Hydration of Zinc Ions: A Comparison with Magnesium and Beryllium Ions

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Abstract: The coordination geometry of divalent zinc cations has been investigated by analyses of the crystal structures of small molecules containing this cation that are found in the Cambridge Structural Database and by *ab initio* molecular orbital calculations on hydrated structures of the form $Zn[H_2O]_n^{2+} \cdot mH_2O$, in which there are n water molecules in the first coordination shell and m water molecules in the second coordination shell. Zinc ions in crystal structures are more commonly found to bind nitrogen and sulfur atoms, in addition to oxygen, while magnesium ions have a tendency to bind oxygen atoms. While most magnesium ion complexes have a metal ion coordination number of six, zinc ion complexes show coordination numbers that are generally four, five, and six. The higher of these coordination numbers for zinc (six) is primarily found when oxygen (or, to a lesser extent, nitrogen) is bound, and the lowest when sulfur is bound. *Ab initio* molecular orbital studies of aquated zinc ions show that the total molecular energies of the three gas-phase complexes $Zn[H_2O]_6^{2+}$, $Zn[H_2O]_5^{2+} \cdot H_2O$, and $Zn[H_2O]_4^{2+} \cdot 2H_2O$ differ by less than 0.4 kcal/mol. This is in contrast to the corresponding results for magnesium and beryllium, where we have previously shown that $Mg[H_2O]_6^{2+}$ is approximately 9 and 4 kcal/mol lower in energy than $Mg[H_2O]_4^{2+} \cdot 2H_2O$ and $Mg[H_2O]_5^{2+} \cdot H_2O$, respectively, while $Be[H_2O]_4^{2+} \cdot 2H_2O$ is 22 kcal/mol lower in energy than $Be[H_2O]_6^{2+}$, and no stable form with five water molecules in the first coordination sphere of a beryllium ion could be found. Thus the energy penalty for changing the local environment (coordination number) of divalent zinc ions surrounded by water is significantly less than that for the corresponding magnesium and beryllium ions. This is in line with the modes of utilization of these cations in enzyme systems, where magnesium ions play a more structural role than do zinc ions which, when bound to oxygen or nitrogen, tend to be involved in catalytic processes, possibly involving coordination number changes. The effects of Be^{2+}, Mg^{2+}, and Zn^{2+} ions on water molecules bound in the first coordination sphere have been assessed by use of values of the H—O—H angle from the *ab initio* molecular orbital studies. It is found that this angle is increased from 105.5° in an isolated water molecule to average values of 106.7° for magnesium, 107.1° for zinc, and 108.8° for beryllium complexes. These values are even larger when other water molecules in the second hydration sphere that are hydrogen bonded to water molecules in the first hydration sphere are taken into account in the calculations, but the overall trend remains the same. This order of the effect of these cations presumably expresses the extent of polarization of water molecules by each metal cation.

Introduction

Approximately one-third of all proteins require a metal ion for their structure or function, and therefore an understanding of the chemical consequences of metal binding is essential to a correct derivation of the mechanism of action of a metalloenzyme.[1] Of the first row transition metals, zinc is second only to iron in its importance in enzyme systems.[2] Divalent zinc, Zn^{2+}, has an ionic radius of approximately 0.74 Å, is at the borderline between hard and soft cations, and can accommodate nitrogen, oxygen, sulfur, and halogen atoms in its coordination polyhedron.[3–5] Since it has a filled d-shell and is not subject to ligand field effects that stabilize octahedral over tetrahedral geometries, zinc binding sites in proteins often have tetrahedral geometries.[1,2,6] Furthermore, zinc does not show any biologi-

cally relevant redox activity, and in this regard is similar to magnesium.[1] Divalent magnesium, Mg^{2+}, however, has a slightly smaller ionic radius of approximately 0.65 Å, is considered a hard cation, and is most often found in an octahedral arrangement where it prefers oxygen ligands.[3–5] The functions of these two metal ions in proteins also differ, the role of divalent magnesium is generally structural, while the role of divalent zinc is often catalytic.[1,2] Thus, in spite of radii that differ by less than 0.1 Å, and similar charges, zinc and magnesium ions have somewhat different properties. It is the aim of this article to provide some measure of these differences.

In two recent studies[7,8] we used the Cambridge Structural Database (CSD)[9] in conjunction with *ab initio* molecular orbital calculations to study the stereochemistry of ligand binding by divalent beryllium and magnesium ions and the manners in which these cations bind water. In the case of Be^{2+}, in which the ionic radius is only 0.34 Å,[4] *ab initio* MP4SDQ/6-31G*// RHF/6-31G* calculations showed that the complex $Be[H_2O]_6^{2+}$

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Hydration of Zinc Ions

J. Am. Chem. Soc., Vol. 117, No. 13, 1995 3755

is a local minimum on the potential energy surface, but it is more than 22 kcal/mol higher in energy than any of several different forms of Be[H$_2$O]$_4^{2+}$·2H$_2$O.[10] Furthermore, two different forms of Be[H$_2$O]$_3^{2+}$·3H$_2$O were found to be at least 12 kcal/mol higher in energy than any of the conformers of Be[H$_2$O]$_4^{2+}$·2H$_2$O. These results suggest that a divalent beryllium ion that is surrounded by water molecules prefers a tetrahedral to an octahedral environment in the primary coordination sphere, no doubt a result of the small size and relatively large charge of the beryllium ion. Indeed, a search of the CSD showed that the maximum coordination number of beryllium ions for 41 entries in this database was 4, and that the six crystal determinations which involved beryllium bonded to oxygen all had a coordination of precisely 4. A comparable *ab initio* study of hydrated divalent magnesium ions showed that Mg[H$_2$O]$_6^{2+}$ is lower in energy than Mg[H$_2$O]$_5^{2+}$·H$_2$O, Mg[H$_2$O]$_4^{2+}$·2H$_2$O, and Mg[H$_2$O]$_3^{2+}$·3H$_2$O, by approximately 4, 9, and 34 kcal/mol, respectively, demonstrating that the optimal binding geometry for a divalent magnesium ion surrounded by water molecules is octahedral and that a significant energy penalty is incurred for altering this octahedral environment. A search of the CSD for divalent magnesium structures bound to oxygen, nitrogen, chlorine, bromine, and/or sulfur atoms showed that most of these complexes (149 out of 189, 79%) were hexacoordinate. Oxygen is the preferred ligand for hexacoordinate magnesium in 122 crystal structures (82% of all hexacoordinate structures), and 31 (21%) of these crystal structures were found to contain hexaaquated magnesium ions. Furthermore, only six structures were found that involved four-coordinate magnesium bound to oxygen, and none of these contained any metal-coordinated water molecules.

The purpose of this article is to report the results of an investigation of the general role of divalent zinc cations by (1) analyses of the crystal structures of small molecules containing Zn^{2+} as found in the CSD and (2) *ab initio* molecular orbital calculations on a selection of hydrated structures of the form Zn[H$_2$O]$_n^{2+}$·mH$_2$O, see deposited Chart 1. Comparisons are made with our previous structural and molecular orbital analyses of divalent beryllium and magnesium ions.[8,9] The results can then be used to further an understanding of the roles of zinc and magnesium ions in metalloproteins.[11-13] We have analyzed the various types of ligands coordinated to zinc ions in crystal structure determinations. In the *ab initio* molecular orbital studies, we specifically investigate the manner in which water molecules are arranged around divalent zinc ions, the energy differences between comparable gas phase clusters, e.g. Zn[H$_2$O]$_6^{2+}$, Zn[H$_2$O]$_5^{2+}$·H$_2$O, and Zn[H$_2$O]$_4^{2+}$·2H$_2$O, and the relationships between water molecules in the first and second coordination spheres. These two types of information (structural and computational) are then considered together so that differences between divalent zinc and magnesium cations can be identified.

Methods

A. Structural Analyses. The three-dimensional data on crystal structure determinations contained in the CSD were used as the basis for our structural analyses.[9] This database was searched for all published crystal structures containing divalent zinc ions by use of the

program QUEST, and a master file of the complexes found in this search was created. Only those compounds with zinc bound to the elements O, N, Cl, Br, and/or S were then considered, because we were interested in crystal structures relevant to zinc—protein and zinc—nucleic acid interactions in an aqueous environment. As a result, 17 entries involving zinc bound to a variety of other chemical elements were eliminated from this analysis (see Table 1). Results of 44 crystal structural analyses were not used by us because of disorder in the structure or high R factors (greater than 0.10). They are listed in deposited Table 1S.

The master file of these crystallographic parameters was then broken down into smaller files, each containing a zinc ion with a specific coordination number (3 to 7). Each of these coordination-number files was studied separately. For example, starting with the file of zinc ions with a coordination number of 6, the program GSTAT was used to extract information from the zinc master file on the coordination geometry of those entries containing only oxygen atoms in the first coordination sphere of the zinc ion [the Zn(O)$_6$ fragment]. This was repeated for other coordination number and ligand types. In many cases the coordination number had to be checked by a detailed inspection of the molecular structure calculated from the published atomic coordinates using the program ICRVIEW.[14] In other cases the coordination number is evident from the chemical formula drawn by the software provided with the CSD program system.

