

We used Gaussian92[10a] and Gaussian94[10b] programs on IBM RS6000 for all ab initio molecular-orbital calculations and the MOLCAT program[11] on a Macintosh for visualization of the molecular structures and vibrational modes.

Results and Discussion

a. Structure of Heptahydrated Metal(II) Ions. The optimized structures, the electronic states, and the total energies of all the heptahydrated cations treated in the present and previous studies are given in Table 1. For seven-coordinate compounds, three regular geometries are known, i.e., the pentagonal bipyramid, capped octahedron, and capped trigonal prism.[12] The optimized structures are pentagonal bipyramidal with a distorted equatorial plane. Figure 1 shows an outline of the optimized structure of the heptahydrated titanium(II) ion. The axial bonds are shorter than any bonds in the equatorial plane for all of the hexahydrated divalent cations, except for copper(II). It is considered that the longer bonds and the distortion of the equatorial plane are due to the strong repulsive interaction between the coordinating water molecules. The point group of heptahydrated calcium(II), titanium(II), vanadium(II), manganese(II), copper(II), and zinc(II) ions is C_2 while that of scandium(II) and chromium(II) is C_1. The structure of the heptahydrated vanadium(II) ion is in agreement with that reported by Rotzinger[13] within 0.02 Å in bond length.

Table 1. Metal–Oxygen Bond Lengths, Electronic Properties, Hydration Energies, and Harmonic Vibrational Frequencies for Heptahydrated Divalent Cations in the First Transition Series

	Ca(II)	Sc(II)$^{a)}$	Ti(II)	V(II)	Cr(II)$^{a)}$	Mn(II)	Cu(II)	Zn(II)
d Configuration	d^0	d^1	d^2	d^3	d^4	d^5	d^9	d^{10}
Bond length								
$M–O_1{}^{b)}$	2.4873	2.3936	2.3498	2.2376	2.2345	2.3434	2.0520	2.2596
$M–O_2{}^{b)}$	2.5105	2.4183	2.3504	2.2350	2.4949	2.3844	2.2917	2.2609
$M–O_3{}^{b)}$	2.5105	2.4462	2.3504	2.2350	2.6276	2.3844	2.2917	2.2609
$M–O_4{}^{b)}$	2.4982	2.4974	2.3872	2.7027	2.6800	2.3561	2.2836	2.3057
$M–O_5{}^{b)}$	2.4982	2.3637	2.3872	2.7027	2.2181	2.3561	2.2836	2.3057
$M–O_6{}^{b)}$	2.4541	2.3394	2.3211	2.2198	2.1444	2.2643	2.2739	2.1522
$M–O_7{}^{b)}$	2.4541	2.3855	2.3211	2.2198	2.1322	2.2643	2.2739	2.1522
Total energy$^{c)}$	−1208.883791	−1291.850794	−1380.501200	−1474.955833	−1575.346272	−1681.850801	−2170.797844	−2309.648693
Electronic state	^1A	^2A	^3B	^4A	^5A	^6A	^2A	^1A
$< S^2 >^{d)}$	0.0000	0.7505	2.0009	3.7517	6.0026	8.7517	0.7509	0.0000
Hydration energy$^{e)}$	−262.6	−283.8	−296.3	−310.8	−307.8	−301.8	−328.7	−328.9
Frequency$^{f)}$	29.4	31.8	35.5	128.7i	73.1i	28.6	189.7i 158.1i	126.8i 86.9i

a) C_1 structure. b) In Å. 1 Å = 100 pm. c) In atomic unit. 1 a.u. = 2628.3 kJ mol^{-1}. d) Total squared-magnitude of the spin. e) In kcal mol^{-1}. 1 kcal mol^{-1} = 4.1884 kJ mol^{-1}. All the values are corrected by BSSE (basis set super-position error). The total energy of a water molecule is −76.046801 a.u. f) In cm^{-1}. 1 cm^{-1} = 1.98648×10^{-23} J. For structures at local minima, the lowest real frequency is given. For the structures at saddle points and second-order saddle points, all the imaginary frequencies are given.

