Organization of Water around a Beryllium Cation

Charles W. Bock

Department of Chemistry, Philadelphia College of Textiles and Science,
Philadelphia, Pennsylvania 19144, and American Research Institute, Suite 1212,
Upper Darby, Pennsylvania 19082

Jenny P. Glusker*

The Institute for Cancer Research, The Fox Chase Cancer Center, Philadelphia, Pennsylvania 19111

Ab initio molecular orbital calculations are used to examine the possible structures of hydrated Be^{2+} ions with up to six water molecules partitioned between the first and second coordination shells. The potential energy surfaces of $Be[H_2O]_4^{2+}$, $Be[H_2O]_5^{2+}$, and $Be[H_2O]_6^{2+}$ are found to have many local minima with different arrangements of the surrounding water molecules. In each of these cases, however, the lowest energy configuration has four water molecules in the first shell with any remaining water molecules relegated to the second shell, suggesting that the hydration number of Be^{2+} is indeed 4. We have further shown some energetic and geometrical details of how the second shell of water molecules is organized around the tetraaquated beryllium ion.

Introduction

The divalent beryllium cation with an ionic radius of only 0.34 Å has a very high charge-to-radius ratio of 6.0.[1] This cation is generally thought to have a coordination number of four although, in view of its high ionization enthalpy, there appears to be considerable covalent character in bonds to Be^{2+}.[1] The beryllium ion shows a strong tendency to form the aquo ion $[Be(H_2O)_4]^{2+}$ in acidic solution. The water molecules are more tightly bound than is normally found for such hydrated cations,[1] apparently the result of a significant transfer of charge from the surrounding water molecules to the Be^{2+} ion. The structure of hydrated beryllium cations and the energetics of the hydration process have been the subject of several recent ab initio molecular orbital studies.[2,3] At the RHF level, Hashimoto et al.[2] using the 3-21G and 3-21G* basis sets[4] and Probst et al.[3] using the Dunning double-zeta valence basis set[5] augmented by p-type polarization functions on the Be and H atoms and d-type polarization functions on O, have shown that stable structures of the form $Be[H_2O]_n^{2+}$ exist for $n = 1$–4. Hashimoto and co-workers[2] went on to show that a Be^{2+} cation surrounded by six equivalent water molecules with T_h symmetry is also stable, despite the small ionic radius of Be^{2+}. This result is consistent with the conclusions of an earlier molecular dynamics simulation by Yamaguchi et al.[6] on an aqueous $BeCl_2$ solution, in which six water molecules were found to bind to a beryllium cation in the first coordination shell. By contrast, the results of an X-ray diffraction study by Yamaguchi and co-workers,[6] also on an aqueous $BeCl_2$ solution, showed conclusively that only four water molecules coordinate directly to a Be^{2+} ion. This led Hashimoto and co-workers[2] to search for an alternative lower-energy structure for the organization of six water molecules surrounding a Be^{2+} ion. On the basis of a partial RHF/

3-21G optimization, these authors suggested that a stable structure exists with four water molecules in the first (inner) coordination shell and two water molecules in the second (outer) coordination shell, which is lower in energy than the stable configuration with six water molecules crowded into the first coordination shell.

The present paper uses ab initio molecular orbital calculations to examine further the geometries, relative energies and charge distributions of divalent beryllium ions hydrated with four, five or six water molecules which are partitioned between the inner and outer coordination shells (see Charts I and II). For comparison, we also provide the corresponding data for Be^{2+} ions hydrated with one to six water molecules all in the inner coordination shell. Our primary goal is to locate the lowest energy configurations for divalent beryllium cations surrounded by up to six water molecules. These calculations will provide valuable insight into the structure of the potential energy surfaces of these hydrates, specifically with regard to the possible ways in which water can organize around a beryllium cation.