B. Molecular Orbital Studies. All of the *ab initio* molecular-orbital calculations were carried out on a CRAY Y-MP computer at the National Cancer Institute, using the GAUSSIAN 90 and GAUSSIAN 92 series of programs.[15,16] Restricted Hartree—Fock (RHF) calculations with gradient optimizations were employed throughout using the 6-31G* basis set[17] for oxygen and hydrogen atoms, and since no standard 6-31G* basis set parameters are currently available for the transition elements, a split-valence Huzinaga ⟨53321/53*/41⟩ basis set was employed for zinc, which includes a p-type polarization function.[18] For convenience we shall refer to this combined basis set as HUZSP*.[19] This choice of basis set represents a compromise between accuracy and our desire to include a significant number of water molecules surrounding the zinc ions. The effects of electron correlation were included by performing single-point Møller—Plesset (MP) perturbation calculations, in some cases up to the MP4SDTQ/ HUZSP*//RHF/HUZSP* level.[20] Vibrational frequencies were obtained from analytical second derivatives calculated at the RHF/HUZSP*// RHF/HUZSP* level in order to verify that the computed structures were indeed stable states and not transition states,[21-24] and to modify calculated reaction energies for zero-point vibrational energy differences. Many of the structures were also reoptimized at the MP2(FC)/ HUZSP*//MP2(FC)/HUZSP* level, where only the valence orbitals are active, to assess the effects of electron correlation on the geometrical

(10) The notation M[H$_2$O]$_n^{2+}$·mH$_2$O denotes a divalent metal ion, M^{2+}, bound to n water molecules in the first coordination shell, with m water molecules in the second coordination shell hydrogen bonded to water molecules in the first coordination shell.

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Table 1. Occurrences of $Zn^{2+} \cdots X$ (X = N, O, S, Cl, Br) Interactions in Crystal Structures Reported in the CSD[a] and a Comparison with Analogous Data for $Mg^{2+} \cdots X$

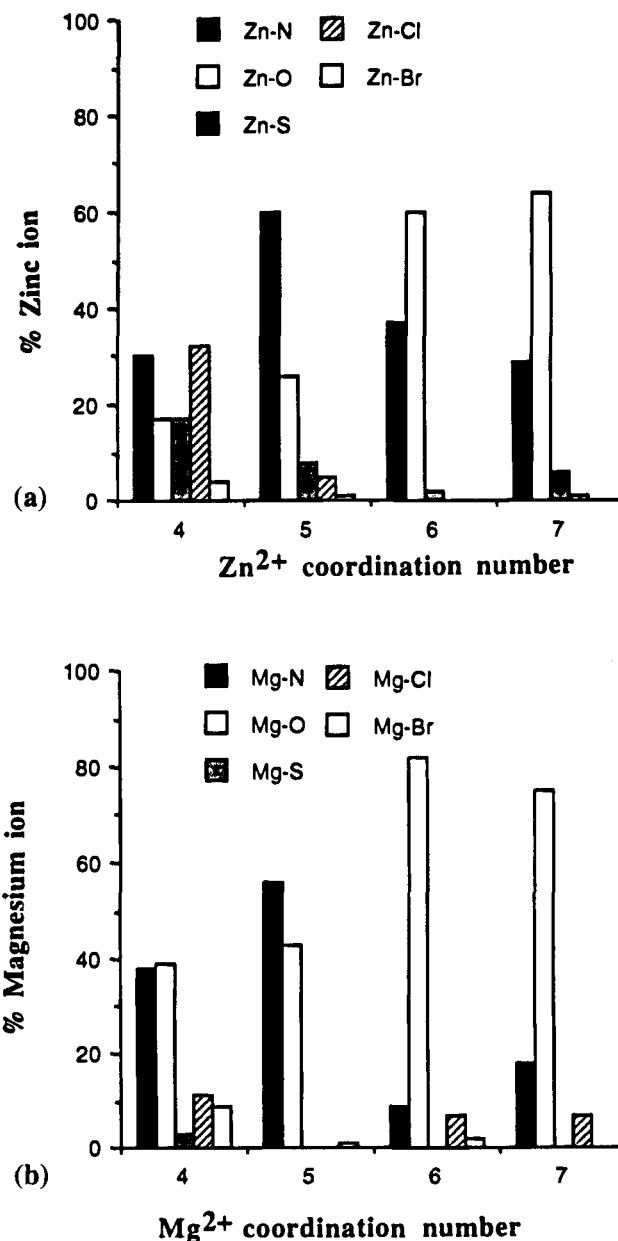| coord no.	$Zn^{2+}-N$			$Zn^{2+}-O$			$Zn^{2+}-S$			$Zn^{2+}-Cl$			$Zn^{2+}-Cl$			total M $\cdots$ X		
	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}	no. of bonds[b]	% Zn^{2+}	% Mg^{2+}
3	0	0	0	0	0	100	3	100	0	0	0	0	0	0	0	3	0.2	0.5
4[c]	246	30	38	149	17	39	141	17	3	272	32	11	36	4	9	844	42	9
5	229	60	56	98	26	43	30	8	0	18	5	0	5	1	1	380	19	7
6[d]	259	37	9	424	60	82	17	2	0	2	0.2	7	0	0	2	702	35	79
7	20	29	18	45	64	75	4	6	0	1	1	7	0	0	0	70	4	4
$Zn^{2+} \cdots X$ for all ligands	754	38		716	36		195	10		293	15		41	2		1999[e]	100	

[a] Data for organic crystal structures, extracted from the CSD. Remeasurements of the same crystal structure are not included in the count. Percentages are for the coordination number listed on the left, except for the last two columns on the right which give the percentages of the total. [b] Number of $Zn^{2+} \cdots X$ bonds. [c] Contains one crystal structure (refcode PASNZN) that might be described as containing octacoordinate zinc, but four of the $Zn \cdots O$ distances range from 2.046 to 2.071 Å, while the other four range from 2.516 to 2.636 Å. Therefore we have considered it here to be four-coordinate. [d] Includes three structures containing $Zn(H_2O)_6^{2+}$. [e] This entry gives the number of M $\cdots$ X bonds. The total number of entries for all elements attached to Zn^{2+} = 476. Other elements bound to Zn (with the number of entries in parentheses) are I(1), Si(2), Se(2), C(2), and Cu(1). In addition, 44 entries were eliminated because they showed disorder, questionable metal ion identity, or other crystallographic problems (listed in Table 1S). The remaining 415 entries are listed in the table above.

parameters. No corrections for basis set superposition errors (BSSE) were incorporated into the results, since MP2 calculations without BSSE corrections often more closely reproduce experimental energy differences than do calculations which include this correction.[25–28] The reason for this is that the increase in the binding energy due to BSSE may be comparable to a decrease resulting for physical reasons, e.g. an improved description of the dispersion interaction, as the basis set becomes more complete. Therefore the two effects may cancel each other out. For a few of the smaller hydrates, further optimizations were performed at both the RHF and MP2 levels, employing basis sets with multiple polarization functions. This was done in order to test the sensitivity of the calculated geometries to the use of more complete basis sets. Finally, generalized second-order densities were calculated at the MP2(FC)/HUZSP*//MP2(FC)/HUZSP* level in order to study the transfer of charge to the zinc cation in a few selected cases.[29]

Results

I. Structural Studies. A list of the 476 crystal structures containing divalent zinc from the CSD is given in deposited Tables 1S to 5S. Our analysis of these zinc structures involved only those in which divalent zinc is coordinated to oxygen, nitrogen, sulfur, chlorine, and/or bromine atoms, a total of 412 entries. The coordination number of zinc in each crystal structure was determined. The percentages of the various ligands for each coordination number are listed in Table 1 and shown in Figure 1 where the corresponding results for magnesium are also included for comparison. There is, in the CSD, only one crystal structure with a three-coordinate zinc ion (refcode SEJZEM[30]), shown in deposited Figure A. One crystal structure that may be considered to have an octacoordinate zinc ion (refcode PASNZN[31]), illustrated in deposited Figure B, is probably (as also noted by the authors) four-coordinate and is so considered here. The general disposition of ligands is indicated in Table 2 with more details in deposited Tables 2S to 5S for which the journal references are given in deposited Table 6S. Approximately 76% of the crystal structures containing divalent zinc have either coordination number 4 or coordina-

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Figure 1. The percentages of various ligands (left to right in each coordination number grouping: N, O, S, Cl, Br) bound to (a) Zn^{2+} and (b) Mg^{2+} in crystal structures extracted from the CSD.

tion number 6, while most (95%) have coordination numbers 4, 5, or 6. Those with coordination number 4 are nearly twice

Table 2. Metal Coordination in Crystal Structures Containing $Zn^{2+} \cdots M$ (M = N, O, S, Cl, Br) in the CSD[a]

Coordination Number 4

4Cl(40)	4N(27)	4S(20)	4O(17)	4Br(3)					
3Cl 1N(6)	3S1N(3)	3N1O(2)	3O1N(3)	3Cl1O(3)	3S1O(2)	3N1Br(1)	3N1Cl(1)	3Br1N(1)	3S1Cl(1)
2N2Cl(20)	2N2S(14)	2N2O(13)	2O2Cl(11)	2N2Br(7)	2S2Cl(6)	2O2Br(3)	2Cl1N1O(3)	2O2S(1)	2O1Cl1N(1) 2Cl1N1S(1)

Coordination Number 5

5N(19)	5O(6)	5S(3)			
4N1O(12)	4N1Cl(7)	4O1N(2)	4N1Br(1)	4S1N(1)	4O1Cl(1)
3N2O(6)	3O2N(5)	3N2Cl(3)	3O2S(2)	3O1N1Cl(2)	3N2Br(1) 3N2S(1) 3O1N1S(1)
2N1Cl1S(1)	2N2Cl1O(1)	2S2Br1N(1)			

Coordination Number 6

6O (42)	6N (21)	6S (2)	
5O1N(2)	5N1O(1)	5N1Cl(1)	5O1S(1)
4O2N(30)	4N2O(13)	4S2N(1)	4O1N1Cl(1)

Coordination Number 7

7O(2)	
6O1Cl(1)	6O1N(1)
5N2O(1)	5O2N(1)
4O3N(2)	
3N2O2S(2)	

[a] Listed are the ligand atoms around one zinc ion and, in parentheses, the number of individual crystal structures in which these are found. Individual refcodes of the CSD entries and their journal references are given in Deposited Tables 2S to 6S.