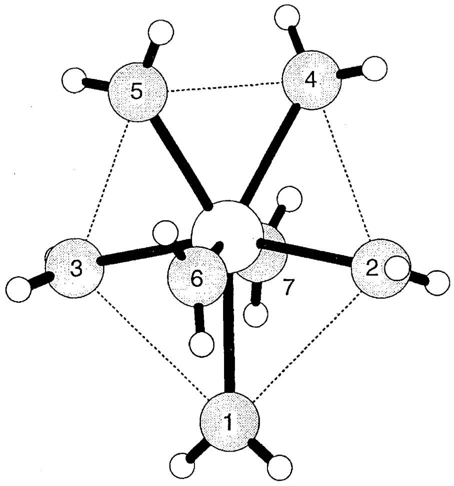


Fig. 1. The numbering of oxygen atoms in heptahydrated ions. The atoms connected by dashed lines are placed on the equatorial plane of a pentagonal bipyramid. This picture shows the optimized structure of heptahydrated titanium(II) ion.

There is an overall decrease in the length of the metal–oxygen bonds across the row of the periodic table. The length of the metal-oxygen bond strongly depends on the d-electron configuration, as will be discussed in the next Section b. For the earlier members, the length of the axial bonds, M–O_6 and M–O_7, (see Table 1) decreases across the row of the periodic table to chromium(II): 2.45 Å for calcium(II), 2.34 and 2.39 Å for scandium(II), 2.32 Å for titanium(II), 2.22 Å for vanadium(II), and 2.13 and 2.14 Å for chromium(II), but increases at manganese(II) (2.26 Å). This trend is also shown by Åkessen et al., although they computed the bond lengths by constrained geometry optimization.[14] The shorter bond length reflects an increase in the effective nuclear charge due to the incomplete shielding of singly occupied non-bonding d-orbitals. The longer axial bonds of the manganese(II) ion are caused by singly occupied σ-anti-bonding d-orbital spreading into this direction.

The molecular structure of manganese(II) is similar to those of closed-shell ions. The lengths of all the metal–oxygen bonds of the heptahydrated manganese(II) ion are between those of the corresponding bonds for closed-shell calcium(II) and zinc(II) (see Table 1). The metal–oxygen bond lengths of the heptahydrated chromium(II) ion range from 2.13 to 2.68 Å, while those of the heptahydrated manganese(II) ion are between 2.26 and 2.39 Å. Therefore, the manganese(II) ion is more spherical than the chromium(II) ion. The sphericity of the manganese(II) ion results from the half-closed 3d shell of the high-spin d^5 configuration, which acts like an isotropic s orbital.

b. Structural Stability of Heptahydrated Metal(II) Ions. Chart 1 shows the structural stability for heptahydrated divalent cations in the first transition series. The lowest real frequencies and all of the imaginary frequencies of their normal modes, as well as the hydration energies are given in Table 1. The heptahydrated ions of the earlier members, calcium(II), scandium(II), titanium(II), and manganese(II) ions, are at the local minima, and are thus regarded as being possible associative intermediates for the water-exchange reaction; those of the members (nickel(II),[13] copper(II), and zinc(II)[4] ions) are located at the second-order saddle points, and are thus neither an associative intermediate nor a transition state. In a previous study,[4] we indicated that the structral stability changes from the local minimum for the earlier members, via the saddle point for the middle members, to a second-order saddle point for the later members. The change in the structural stability is not so simple because the heptahydrated vanadium(II) and chromium(II) ions are at the saddle points, while the heptahydrated manganese(II) is at the local minimum. This behavior concerning the structural stability of vanadium(II) and chromium(II) seems to be anomalous. It is suggested that the stability is dependent on the electron configuration, and is independent of a simple balance between the electrostatic attractive interaction and the repulsive interaction of the ligands. Although the heptahydrated divalent cations with a d^0, d^1, d^2, or high-spin d^5 configuration are at the local minima, those with a high-spin d^3 or d^4 configuration are at the saddle points. This trend is also expected in heptahydrated trivalent cations, because of a resemblance to the divalent cations concerning the characteristics of the bonding and the electronic structure. For example, there are several seven-coordinate compounds of vanadium(III)[15] which have a d^2-electron configuration, like that of titanium(II).

Divalent cation	Ca(II)[a]	Sc(II)[a]	Ti(II)	V(II)	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. Structural stability of heptahydrated ions in the first transition series. Theoretically identified stationary points up to the second-order transition state are marked by "√" and the region marked "?" is not yet elucidated. a) The previous work (Ref. 4). b) Ref. 13.