Computational Methods

All calculations were carried out on the CRAY Y-MP computer at the National Cancer Institute, using the GAUSSIAN 90 series of programs.[7] RHF calculations with gradient optimizations were employed throughout using the 6-31G* basis set.[8] The effects of electron correlation were included by performing single-point Møller–Plesset (MP) perturbation calculations, in some cases up to the MP4SDTQ/6-31G*//RHF/6-31G* level.[9–11] Vibrational frequencies were obtained from analytical second derivatives calculated at the RHF/6-31G*//RHF/6-31G* level in order to verify that the computed structures were indeed stable states and not transition states,[12–14] and to correct reaction energies for zero point vibrational energy differences. Many of the structures were also reoptimized at the MP2/6-31G*//MP2/6-31G* level in order to assess

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience Publishers: New York, 1972.
(2) (a) Hashimoto, K.; Yoda, N.; Iwata, S. *Chem. Phys.* **1987**, *116*, 193. (b) Hashimoto, K.; Iwata, S. *J. Phys. Chem.* **1989**, *93*, 2165. (c) Hashimoto, K.; Yoda, N.; Osamura, Y.; Iwata, S. *J. Am. Chem. Soc.* **1990**, *112*, 7189.
(3) Probst, M. M.; Limtrakul, J. P.; Rode, B. M. *Chem. Phys. Lett.* **1986**, *132*, 370.
(4) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(5) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
(6) Yamaguchi, T.; Ohtaki, H.; Spohr, E.; Palinkas, G.; Heinzinger, K.; Probst, M. M. *Z. Naturforsch* **1969**, *41a*, 1175.

(7) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN90, *Revision F*. Gaussian Inc.: Pittsburgh, PA, 1990.
(8) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(9) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(10) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.
(11) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10S*, 1.
(12) McIver, J. W., Jr.; Kormornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.
(13) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1979**, *13*, 225.