Table 3. Average $O-Zn-O$ Bond Angles (in deg) as a Function of Coordination Number for Crystal Structures in the CSD

	coordination number			
	4	5	6	7
av $O-Zn-O$ angle	109.0	93.1	90.6	85.0
standard dev	2.2	8.4	0.9	2.0
av mo values (RHF level)	109.6	100.1	90.0	

as common as those with 6 and, as found for many other cations,[32] a coordination number of 5 is less common.

A. Crystal Structures with Four-Coordinate Zinc Ions. A total of 211 crystal structures were found in the CSD in which a divalent zinc cation has a coordination number of 4, representing approximately 50% of all the zinc-containing crystal structures used in the present study. Chlorine (e.g. as the $ZnCl_4^{2-}$ anion) and nitrogen are the most common ligands found in these four-coordinate zinc structures, as seen in Table 1. Other important ligands are sulfur and oxygen. In deposited Table 2S the refcodes are given for the various combinations of ligands that are bound to zinc with a coordination number of four.

Seven of the four-coordinate zinc ion crystal structures were found to contain coordinating water molecules; six contain two water molecules and one contains a single water molecule. Interestingly, magnesium, by contrast, shows no four-coordinate compounds in the CSD that contain any coordinating water molecule. In 65 (30%) of the crystal structures containing four-coordinate zinc, at least one nitrogen atom is part of a ring structure bound to the zinc ion; this is in line with the finding that in proteins zinc ions often bind one of the ring nitrogen atoms of histidine. The percentage of structures containing oxygen as a ligand to four-coordinate zinc (17%) is less than half of that for four-coordinate magnesium (39%).

B. Crystal Structures with Five-Coordinate Zinc Ions. Of the 76 pentacoordinate divalent zinc complexes listed in deposited Table 3S, 19 have five nitrogen atoms bound to the metal ion, and 16 contain porphyrin-like polycyclic ring systems, each with four bonds to the metal ion and one additional axially bound group which is either water, chloride, pyridine, nitrogen, methanol, perchlorate, methylimidazole, or N-methylpyrrolidin-2-one. Thus 46% of the entries have four or five nitrogen atoms

bound to the zinc. Examples of five-coordinate zinc complexes (KIMPAX and MPZHZN[33,34]) are shown in deposited Figure C.

**C. Crystal Structures with Six- and Seven-Coordinate Zinc Ions.** There are 117 crystal structures, listed in deposited Table 4S, where the divalent zinc cation has a coordination number of 6. Of these, only three crystal structures (4% of the total) contain a hexaaquated zinc ion. This is in contrast to the situation for hexacoordinate magnesium compounds where 25% of oxygen-bound compounds are hexaaquated, compared with 4% for zinc. As expected, because chlorine and sulfur are so much larger than oxygen or nitrogen atoms, there are very few entries in the CSD with chlorine or sulfur atoms around hexacoordinate zinc ions. The coordination of nitrogen atoms is more common at coordination number 5, while that of oxygen atoms is more common at coordination number 6.

Many of the crystal structures in which the zinc has a coordination number of 7, listed in deposited Table 5S, are crown ether complexes or their analogues. The overall proportion of each heptacoordinate structure is about the same as that found in magnesium complexes.

D. Variation in Coordination Number. The geometries of the coordination spheres of zinc and magnesium in their complexes were investigated in the wide variety of crystal structure determinations listed in the CSD. Since most of the crystal structures in this database were studied for a variety of different reasons, it seems reasonable to study the statistics of the results with respect to the coordination number and the nature of the liganding atoms. In our study of divalent magnesium coordination[7] it was shown that approximately 79% of the crystal structures of magnesium complexes in the CSD have a coordination number of six, and in 82% of these structures the liganding species are oxygen atoms. An analysis of the 5- and 7-coordinate magnesium-containing structures in the CSD showed that these were primarily porphyrins and crown ether complexes, in which the geometries are forced by the nature of the complexing agent, and only 9% of the magnesium-containing structures have a coordination number of 4. Thus, divalent magnesium ions apparently prefer all, or almost all, oxygen atoms in an octahedral coordination polyhedra. On the

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3758   *J. Am. Chem. Soc., Vol. 117, No. 13, 1995*

Bock et al.

(a)

(b)

(c)

(d)

(e)

(f)