The hydration energies of the heptahydrated divalent cations at the saddle points are larger than those at the local minima, though an overall increase in the energy occurs across the row. The structural stability is independent of the magnitude of the hydration energy, dominated by an electrostatic interaction between the central cation and the coordinating ligands.

It was mentioned in a previous paper[4] that the d-electron configrations significantly influence the structural stability of heptahydrated divalent cations. In the seven-coordinate pentagonal-bipyramidal structure, five 3d orbitals interact with the a_1 orbitals of the coordinating water molecules and split into two lower non-bonding orbitals (e_1'') and three higher σ-anti-bonding ones (e_2',a_1'). For heptahydrated cations with d^0, d^1, and d^2 configurations, their structural stability, dependent upon the bonding between the central cation and oxygen atoms, is not affected, because only the non-bonding orbitals are occupied. Thus, the heptahydrated species with these electron configurations are at the local minima. For cations with a high-spin d^3 configuration, such as vanadium(II), a σ-anti-bonding d-orbital is also occupied. The orbitals mentioned here are shown in Fig. 2. The V–O bonds along the singly occupied σ-anti-bonding d-orbital become longer and the transition vector follows a movement breaking one of the bonds (see Fig. 3a). Bader–Pearson's second-order perturbation theory states that the movement is induced by excitation from the σ-anti-bonding orbital to the unoccupied 4s orbital. For cations with a high-spin d^4 configuration, such as chromium(II), two of the σ-anti-bonding d-orbitals are singly occupied and the heptahydrated chromium(II) ion is at the saddle point. The elongation on the bonds between the chromium and the oxygen atoms (2, 3, and 4) results from the occupation of the σ-anti-bonding d-orbitals. The transition vector follows the stretching of the longest bond with the 4-th oxygen atom (see Fig. 3b).

The characteristic of manganese(II) is different from that

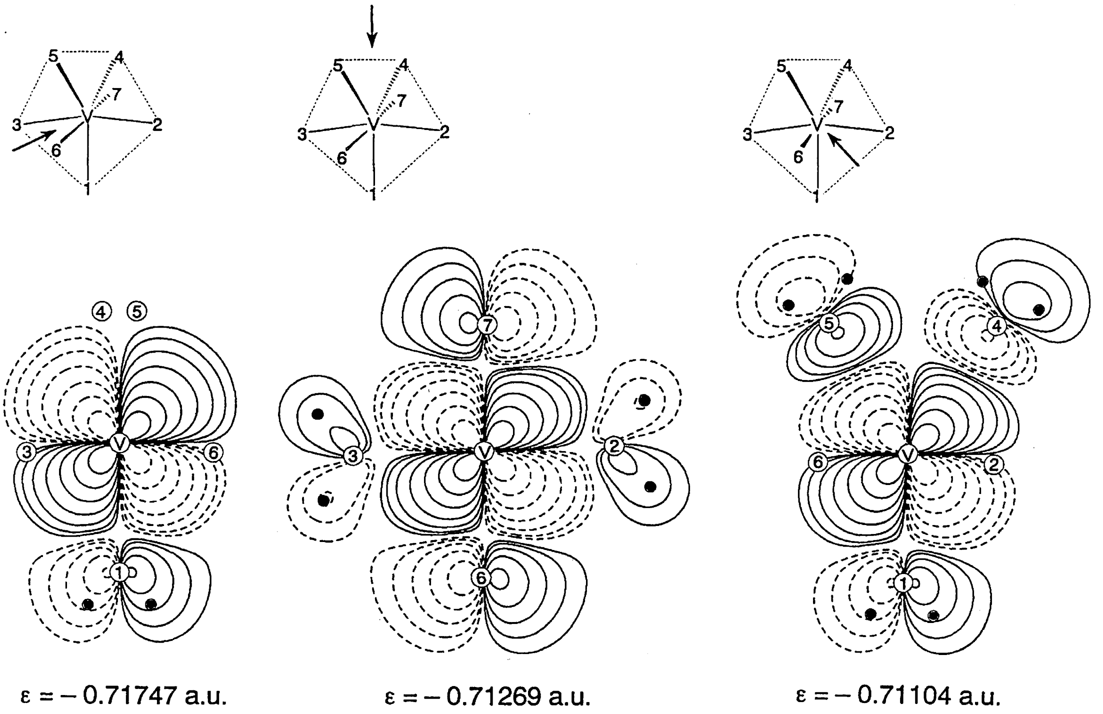
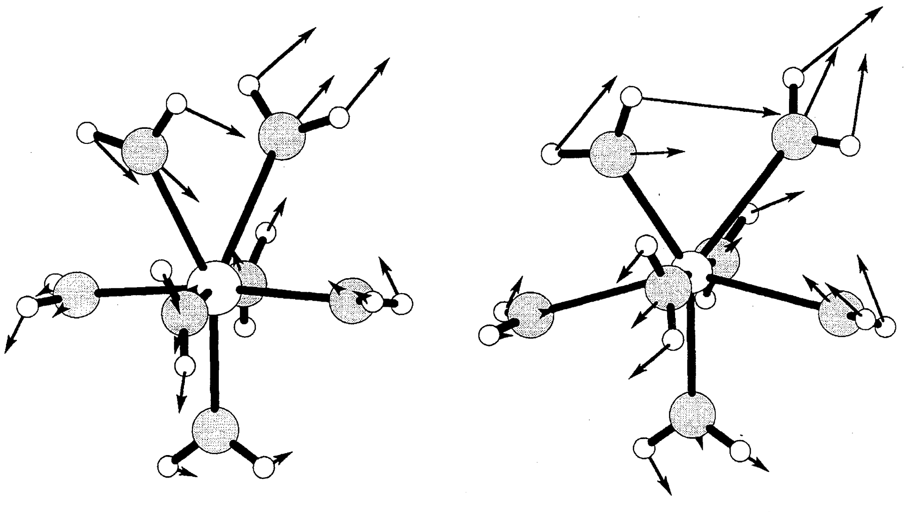