Chart I

A

B

C

D

E

F

G

H

I
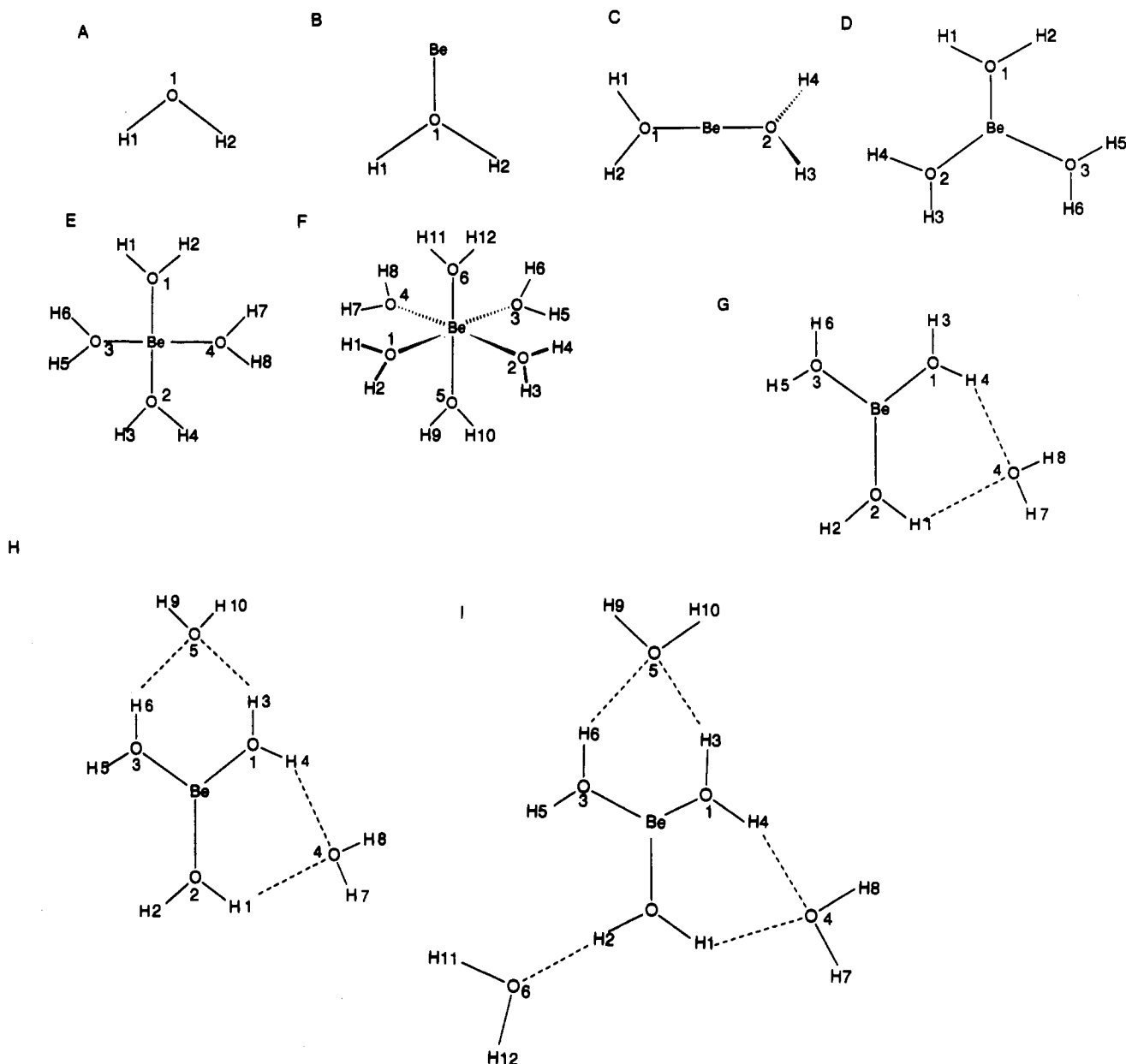
the effects of electron correlation on the geometrical parameters. For a few of the smaller hydrates, further optimizations were performed at both the RHF and MP2 levels, employing basis sets with multiple polarization functions, in order to test the sensitivity of the calculated geometries to the use of more complete basis sets. Finally, generalized second order densities were computed at the MP2/6-31G**//MP2/6-31G* level in order to study the transfer of charge in a few selected cases.[15]