(g)
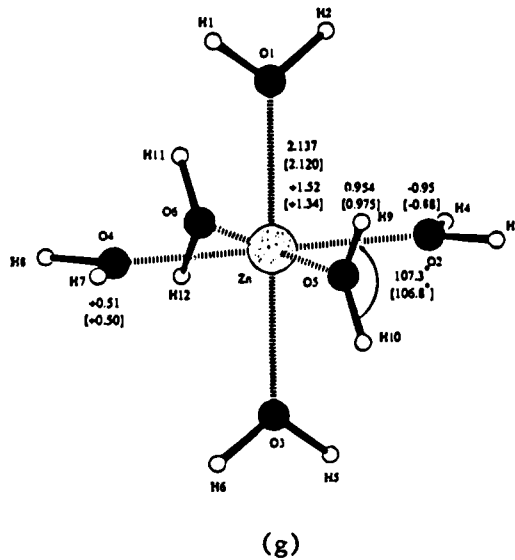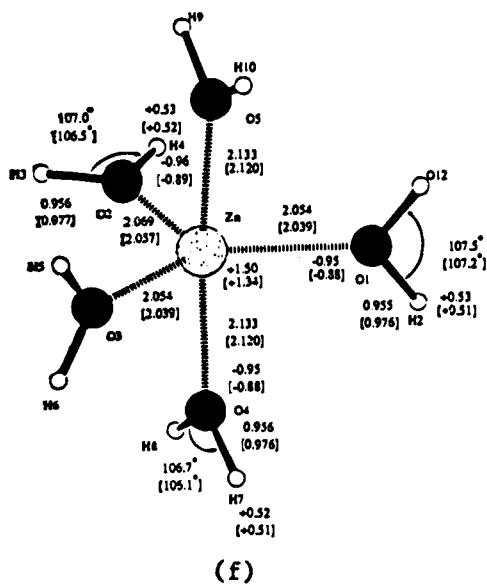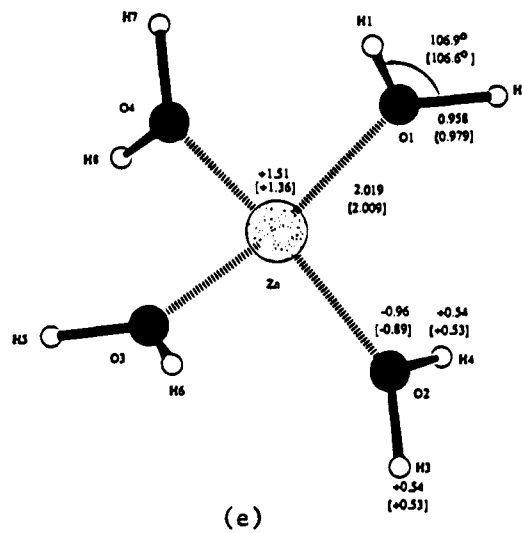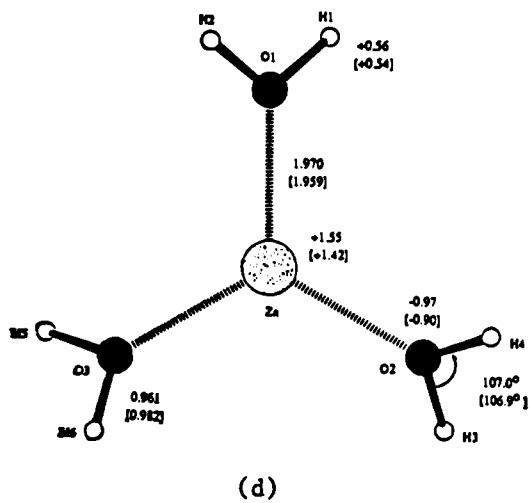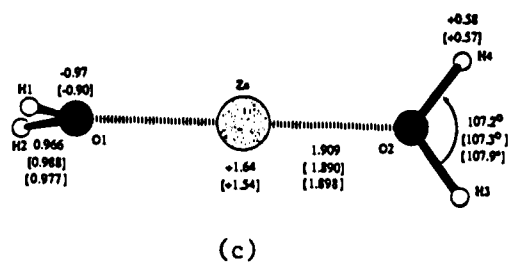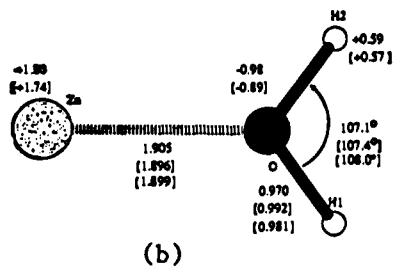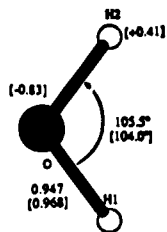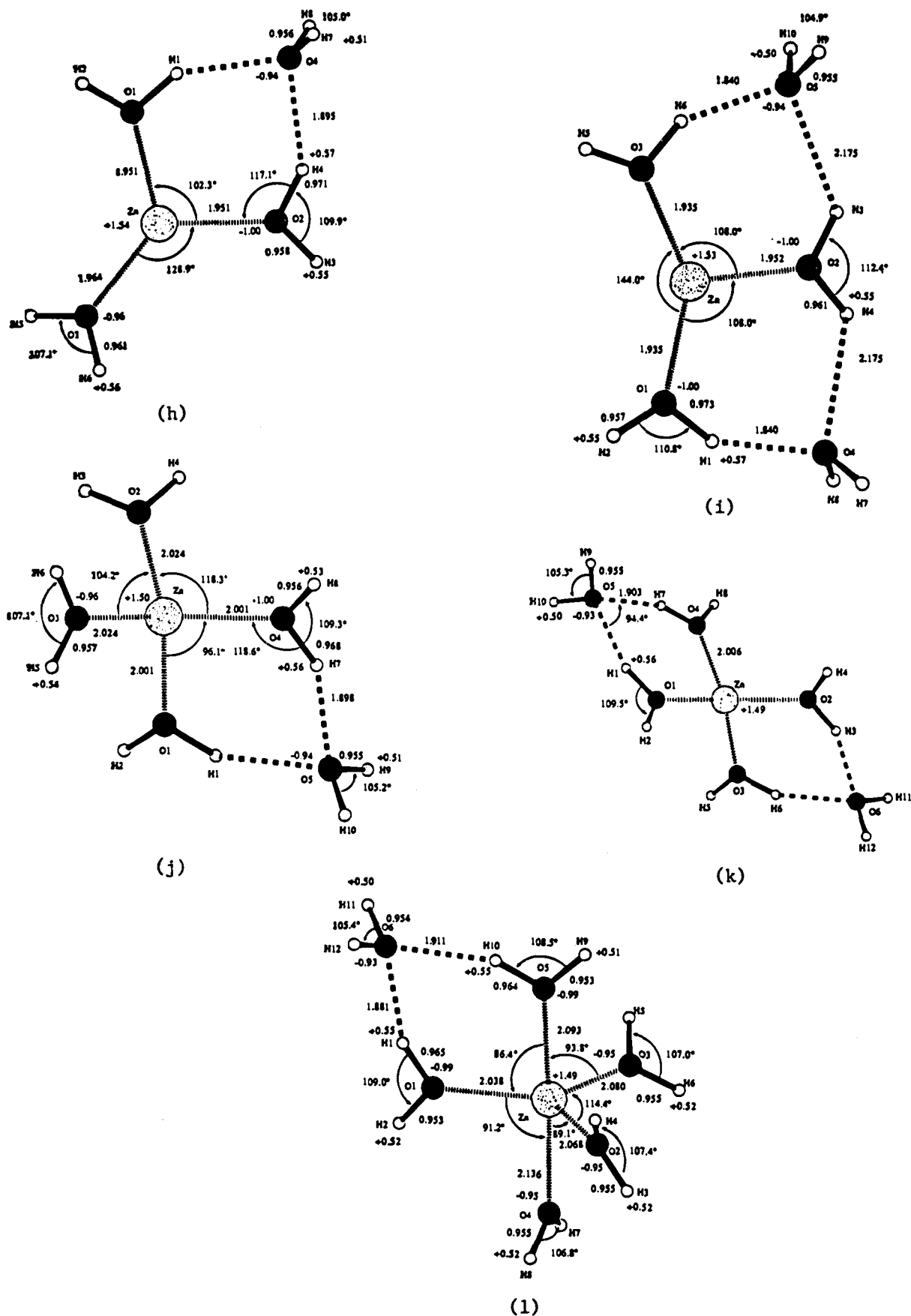
Figure 2. Molecular geometries from *ab initio* molecular orbital calculations: (a) H₂O, (b) Zn[H₂O]²⁺, (c) Zn[H₂O]₂²⁺, (d) Zn[H₂O]₃²⁺, (e) Zn[H₂O]₄²⁺, (f) Zn[H₂O]₅²⁺, (g) Zn[H₂O]₆²⁺, (h) Zn[H₂O]₃²⁺·H₂O, (i) Zn[H₂O]₃²⁺·2H₂O, (j) Zn[H₂O]₄²⁺·H₂O, (k) Zn[H₂O]₄²⁺·2H₂O, and (l) Zn[H₂O]₅²⁺·H₂O. Shown in these diagrams are bond lengths (Å), bond angles (deg), and Mulliken charges (electron units). Values without brackets are at the RHF/HUZSP*//RHF/HUZSP* level, with square brackets are at the MP2(FC)/HUZSP*//MP2(FC)/HUZSP* level, and with curly brackets are at the MP2(FULL) level using a ⟨5,3,3,1,1,1/5,3,*,*/3,1,1⟩ basis set on zinc and using the 6-31G** basis set for oxygen and hydrogen, see the text.

Table 4. Total Molecular Energies (au) and Zero-Point Vibrational Energies (kcal/mol) of Hydrated Zinc Cations

structure	RHF//RHF^a (ZPE)^b	MP2//RHF (FC)	MP2//RHF (FC)	MP4SDQ//RHF (FC)	MP4SDTQ//RHF (FC)	MP2//MP2 (FC)
Zn[H$_2$O]$^{2+}$	−1852.610958 (16.22)	−1852.946085	−1852.924758	−1852.941928	−1852.952901	−1852.946960
Zn[H$_2$O]$_2^{2+}$	−1928.752798 (32.91)	−1929.283705	−1929.265095	−1929.286998	−1929.300963	−1929.285527
Zn[H$_2$O]$_3^{2+}$	−2004.859922 (49.75)	−2005.580700	−2005.567163	−2005.591860	−2005.608109	−2005.583178
Zn[H$_2$O]$_4^{2+}$	−2080.947968 (66.37)	−2081.858124	−2081.850060	−2081.877328		−2081.861386
Zn[H$_2$O]$_5^{2+}$	−2157.009398 (83.42)	−2158.108704	−2158.106335	−2158.135850		−2158.112924
Zn[H$_2$O]$_6^{2+}$	−2233.066732 (100.09)	−2234.355145	−2234.358726	−2234.390306		−2234.360341
Zn[H$_2$O]$_3^{2+}$[H$_2$O]	−2080.920870 (67.67)	−2081.834930				
Zn[H$_2$O]$_4^{2+}$[H$_2$O]	−2157.004800 (84.33)	−2158.107690				
Zn[H$_2$O]$_5^{2+}$[H$_2$O]	−2233.063393 (100.95)	−2234.354803				
Zn[H$_2$O]$_3^{2+}$[H$_2$O]$_2$	−2156.976624 (85.08)	−2158.082115				
Zn[H$_2$O]$_4^{2+}$[H$_2$O]$_2$	−2233.060320 (102.16)	−2234.355364				
Zn^{2+}	−1776.455266	−1776.593945	−1776.570446	−1776.582877	−1776.590961	−1776.593945
H$_2$O	−76.010746 (14.42)	−76.195960	−76.201969	−76.204626	−76.206358	−76.196848

^{a} RHF//RHF = RHF/HUZSP*//RHF/HUZSP*; MP4SDQ//RHF = MP4SDQ(FC)/HUZSP*//RHF/HUZSP*; MP2//RHF = MP2(FC)/HUZSP*//RHF/HUZSP*; MP4SDTQ//RHF = MP4SDTQ(FC)/HUZSP*//RHF/HUZSP*; MP3//RHF = MP3(FC)/HUZSP*//RHF/HUZSP*; MP2//MP2 = MP2(FC)/HUZSP*//MP2(FC)/HUZSP*.

Table 5. Hydration Energies (kcal/mol)

n	m	RHF//RHF^a	MP2//RHF (FC)	MP3//RHF (FC)	MP4SDQ//RHF (FC)	MP4SDTQ//RHF (FC)	MP2//MP2 (FC)
			(A) Reaction Energies^b for Zn[H$_2$O]$_n^{2+}$ + H$_2$O → Zn[H$_2$O]$_{n+1}^{2+}$				
0		−89.16	−96.20	−93.80	−95.10	−96.83	−96.20
1		−79.99	−86.65	−84.56	−85.86	−86.65	−86.66
2		−58.06	−60.98	−60.39	−66.48	−60.83	−60.83
3		−46.31	−48.92	−48.58	−48.53		−48.85
4		−29.17	−31.64	−31.45	−31.18		−31.69
5		−26.98	−29.43	−29.39	−29.01		−29.48
			(B) Reaction Energies^b for Zn[H$_2$O]$_n^{2+}$[H$_2$O]$_m$ + H$_2$O → Zn[H$_2$O]$_n^{2+}$[H$_2$O]$_{m+1}$				
3	0	−28.00	−33.07				
3	1	−25.25	−28.88				
3	2						
4	0	−25.38	−30.10				
4	1						
5	0	−24.03	−28.35				

^{a} See footnote to Table 4. ^{b} Corrected for differences in zero-point energies.

other hand, the CSD entries for divalent zinc complexes show a more variable coordination number, see Table 1, although most of the entries with O, N, Cl, Br, or S in the coordination sphere are primarily either tetra- or hexacoordinate.

The geometry of the coordination sphere was investigated to establish its flexibility in this variety of crystal structure determinations. Since all angles in a regular octahedron are 90°, we examined the average values of Zn^{2+} ··· O distance and O ··· Zn^{2+} ··· O angles for various coordination numbers. The results are given in Table 3. Note that the average O ··· Zn^{2+} ··· O angle for coordination number four is very close to the expected value for a perfect tetrahedron, which is 109.5°. By contrast, the O ··· Mg^{2+} ··· O angle for coordination number 4 is only 103.1°, suggesting that magnesium complexes with coordination number 4 are rearranged from an angle of 109.5° to a value somewhat nearer to the regular octahedral value of 90°.