Fig. 2. Contour maps of the singly occupied molecular orbitals of heptahydrated vanadium(II) ion viewed from the direction of the arrow in the upper picture. The planes of the maps contain the central cations. Dots mean hydrogen atoms and numbered circles mean oxygen atoms projected into the plane. The numbering of oxygen atoms is shown in Fig. 1. ε means the UHF orbital energy in atomic unit (1 a.u. = 2628.3 kJ mol^{-1}).



(a) $[V(H_2O)_7]^{2+}$ (b) $[Cr(H_2O)_7]^{2+}$

Fig. 3. Transition vectors of heptahydrated vanadium(II) (a) and chromium(II) (b) ions.

of the other earlier members. The finding that the heptahydrated manganese(II) ion is at the local minimum is in disagreement with the trend in the stability mentioned above. The high-spin d^5 configuration of manganese(II) constructs a half-closed-shell, and the d-shell behaves isotropically like an s orbital. In this case, stabilization with the maximum exchange correlation and with the isotropic dispersion of the positive charge is more effective than an increase in the instability due to occupation of the σ-anti-bonding d-orbital.

The stability of the pentagonal bipyramidal structures of earlier members in the first transition series, i.e., at the local minimum or at the saddle point, strongly depends on the change in the d-configuration. This tendency is not observed in hexahydrated or pentahydrated analogues which are at the local minima, and their structural stability is independent of the d-configuration. In such hydrates, the repulsive interaction among ligands is competitive with the stabilization resulting from electrostatically attractive interaction between the central cation and the ligands. Pentahydrated and hexahydrated divalent cations are at the local minima because the attractive interaction is substantially larger than the repulsive interaction among coordinating water molecules. On the other hand, for heptahydrated divalent cations, the repulsive interaction becomes larger due to an increase in the number of coordinating water molecules. In such a critical case, the occupancy of the σ-anti-bonding orbital becomes an important factor in the stability.

c. Water-Exchange Reaction and Stability of Seven-Coordinate Complexes. According to our previous study, the possibility of the operation of the associative mechanism depends on the existence of a seven-coordinate species at the local minima or at the saddle points.4) The present results, that the heptahydrated divalent cations of the earlier members in the first transition series are at the local minima or saddle points, indicate that in principle an associative mechanism is possible for the water-exchange reaction on all of these cations.