Results and Discussion

The RHF/6-31G*//RHF/6-31G* and, where available, the MP2/6-31G*//MP2/6-31G* structures of divalent beryllium cations surrounded by up to six water molecules are shown in Figure 1, and complete details of the geometries can be found in Table 1S of the supplementary materials. The total molecular energies of the structures in Figure 1 at a variety of computational levels are given in Table I and Figure 2. All the structures in Figure 1 have been verified to be local minima by frequency
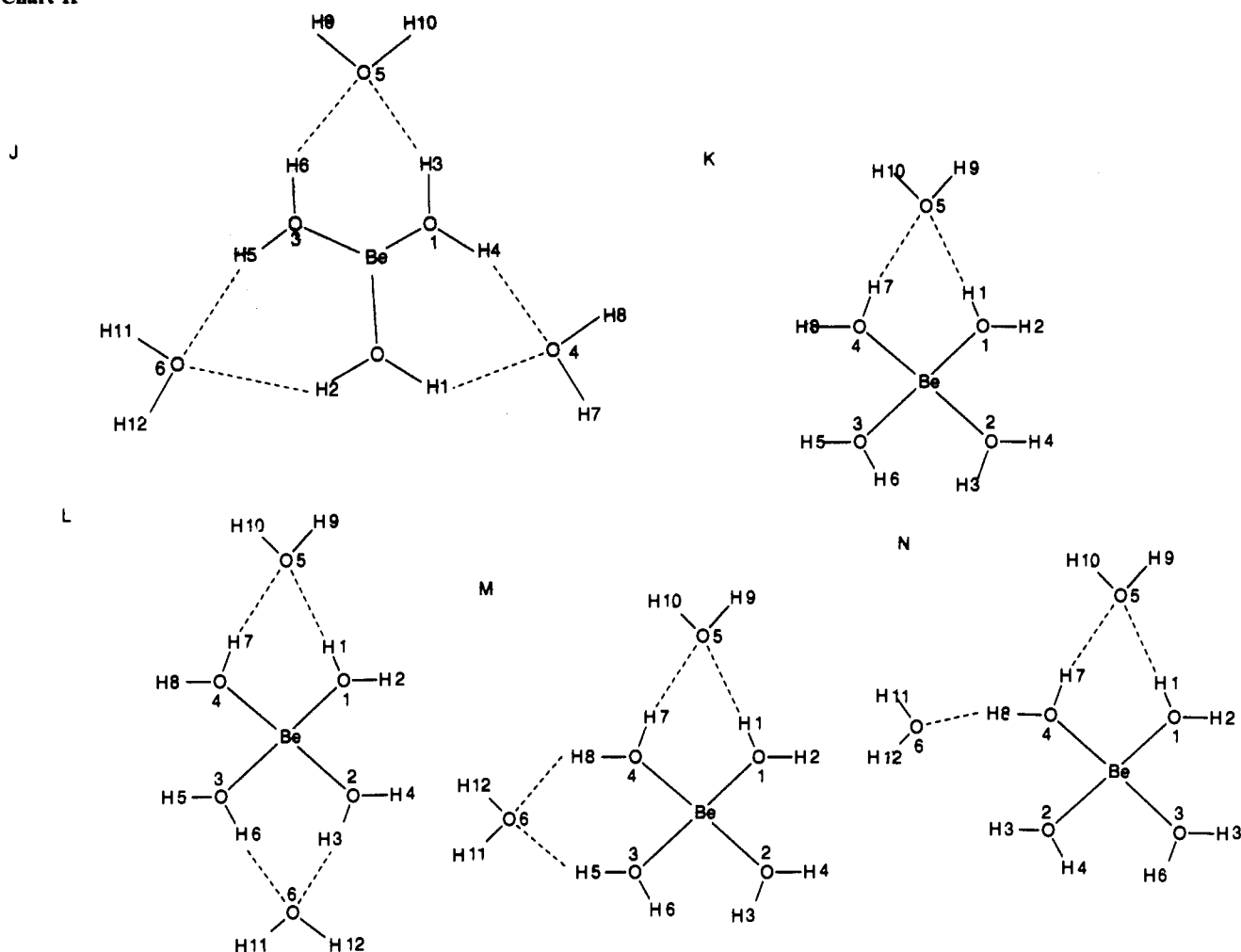
analyses at the RHF/6-31G*//RHF/6-31G* level. The energetics of various hydration processes are summarized in Table II.

Since no direct experimental data are available for the individual species of the hydrated Be^{2+} ions under consideration, it is important to establish the degree to which the 6-31G* basis set adequately describes such structures. Thus, in the case of H_2O and $Be[H_2O]_n^{2+}$ ($n = 1, 2$), we carried out RHF and MP2 level optimizations using both the 6-31G* basis set and the more complete 6-311G** basis set.[16] At both the RHF and MP2 levels, the larger basis set reduces the computed O–H and Be–O bond lengths ~0.01 Å, see Figure 1A–C. However, the predicted *changes* in the O–H bond lengths in going from H_2O to Be-$[H_2O]^{2+}$ to $Be[H_2O]_2^{2+}$ and the predicted *changes* in the Be–O bond length in going from $Be[H_2O]^{2+}$ to $Be[H_2O]_2^{2+}$ are consistent to approximately ±0.004 Å at all four computational levels considered. This suggests that the 6-31G* basis set should be adequate for understanding most of the structural changes that occur as the degree of hydration is varied.

(14) Schlegel, H. B. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertrán, J., Csizmadia, I. G., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; pp 33–53.

(15) Handy, N. C.; Schaefer, H. F., III. *J. Chem. Phys.* **1984**, *81*, 5031.