An analysis of 4-, 5-, 6-, and 7-coordinate zinc complexes in the CSD showed that the predominate liganding species was dependent upon the coordination number of the zinc in the complex. This was not the case for magnesium. Magnesium was primarily bound to oxygen regardless of its coordination number, except in the case of a coordination number of 5 when nitrogen was preferred to oxygen. In magnesium complexes of porphyrin derivatives the magnesium ion was coordinated to four nitrogen atoms in the ligand, with a single oxygen-containing ligand (usually water) in the one axial position. Zinc, however, does not show a preference for porphyrin derivatives.

II. Molecular Orbital Studies. Diagrams of the results of RHF/HUZSP*//RHF/HUZSP* and, where available, the MP2-(FC)/HUZSP*//MP2(FC)/HUZSP* *ab initio* molecular orbital

calculations of the structures of divalent zinc cations surrounded by up to six water molecules partitioned between the first and second coordination shells are shown in deposited Chart 1. Complete details of the geometries can be found in Figure 2 and deposited Table 7S of the supplementary material. Total molecular energies of all the structures in Figure 2 are given in Table 4 at a variety of computational levels. All of the structures in Figure 2 have been verified to be local minima on their respective potential energy surfaces by frequency analyses at the RHF/HUZSP*//RHF/HUZSP* level. The energetics of various processes in which zinc ions are hydrated are summarized in Table 5 and compared with the corresponding results for magnesium and beryllium ions in Table 6.

Since no direct experimental data are available for the individual species of hydrated Zn^{2+} ions under consideration, it is important to establish the degree to which RHF/HUZSP* and MP2(FC)/HUZSP* level calculations adequately describe such structures. Thus, in the case of Zn[H$_2$O]$_n^{2+}$ ($n = 1, 2$), we carried out MP2 optimizations with all the orbitals active, i.e. MP2(FULL) optimizations, using a less contracted basis set for zinc which includes two p-type polarization functions, e.g. ⟨5,3,3,1,1,1/5,3,*,*/3,1,1⟩; a p-type polarization function was also added to the hydrogen atom basis set. The optimized geometries at this level are also shown in Figure 2. While there are some small differences in the calculated bond lengths and angles, the *changes* in these geometrical parameters as a function of the computational level as one proceeds from Zn[H$_2$O]$^{2+}$ to Zn-[H$_2$O]$_2^{2+}$ are generally consistent with each other, particularly if correlation effects are included in the optimization.

A. Zn[H$_2$O]$_n^{2+}$ ($n = 1−6$). We consider first hydrated divalent zinc ions with water only in the inner coordination shell.

Hydration of Zinc Ions

J. Am. Chem. Soc., Vol. 117, No. 13, 1995 3761

Table 6. Comparison of the Computed Hydration Energies for Be^{2+}, Mg^{2+}, and Zn^{2+}

$$M[H_2O]_n^{2+} + H_2O \rightarrow M[H_2O]_{n+1}^{2+}$$

	M		
n	Be^b	Mg^b	Zn^c
0	−148.67	−84.81	−95.10
1	−123.36	−76.58	−85.86
2	−82.86	−63.16	−60.48
3	−54.70	−52.16	−48.53
4		−35.41	−31.18
5		−32.92	−29.01

[a] Corrected for zero-point vibrational energy differences. [b] Calculated at the MP4SDQ(FC)/6-31G*//RHF/6-31G* computational level. [c] Calculated at the MP4SDQ(FC)/HUZSP*//RHF/HUZSP* computational level.
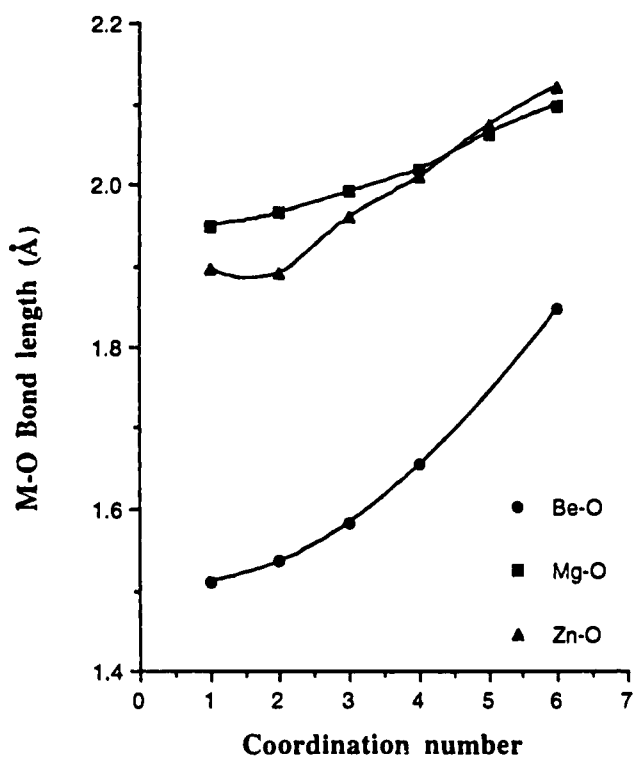

Figure 3. Variation of M···O bond length with coordination number $(M = Be^{2+}, Mg^{2+}, Zn^{2+})$.

Stable structures, as verified by frequency analyses, were found for $Zn[H_2O]_n^{2+}$ with $n = 1-6$ as shown in Figure 2b−g. A partial RHF optimization of the hexahydrated divalent zinc ion, in which the geometries of the water molecules were all held fixed, was reported previously by Stromberg and co-workers,[35] who found the Zn−O distance to be 2.12 Å, in reasonable agreement with our results. Garmer and Krauss,[36] using effective core potential RHF calculations to optimize the structure of $Zn[H_2O]_6^{2+}$, found the Zn−O distance to be 2.14 Å. Marcos et al.[37] at the RHF/3-21G*//RHF/3-21G* level found the Zn−O distance to be somewhat shorter, 2.050 Å, and that embedding $Zn[H_2O]_6^{2+}$ in a solvent reaction field to simulate a water continuum lengthens the Zn−O distance ∼0.02 Å. Kitchen and Allen[11] used effective core potentials to investigate a number of zinc complexes of chemical and biological

(35) Stromberg, D.; Sandstrom, M.; Wahlgren, U. *Chem. Phys. Lett.* **1990**, *172*, 49−54.

(36) Garmer, D. R.; Krauss, M. *J. Am. Chem. Soc.* **1992**, *114*, 6487−6493.

(37) Marcos, E. S.; Pappalardo, R. R.; Rinaldi, D. *J. Chem. Phys.* **1991**, *95*, 8928−8932.
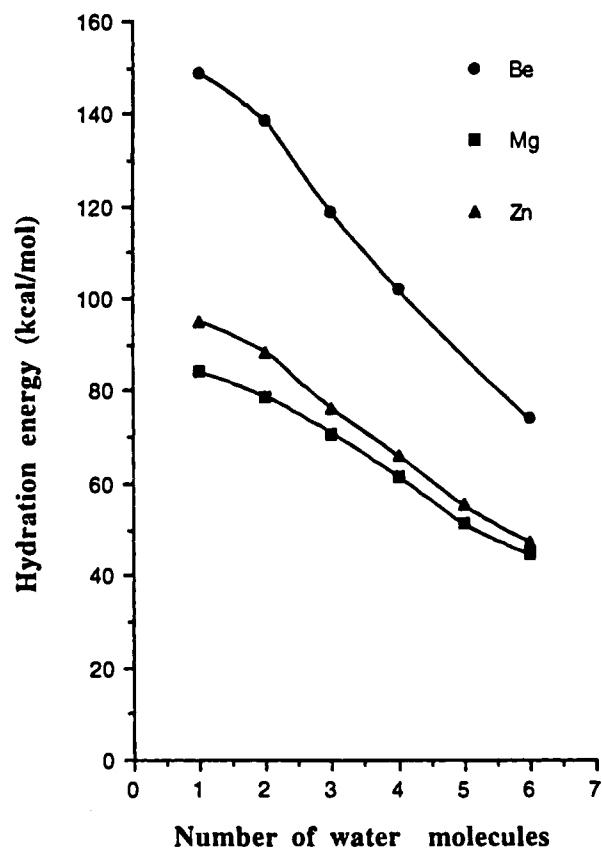
Figure 4. The hydration energy (kcal/mol) per water molecule (defined in eq 2) for Be^{2+}, Mg^{2+}, and Zn^{2+}.
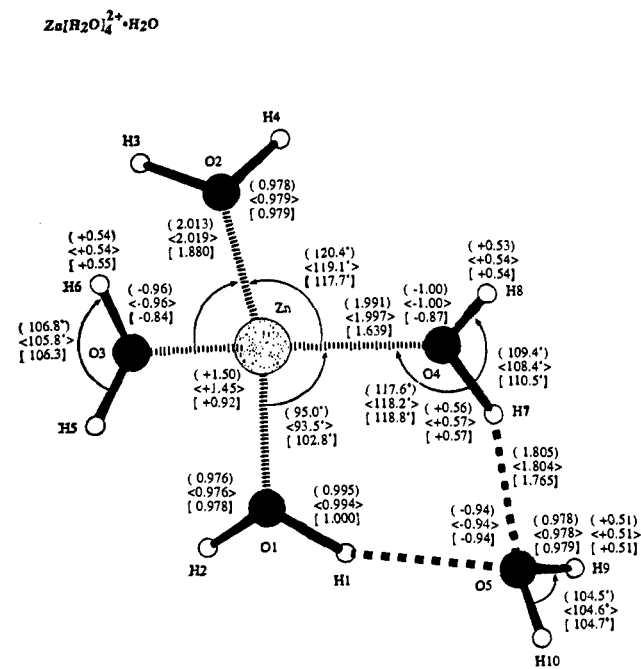
significance, including $Zn[H_2O]^{2+}$ and $Zn[H_2O]_6^{2+}$, where the Zn−O distances were found to be 1.901 and 2.10 Å, respectively. Earlier pseudopotential calculations on $Zn[H_2O]_n^{2+}$ ($n = 1, 2, 4, 6$) were performed by Pullman and Demoulin,[13] who found Zn−O distances of 1.90, 1.91, 1.98, and 2.10 Å, respectively. The average Zn−O distance for structures in the CSD in which a zinc ion is surrounded by six water molecules is approximately 2.09 Å. These $Zn[H_2O]_n^{2+}$ ($n = 1-6$) structures are all analogous to the corresponding structures found for $Mg[H_2O]_n^{2+}$ and $Be[H_2O]_n^{2+}$, except that no stable structure for $Be[H_2O]_5^{2+}$ was found. Several attempts to find a local minimum with seven water molecules in the inner coordination shell, $Zn[H_2O]_7^{2+}$, were not successful for either Zn^{2+} or Mg^{2+} at the RHF/HUZSP*//RHF/HUZSP* level. The optimizations invariably led to structures with at least one water molecule in the second coordination shell.