Though the heptacoordination is less familiar for the complexes of metal ions in the first transition series, there are several seven-coordinate compounds with multidentate ligands.12) Some aminopolycarboxylate complexes of manganese(II) and iron(II) hydrated by a water molecule are seven-coordinate.16) Manganese(II)16d) and iron(III)16e) complexes with *o*-phenylenediamine-*N,N,N′,N′*-tetraacetate are seven-coordinate, while its copper(II)16f) and zinc(II)16g) complexes are six-coordinate. This finding corresponds to our conclusion concerning the structural stability, that the seven-coordinate structure of manganese(II) and iron(II) with a d^5 configuration is stable, but that of copper(II) with a d^9 configuration and zinc(II) with a d^{10} configuration is unstable. Recently, Kanamori et al. prepared $[V_2(SO_4)_3\{$*N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamime$\}_2]$ and $[V(SO_4)\{$*N,N,N′N′*-tetrakis(2-pyridylmethyl)-1,2-ethanediamime$\}]^+$ with a seven-coordinate pentagonal bipyramidal structure.15) They claimed that the heptacoordination of these complexes results from an insufficiently large chelate-ring system encircling the vanadium(III) center. Taking into account the structrual stability obtained in our study, the d^2 configuration of vanadium(III) also encourages the existence of these seven-coordinate structures because of the unoccupancy of the σ-anti-bonding d-orbitals.

Conclusions

1. We studied the stability of the heptahydrated divalent cations as model intermediary species on associative reaction pathways for earlier members of the first transition series in order to explain the change in the mechanistic behavior of the water-exchange reaction on the hexahydrated divalent cations as the central elements are changed.
2. All of the structures of the heptahydrated divalent cations are pentagonal bipyramidal with a distorted equatorial plane. Although the cation with a d^0, d^1, d^2, or high-spin d^5 configuration is at the local minimum, that with a high-spin d^3 or d^4 configuration is at the saddle point. The trend in the structural stability differs significantly in the case of penta- or hexahydrated divalent cations that are at the local minima. The stability depends on the occupancy of the σ-anti-bonding d-orbitals. Manganese(II), with a high-spin d^5 configuration, behaves like a closed-shell ion due to its half-closed shell.
3. It is concluded that the associative mechanism is possible for water-exchange reactions on hexahydrated divalent cations of the earlier members via the seven-coordinate species located at the local minima or at the saddle points on the potential surface.

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8) We examined the difference in the structures optimized by MP2 and SCF calculations. We selected three types of model molecules: the heptahydrated titanium(II), the heptahydrated vanadium(II), and the heptahydrated manganese(II) ions. The heptahydrated titanium(II) ion is a molecule of which only the nonbonding d-orbitals are occupied. The heptahydrated vanadium(II) ion is a molecule of which one of the σ-anti-bonding d-orbitals is occupied. The heptahydrated manganese(II) ion is a species with the half-filled shell. We carried out geometry optimizations using

the same basis set in the text except for the polarization function for hydrogen ([8s6p3d] for metal, [4s2p1d] for oxygen, and [2s] for hydrogen) at the UHF and MP2 levels. All the optimized structures were in C_2 symmetry as shown in Fig. 1. The bond lengths (Å) of M–O$_1$, M–O$_2$, M–O$_4$, and M–O$_6$ for the optimized structures at the MP2 level (in parentheses, the structural parameters at the UHF level) were 2.284 (2.350), 2.294 (2.349), 2.335 (2.386), and 2.277 (2.320) for titanium(II), 2.190 (2.239), 2.194 (2.237), 2.629 (2.692), and 2.180 (2.221) for vanadium(II), and 2.292 (2.340), 2.358 (2.386), 2.303 (2.352), and 2.229 (2.264) for manganese(II), respectively. The numbering of oxygen atoms was defined in Fig. 1. The bond angles (degree) of $\angle O_2MO_1$, $\angle O_4MO_1$, and $\angle O_6MO_1$ in the optimized structures were 80.9 (80.4), 142.5 (143.3), and 81.6 (81.2) for titanium(II), 86.2 (86.1), 146.4 (146.9), and 85.4 (85.6) for vanadium(II), and 75.8 (76.2), 142.9 (143.3), and 82.9 (82.2) for manganese(II), respectively. The difference in bond length is from 0.04 to 0.07 Å, the difference in bond angle is less than 1°, and the difference in dihedral angle is less than 3°. The dynamical correlation estimated by the MP2 calculation has no significant effect on the pentagonal bipyramid with the distorted equatorial plane as described in the text (vide infra).

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