(16) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

Chart II

J

H9 H10
O5
H6   H3
O   O
3   1
Be
H5   H4
H11   O   O   O   H8
6   6   H2   H1   4
H12   H7

K

H10 H9
O5
H7   H1
H8—O   O—H2
4   Be   1
H5—O   O—H4
3   H6 H3 2

L

H10 H9
O5
H7   H1
H8—O   O—H2
4   Be   1
H5—O   O—H4
3   H6 H3 2
O
6
H11   H12

M

H10 H9
O5
H7   H1
H8—O   O—H2
H12   4   Be   1
O6   O—H4
H11   H5—O   2
3   H6   H3

N

H10 H9
O5
H7   H1
H11   H8—O   O—H2
O   4   Be   1
H12 6   O—H3
H3—O   3
2   H4   H6

In the case of Be[H$_2$O]$^{2+}$ we also carried out MP2/6-31G-(2d,2p)//MP2/6-31G(2d,2p) and MP2/6-31G(2df,2p)//MP2/6-31G(2df,2p) optimizations to try to establish a better absolute value for the length of the Be–O bond. The second d- and p-functions reduce the Be–O bond length to 1.503 Å, from 1.505 Å at the MP2/6-31G(d,p) level, and the f-functions reduce the Be–O length further to 1.490 Å. Addition of a third set of d functions on the heavy atoms only reduces the Be–O bond length another ~0.001 Å. These results suggest that MP2/6-31G* optimizations yield Be–O bond lengths which are too long by approximately 0.02 Å. Interestingly, the added f-functions have little effect on the O–H bond length or the H–O–H bond angle in Be[H$_2$O]$^{2+}$.

A. Be[H$_2$O]$_n$$^{2+}$ (n = 1–4, 6). We consider first hydrated beryllium ions with water constrained to the inner coordination shell. Stable structures, as verified by a frequency analysis, were found for Be[H$_2$O]$_n$$^{2+}$ with n = 1–4, 6 as shown in Figure 1B–F. Attempts to find a stable structure with five water molecules in the first coordination shell failed: the optimizations inevitably led to structures with four water molecules in the first shell and one in the second shell. The computed structures at the RHF/6-31G*//RHF/6-31G* level are in reasonable agreement with those of Hashimoto et al.[2] and Probst et al.[3] It should be noted that our computed Be[H$_2$O]$_2$$^{2+}$ structure has D_{2d} symmetry, in agreement with the results of Hashimoto and co-workers,[2] and not D_{2h} symmetry as found by Probst and co-workers.[3] At the RHF/6-31G* level the D_{2h} structure proved to be a rotational transition state. We also carried out an MP2/6-31G*//MP2/6-31G* optimization on the neutral beryllium hydrate, Be[H$_2$O]$_2$^{0},

and, as might be expected based on the electronic structure of a neutral beryllium atom, the Be–O distance expands to over 3.4 Å.

As can be seen in Figure 1, optimizations at both the RHF/6-31G* and MP2/6-31G* computational levels find the Be–O bond lengths increase in the Be[H$_2$O]$_n$$^{2+}$ structures as n increases. The O–H bond lengths decrease as n increases, but in all cases remain longer than the O–H bond length in an isolated water molecule. The H–O–H bond angle is almost the same for all the hydrated beryllium structures and is a few degrees larger than that computed at the same computational level for isolated water.