In Figure 3 we compare the bond lengths between the metal ions and oxygen atoms in $M[H_2O]_n^{2+}$ ($n = 1-6$) for M = Be, Mg, and Zn. In general, as n increases, the M−O bond lengths increase. In going from $Zn[H_2O]^{2+}$ to $Zn[H_2O]_2^{2+}$, however, the Zn−O bond length actually decreases slightly when correlation effects are included in the optimization. It is interesting to note that for $n = 1-4$ the Zn−O distances are shorter than the corresponding Mg−O distances, despite the fact that the ionic radius of Zn^{2+} is larger than that of Mg^{2+}. For $n = 6$, however, the Zn−O distance has increased to 2.12 Å and is more than 0.02 Å larger than the corresponding Mg−O distance. Clearly, Zn^{2+}−O distances increase far more rapidly than Mg^{2+}−O distances in $M[H_2O]_n^{2+}$ as the number of water molecules in the first coordination shell increases, see Figure 3, and Be^{2+}−O distances increase even more rapidly.
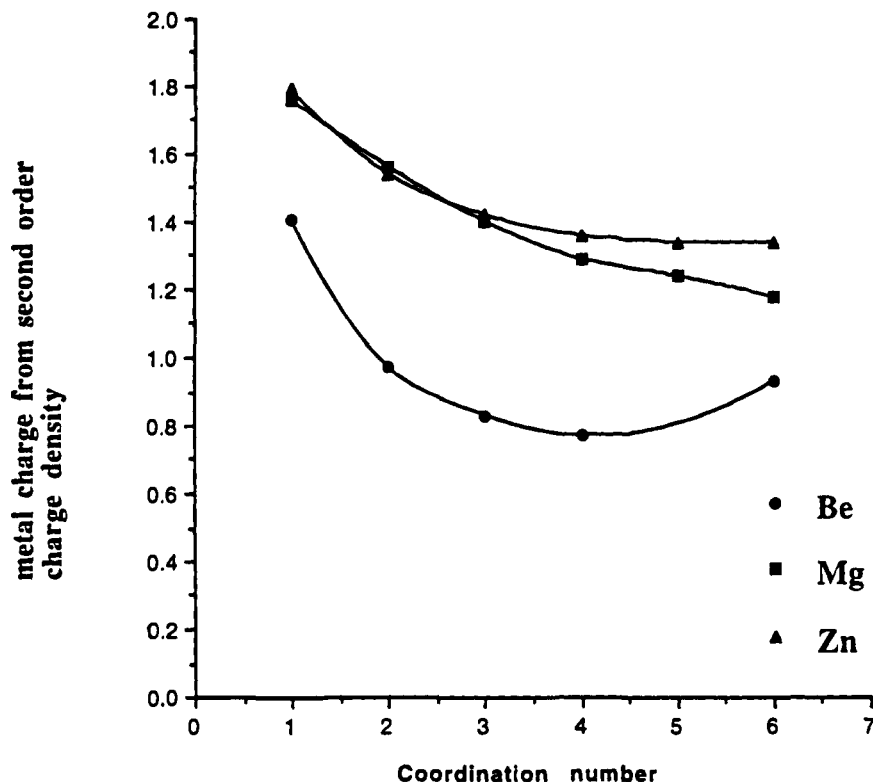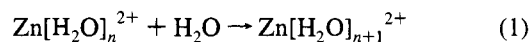
Figure 5. Net charge on metal cation (M) in the structures $M[H_2O]_n^{2+}$ (M = Be, Mg, Zn; n = 1–6) computed from the MP2/6-31G*//MP2/6-31G* charge density for Be and Mg and from the MP2/HUZSP* charge density for Zn.

Figure 6. Comparison of the calculated geometries of $Zn[H_2O]_4^{2+}$: ( ) for Zn, ⟨⟩ for Mg, and [ ] for Be. Bond lengths are computed at the MP2//MP2 level and charges at the RHF//RHF level.

The change in energy, ΔE, for the hydration reactions

$$Zn[H_2O]_n^{2+} + H_2O \rightarrow Zn[H_2O]_{n+1}^{2+} \qquad (1)$$

for n = 0–5 is given in Table 5 at a variety of computational levels and compared with the corresponding results for magnesium and beryllium in Table 6 and deposited Figure D. As can be seen from Table 5, once correlation effects are included in the calculations at the MP2 computational level, there is

relatively little difference in the hydration energies as higher-order perturbation corrections are included in the calculations. This is consistent with what was observed for the corresponding beryllium and magnesium reactions. As shown in deposited Figure D, as n increases the hydration reactions become less exothermic for all three metal ions. For n = 0 and 1, the zinc ion hydrations are approximately 10 kcal/mol *more* exothermic than the corresponding magnesium reactions,[7] but significantly less exothermic than the beryllium reactions.[8] For the larger n values, however, the hydration energies are actually a few kcal/mol *less* exothermic for zinc than for magnesium. Thus, for example, it is thermodynamically more favorable for $Mg[H_2O]_4^{2+}$ or $Mg[H_2O]_5^{2+}$ to gain additional water molecules in the first coordination shell than it is for the corresponding Zn complexes.

The hydration energy per water molecule,

$$E_{per} = \frac{[E(Zn^{2+}) + nE(H_2O) - E(Zn[H_2O]_n^{2+})]}{n} \qquad (2)$$

is plotted in Figure 4, where it is compared with the corresponding values of E_{per} for beryllium and magnesium. In all cases E_{per} decreases as the value of n increases; the rate of decrease is largest for beryllium and lowest for magnesium.

In Figure 5, the net charge on the zinc atom in $Zn[H_2O]_n^{2+}$ (n = 1–6), calculated from the generalized density at the MP2-(FC)/HUZSP*//MP2(FC)/HUZSP* level, is plotted as a function of the hydration number and compared to the analogous data for Be^{2+} and Mg^{2+}, using the 6-31G* basis set. It is clear that a significant amount of charge is transferred to the central metal atom for all the hydrates $M[H_2O]_n^{2+}$ (M = Be, Mg, and Zn), suggesting that the interaction of M^{2+} with water is not entirely electrostatic in nature but that dative bonds are formed using the lone pair of electrons on the oxygen atoms.[26] The maximum charge transferred to the beryllium ion from the surrounding water occurs for coordination number 4, whereas the charge transferred from the water to the magnesium ion increases
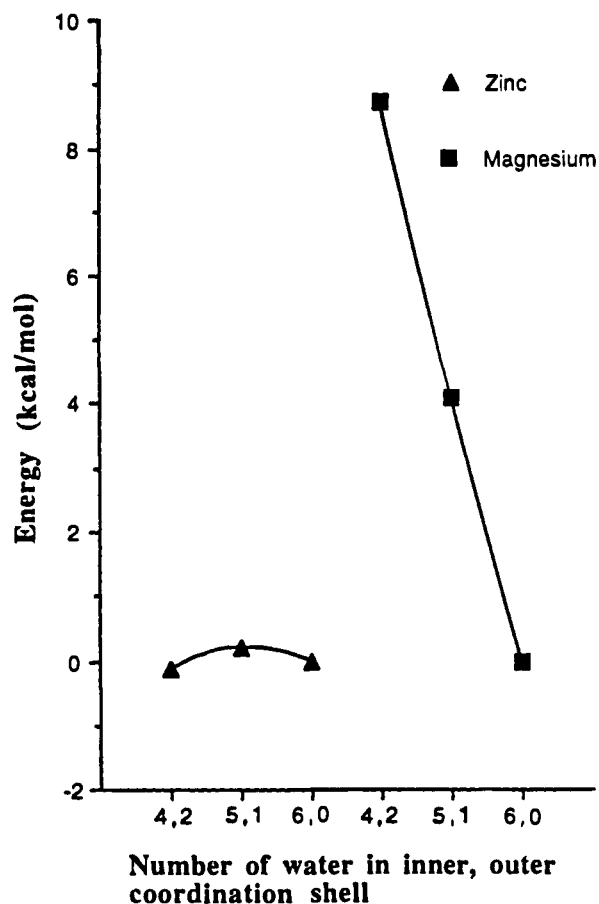
Hydration of Zinc Ions