Perhaps the most interesting of the Be[H$_2$O]$_n$$^{2+}$ structures is that with n = 6. A frequency analysis at the RHF/6-31G*//RHF/6-31G* level confirms this hydrate is indeed stable. This agrees with the RHF/3-21G//RHF/3-21G calculations of Hashimoto et al.,[2] although no frequency analysis was reported by these authors. Be[H$_2$O]$_6$$^{2+}$ remains stable even when correlation effects are included in the optimization at the MP2/6-31G*//MP2/6-31G* level. Consider, for example, the reaction

$$Be[H_2O]_6^{2+} \rightarrow 2H_2O + Be[H_2O]_4^{2+} \quad (1)$$
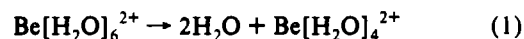
for which the computed energy change, ΔE, is +44.6 kcal/mol, the enthalpy change, $\Delta H°_{298}$, is +40.1 kcal/mol, and the Gibbs free energy change, $\Delta G°_{298}$, is +18.5 kcal/mol. In calculating these values we have used MP2/6-31G*//MP2/6-31G* level energy differences and RHF/6-31G*//RHF/6-31G* level thermal and entropy corrections. For comparison, the analogous

Table I. Total Molecular Energies (au) and Zero Point Vibrational Energies (kcal/mol)[a] of Hydrated Beryllium Cations

structure[b]	RHF/6-31G*//RHF/6-31G*	MP2/6-31G*//RHF/6-31G*	MP3/6-31G*//RHF/6-31G*	MP4SDQ/6-31G*//RHF/6-31G*	MP4SDTQ/6-31G*//RHF/6-31G*	MP2/6-31G*//MP2/6-31G*
Be[H₂O]²⁺ (B)	-89.854609 (16.66)	-90.047157	-90.051780	-90.054856	-90.057580	-90.054482
Be[H₂O]₂²⁺ (C)	-166.060291 (34.15)	-166.445035	-166.455037	-166.460953	-166.466404	-166.456534
Be[H₂O]₃²⁺ (D)	-242.203181 (52.53)	-242.779901	-242.795552	-242.803929	-242.811956	-242.795363
Be[H₂O]₃²⁺·[H₂O] (G)	-318.272410 (70.22)	-319.042894	-319.062530	-319.073631	-319.084471	-319.062877
Be[H₂O]₃²⁺·[H₂O]₂ (H)	-394.337196 (87.87)	-395.299918	-395.323939	-395.337770		
Be[H₂O]₃²⁺·[H₂O]₃ (I)	-470.394580 (104.46)	-471.547972	-471.576589	-471.593022		
Be[H₂O]₃²⁺·[H₂O]₃ (J)	-470.394208 (104.88)	-471.546470	-471.575686	-471.592271		
Be[H₂O]₄²⁺ (E)	-318.299201 (69.63)	-319.068215	-319.089106	-319.099995	-319.110712	-319.087418
Be[H₂O]₄²⁺·[H₂O] (K)	-394.361147 (87.60)	-395.323468		-395.362117		-395.347118
Be[H₂O]₄²⁺·[H₂O]₂ (L)	-470.420341 (105.01)	-471.574648	-471.604152	-471.620390		-471.602284
Be[H₂O]₄²⁺·[H₂O]₂ (M)	-470.416281 (105.13)	-471.575222	-471.600118	-471.616434		
Be[H₂O]₄²⁺·[H₂O]₂ (N)	-470.413504 (104.26)	-471.566282	-471.596035	-471.612241		
Be[H₂O]₆²⁺ (F)	-470.374346 (102.97)	-471.530558	-471.560297	-471.576939		-471.556921
Be²⁺	-13.609800	-13.609800	-13.609800	-13.609800	-13.609800	-13.612738
H₂O (A)	-76.010746 (14.42)	-76.195960	-76.201969	-76.204626	-76.206358	-76.199244

[a] The zero point vibrational energies computed at the RHF/6-31G*//RHF/6-31G* level are given in parentheses after the RHF/6-31G*//RHF/6-31G* energies. [b] See Figure 1 for structures.

reaction with Mg^{2+} in place of Be^{2+} has $\Delta E = +67.5$ kcal/mol, $\Delta H°_{298} = +62.5$ kcal/mol and $\Delta G°_{298} = +46.4$ kcal/mol.[17] As expected, the energies for the magnesium salts are all substantially more positive than those for the corresponding beryllium salts, reflecting the fact that Mg^{2+}, with its available d-orbitals, routinely accommodates six atoms in the first coordination shell. It is interesting to note that reaction 1, which removes two water molecules from $Be[H_2O]_6^{2+}$, is substantially *less* endothermic than the corresponding reactions for removing a single water molecule from any of the other $Be[H_2O]_n^{2+}$ ($n = 1$–4) structures, see Table II.

In Figure 3, we plot the hydration energy per water molecule, defined as

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

computed at the MP4SDQ/6-31G*//RHF/6-31G* level, and corrected for zero point vibrational energy differences computed at the RHF/6-31G*//RHF/6-31G* level. E_{per} decreases as n increases, and, at $n = 6$, E_{per} has been reduced to approximately 50% of its value at $n = 1$. E_{per} does not decrease uniformly at this computational level (e.g. from $n = 1$ to $n = 2$ E_{per} drops 12.6 kcal/mol, while from $n = 2$ to $n = 3$ E_{per} drops 17.7 kcal/mol), showing clearly that the hydration energies are not simply additive.

In Figure 4, the net charge on the beryllium atom, computed from the generalized charge density at the MP2/6-31G**//MP2/6-31G* level with all orbitals active, is plotted as a function of n. It is clear that a significant amount of charge is transferred from the surrounding water to the central beryllium atom for all the hydrates, $Be[H_2O]_n^{2+}$ ($n = 1$–4, 6), substantiating the conclusion of Hashimoto et al.[2] that the interaction of Be^{2+} and water is not entirely electrostatic, but that a dative bond is formed using the lone pair of electrons on oxygen. It is important to note that the amount of charge transferred to the beryllium ion increases as n increases from $n = 1$ to 4, reducing the net positive charge on beryllium 45% from $+1.40$ ($n = 1$) to $+0.77$ ($n = 4$). For $n = 6$, however, the charge transferred is *less* than that for $n = 4$, and the net charge on beryllium is back up to $+0.98$. This reduced charge transfer for $Be[H_2O]_6^{2+}$ is certainly correlated with the fact that the Be–O bond length has become very large for $Be[H_2O]_6^{2+}$, i.e. 1.85 Å, compared to 1.65 Å for $Be[H_2O]_4^{2+}$.