J. Am. Chem. Soc., Vol. 117, No. 13, 1995 3763

Figure 7. Energies of $M[H_2O]_4^{2+}\cdot 2H_2O$, $M[H_2O]_5^{2+}\cdot H_2O$, and $M[H_2O]_6^{2+}$ (listed as 4,2; 5,1; and 6,0 respectively) for $M = Zn$ (left) and $M = Mg$ (right). Energies are listed relative to 0.0 kcal/mol for both $Zn[H_2O]_6^{2+}$ and $Mg[H_2O]_6^{2+}$.

monotonically from coordination numbers 1−6, and no magnesium complex with 7 waters in the inner shell was found. Although the charge transferred to the zinc ion is a maximum at coordination number 5, it is nearly the same for coordination numbers 4, 5, and 6. Interestingly, all the structures in the CSD which involved beryllium bonded to oxygen had coordination number 4, and of the 145 structures in the CSD in which magnesium was bonded to oxygen, 122 had coordination number 6. As shown in Table 1, however, there are a substantial number of entries in the CSD in which zinc ions are bound to 4, 5, and 6 oxygen atoms, suggesting a strong correlation between the maximum charge transferred and the preferred coordination number of the central metal ion.

B. $Zn[H_2O]_n^{2+}\cdot mH_2O$. Several structures of the form Zn-$[H_2O]_n^{2+}\cdot mH_2O$, with n water molecules in the first coordination shell and m water molecules in the second coordination shell, were found to be stable, see Figure 2. In all of these calculations no symmetry was imposed a priori to lessen the chance of optimizing to transition states.

$Zn[H_2O]_n^{2+}\cdot H_2O$ ($n = 3, 4, 5$). Stable structures were found with three, four, or five water molecules bound to zinc in the first coordination shell, and with a single water molecule in the second coordination shell (hydrogen bonded to two water molecules in the first shell), see Figure 2h,j,l. In the case of $Zn[H_2O]_3^{2+}\cdot H_2O$ and $Zn[H_2O]_4^{2+}\cdot H_2O$, symmetrical six-membered rings are formed, whereas for $Zn[H_2O]_5^{2+}\cdot H_2O$ the ring is not symmetrical.

In Figure 6, we compare the structures $M[H_2O]_4^{2+}\cdot H_2O$ for $M = Be, Mg,$ and Zn. Clearly, the geometrical parameters for the five water molecules are nearly identical in all three cases.

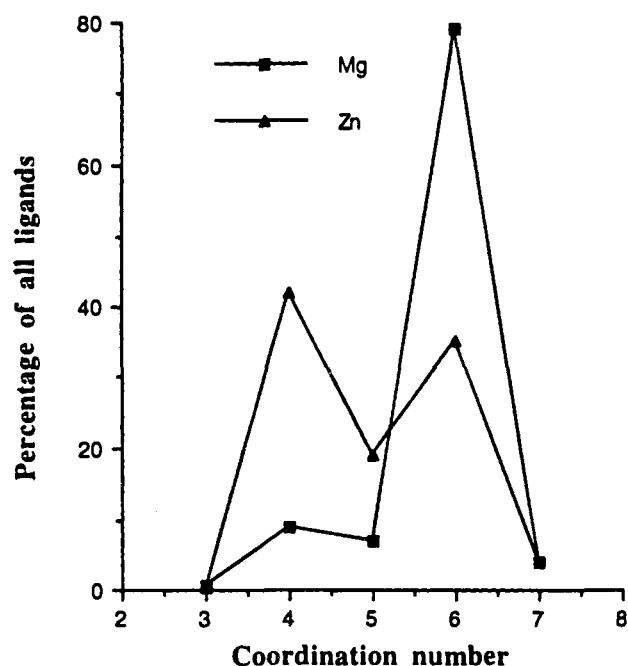**Figure 8.** Ligands of Mg^{2+} and Zn^{2+} in the CSD expressed as percentages of all entries for Zn^{2+} and Mg^{2+}. Note the different distribution for the two types of cations.

The hydrogen bonding of the water in the second coordination shell, however, is significantly stronger for beryllium as the central atom rather than for magnesium or zinc. It is interesting to note that all the structural parameters and charges are nearly the same for the Mg^{2+} and Zn^{2+} hydrates. This manifests itself energetically in that the water transfer reaction

$$Zn[H_2O]_4^{2+}\cdot H_2O + Mg[H_2O]_4^{2+} \rightarrow Zn[H_2O]_4^{2+} +$$

$$Mg[H_2O]_4^{2+}\cdot H_2O$$
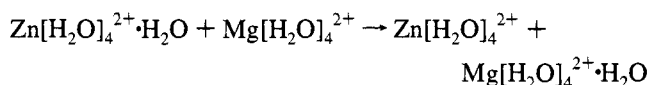
is calculated to be thermoneutral to within approximately 0.25 kcal/mol at the MP2//RHF computational level. The energies of $Zn[H_2O]_n^{2+}\cdot H_2O$, $n = 3, 4,$ and 5, are higher than the corresponding energies of $Zn[H_2O]_m^{2+}$, $m = 4, 5,$ and 6, by 14.6, 0.6, and 0.2 kcal/mol, respectively, at the MP2(FC)/HUZSP*//RHF/HUZSP* level. The corresponding values for the magnesium hydrates are significantly higher, 19.1, 5.3, and 4.1 kcal/mol at the MP2/6-31G*//RHF/6-31G* level. Thus for $Zn[H_2O]_5^{2+}$ and $Zn[H_2O]_6^{2+}$ a water molecule can quite readily be lost to the second coordination sphere giving $Zn[H_2O]_4^{2+}\cdot H_2O$ and $Zn[H_2O]_5^{2+}\cdot H_2O$, respectively.

$Zn[H_2O]_3^{2+}\cdot 2H_2O$ and $Zn[H_2O]_4^{2+}\cdot 2H_2O$. Structures with three or four water molecules in the first coordination shell and with two water molecules in the second coordination shell were also investigated, see Figures 2i and 2k. These structures were found to be stable with the two water molecules in the second coordination shell and with each hydrogen bonded to two water molecules in the first shell. The two six-membered rings so formed are identical but not symmetrical in the structure of Zn-$[H_2O]_3^{2+}\cdot 2H_2O$, see Figure 2i, while the two rings are identical and symmetrical in the structure of $Zn[H_2O]_4^{2+}\cdot 2H_2O$ shown in Figure 2k. $Zn[H_2O]_3^{2+}\cdot 2H_2O$ is 16.7 kcal/mol higher in energy than $Zn[H_2O]_6^{2+}$ at the MP2(FC)/HUZSP*//RHF/HUZSP* level, but $Zn[H_2O]_4^{2+}\cdot 2H_2O$ is actually 0.1 kcal/mol lower in energy than $Zn[H_2O]_6^{2+}$. $Be[H_2O]_4^{2+}\cdot 2H_2O$ is 27.7 kcal/mol lower in energy than $Be[H_2O]_6^{2+}$, while Mg-$[H_2O]_4^{2+}\cdot 2H_2O$ is 8.7 kcal/mol higher in energy than Mg-$[H_2O]_6^{2+}$.
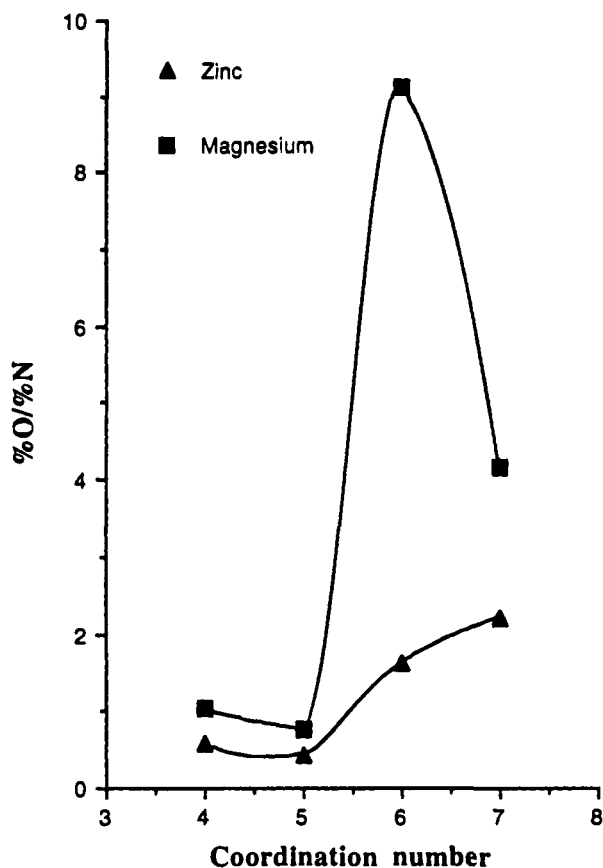
Figure 9. Values of the ratio of O to N coordination for Zn^{2+} and Mg^{2+} for various coordination numbers.

Finally, the energies of the structures $Zn[H_2O]_6^{2+}$, $Zn[H_2O]_5^{2+}\cdot H_2O$, and $Zn[H_2O]_4^{2+}\cdot 2H_2O$, in which divalent zinc ions are surrounded by six water molecules partitioned between the first and second coordination spheres, are compared at the MP2(FC)/HUZSP*//RHF/HUZSP* computational level (at 0 K). (The "tile" form of $Zn[H_2O]_3^{2+}\cdot 3H_2O$, which was a stable species in the case of beryllium,[8] proved to be a third-order transition state in the case of zinc.) The four-coordinate structure, $Zn[H_2O]_4^{2+}\cdot 2H_2O$, in which the zinc ion is in a tetrahedral environment, has the lowest total molecular energy of these three water complexes. The hexacoordinate structure, $Zn[H_2O]_6^{2+}$, in which the zinc is in an octahedral environment, however, is only 0.14 kcal/mol higher in energy, and the pentacoordinate structure, $Zn[H_2O]_5^{2+}\cdot H_2O$, is only 0.35 kcal/mol higher in energy than $Zn[H_2O]_4^{2+}\cdot 2H_2O$ (Figure 7). If thermal corrections, computed at the RHF/HUZSP*//RHF/HUZSP* level, are added to the MP2(FC)/HUZSP*//RHF/HUZSP* total molecular energies, $Zn[H_2O]_6^{2+}$ is 0.77 kcal/mol lower in energy than $Zn[H_2O]_5^{2+}\cdot H_2O$ and 0.93 kcal/mol lower in energy than $Zn[H_2O]_4^{2+}\cdot 2H_2O$. Thus, the energy differences remain small at 298 K, although the ordering of the structures is somewhat different. Clearly, there is a much smaller energy penalty for changing the local environment of the zinc ion than there is for changing the local environment of the magnesium ion.[7]

Discussion

The behavior of zinc and magnesium ions in the presence of water molecules is found to differ in several respects. First of all, studies of crystal structures in the CSD show that magnesium tends to form 6-coordinate structures, while zinc forms 4-, 5-, and 6-coordinate structures with approximately equal ease. This
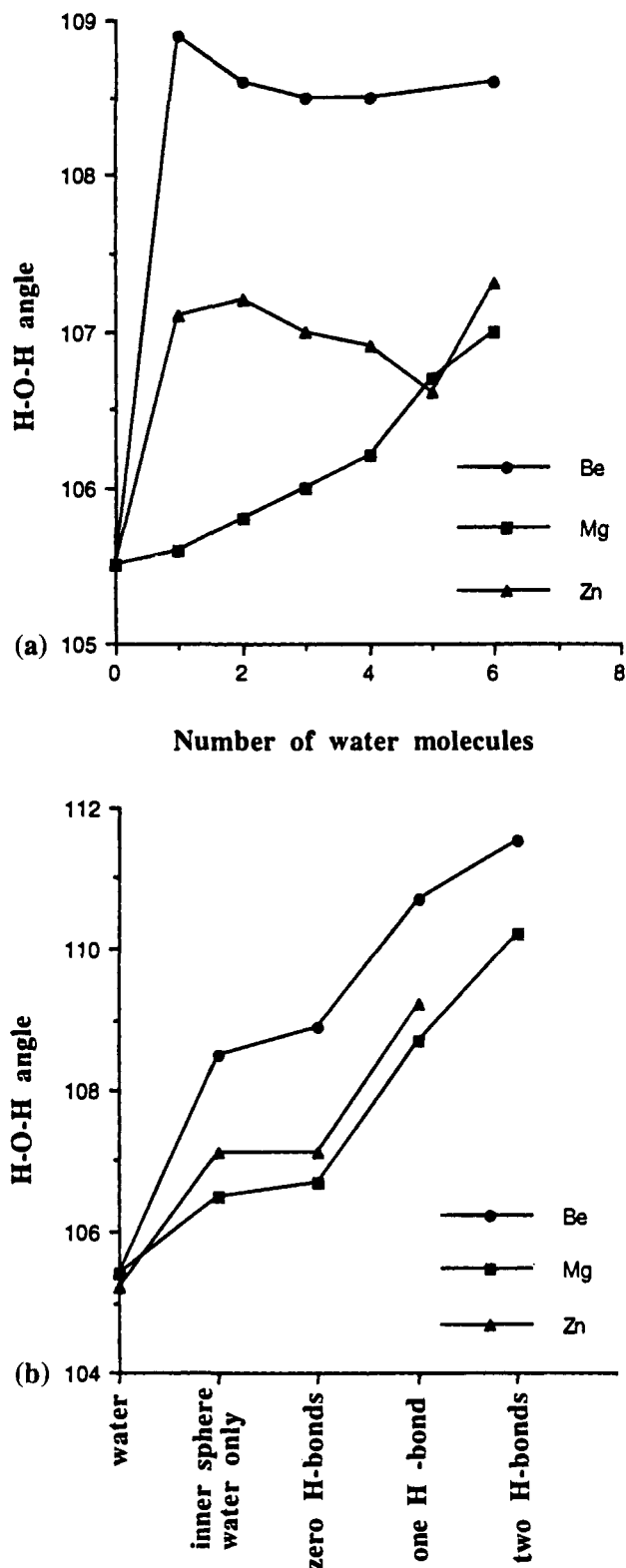
Figure 10. Effect of metal ions on water molecules: (a) The effect of metal ions M (M = Be^{2+}, Mg^{2+}, and Zn^{2+}) on the H—O—H angle of water in $M[H_2O]_n^{2+}$ as a function of the number of water molecules n. (b) The effect of further hydrogen bonding on water H—O—H angles in hydrates of Be^{2+}, Mg^{2+}, and Zn^{2+}.

result is seen in the liganding properties shown in Figure 8, where the percentages of each coordination type (see Figure 1) are shown. *Ab initio* molecular orbital studies show that the gas phase clusters $Zn[H_2O]_6^{2+}$, $Zn[H_2O]_5^{2+}\cdot H_2O$, and $Zn[H_2O]_4^{2+}\cdot H_2O$ differ in energy by less than 1 kcal/mol. The corresponding results for magnesium show that $Mg[H_2O]_6^{2+}$ is 8.7 and 4.1 kcal/mol lower in energy than $Mg[H_2O]_4^{2+}\cdot 2H_2O$

and $Mg[H_2O]_5^{2+} \cdot H_2O$, respectively. Thus, these calculations support the inference that the energy penalty for changing the immediate environment of Zn^{2+} is much less than that for changing the immediate environment of Mg^{2+}.

The types of atoms to which the metal prefers to bind in crystal structures listed in the CSD vary somewhat, as shown in Figure 9 for the binding of oxygen and nitrogen atoms. Zinc does not show the high peak at coordination number 6 seen for magnesium complexes. It is also seen in Table 1 that zinc binds sulfur at low coordination numbers as is well-known from its chemistry and is in accord with its description as "borderline soft" (while magnesium is "hard", that is, not readily deformable).

The effect of the metal ion on water molecules was also addressed. The extent of polarization of the water molecule was estimated by examining the H−O−H angle in water molecules that are bound directly to a beryllium, magnesium, or zinc cation. Neutron diffraction studies of some hydrates (in which hydrogen atoms are better located than in X-ray crystal structures) indicate that metal ions can affect the H−O−H angle and that different metal cations do so to different extents. An average H−O−H angle for divalent cations bound to water in some well-done neutron diffraction studies is 107.7° (Cu^{2+} 105.2−106.8°, Mn^{2+} 108.4−109.1°, Cd^{2+} 112.8°; references in deposited Table 8S). As seen in Figure 10a, the largest effect of a metal ion on water molecules in the *ab initio* molecular orbital calculations that we have carried out is seen for the beryllium ion which increases the H−O−H angle from 105.5° in isolated water molecules to about 108.5°, even when only one water molecule is bound. The H−O−H angle then stays fairly constant, independent of the coordination number. Zinc acts similarly and increases the H−O−H angle from 105.5° to about 107° and, again, the angle appears to be independent of coordination number. Magnesium, on the other hand, does not have much effect on water until several water molecules have bound and, by coordination number 6, its effect is similar to that of zinc. When the water molecules are further hydrogen bonded to others in the second coordination spheres and beyond, the angle is increased further as shown in Figure 10b, but the effect is similar for each ion, although still in the order that beryllium has the greatest effect and magnesium the least. Thus, while magnesium and zinc have similar effects at coordination number 6, the ability of zinc to form complexes of equal or lower energy in lower coordination states may be used to effect catalysis in enzyme systems.

These studies show that Zn^{2+} accommodates better than Mg^{2+} to different coordination numbers (4 to 6, versus 6 only for Mg^{2+}) and have provided a measure of the energy penalty for this variation in coordination number. They also show that Zn^{2+} and Mg^{2+} have different profiles for their effects on water molecules. The energetic cost of varying the inner coordination sphere of a metal ion must be taken into account, using the values derived here, in any consideration of mechanisms. We are now studying other cations to determine whether some more definitive rules can be derived.

Supplementary Material Available: Table 1S, a list of entries that were eliminated from the CSD search; Tables 2S−5S, Refcodes and metal coordination of crystal structures containing Zn^{2+}−N, Zn^{2+}−O, Zn^{2+}−S, Zn^{2+}−Cl, or Zn^{2+}−Br in the CSD for coordination numbers four through seven; Table 6S, journal references of articles; Table 7S. X, Y, and Z coordinates (Z-matrices orientation) of all *ab initio* molecular orbital structures described in the text; Chart 1, Molecular orbital calculations on selected hydrated structures of the form $Zn[H_2O]_n^{2+} \cdot mH_2O$; Figure A, three-coordinate zinc in SEJZEM; Figure B, four-coordinate zinc in PASNZN; Figure C, examples of five-coordinate Zn^{2+} complexes; Figure D, reaction energy of eq 1 for various values of n (56 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.