B. Be[H₂O]ₙ²⁺·[H₂O]ₘ ($n = 3$, 4; $1 \le m \le 3$; $4 \le n + m \le 6$). Several structures of the form $Be[H_2O]_n^{2+}·[H_2O]_m$, 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 1G–N. In these calculations no symmetry was imposed
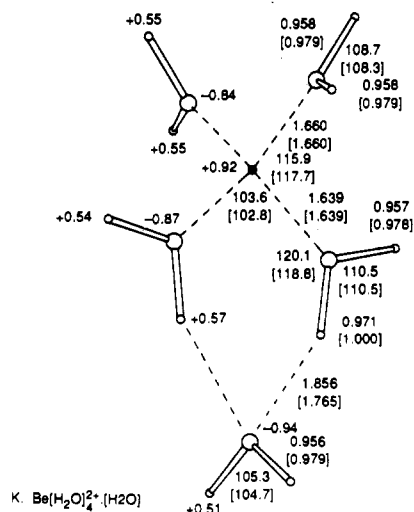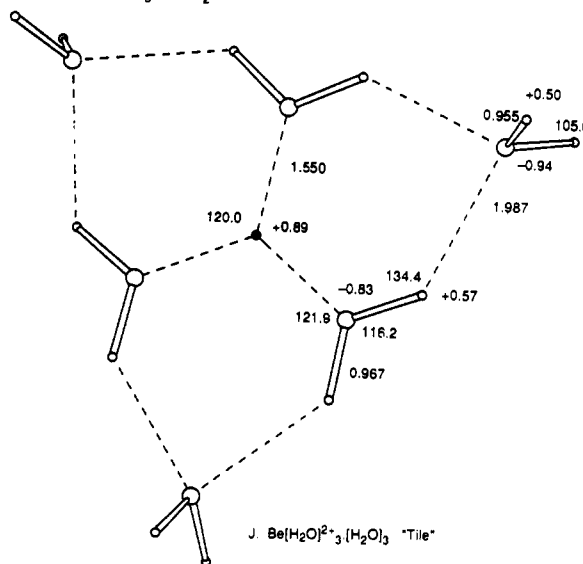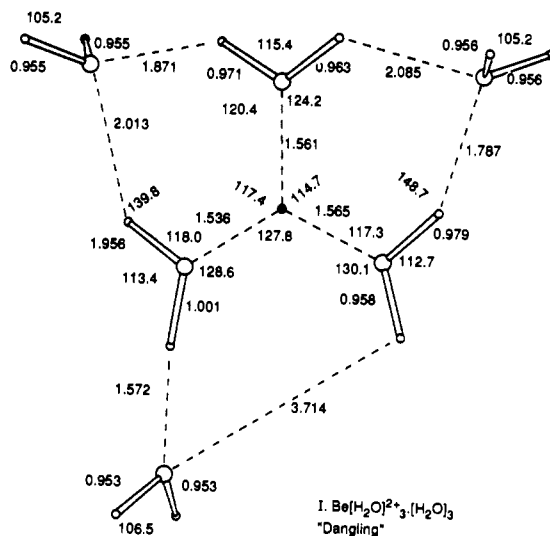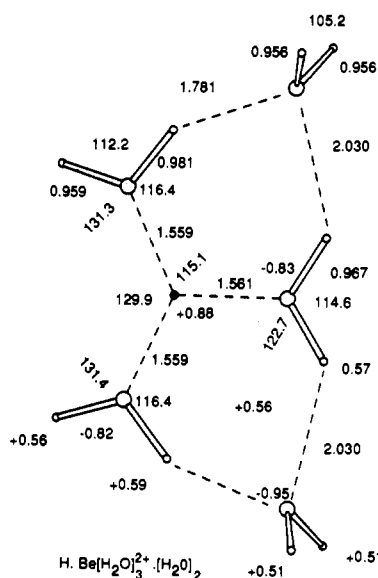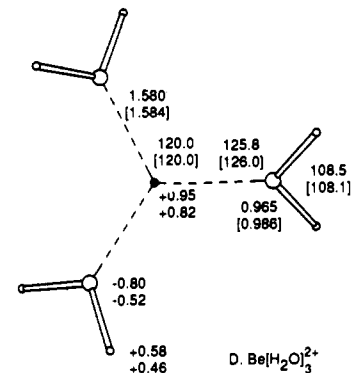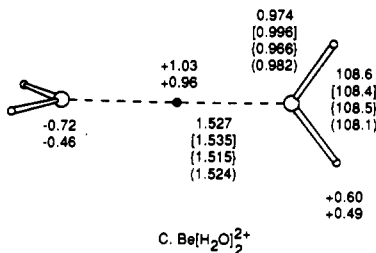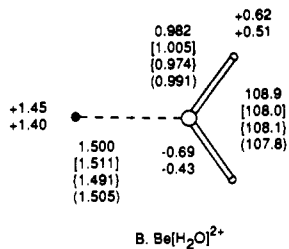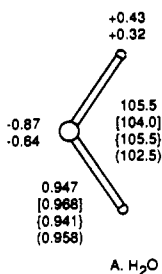
a priori to lessen the chance of optimizing to transition states. We were unable to find a stable species of the form $Be[H_2O]^{2+}·H_2O$, i.e. a beryllium cation bound to a water dimer. The optimizations led to $Be[H_2O]_2^{2+}$, $BeOH^- + H_3O^+$ or to a transition state, depending on the initial geometry. No attempt was made to search for stable structures of the form $Be[H_2O]_2^{2+}·H_2O$.
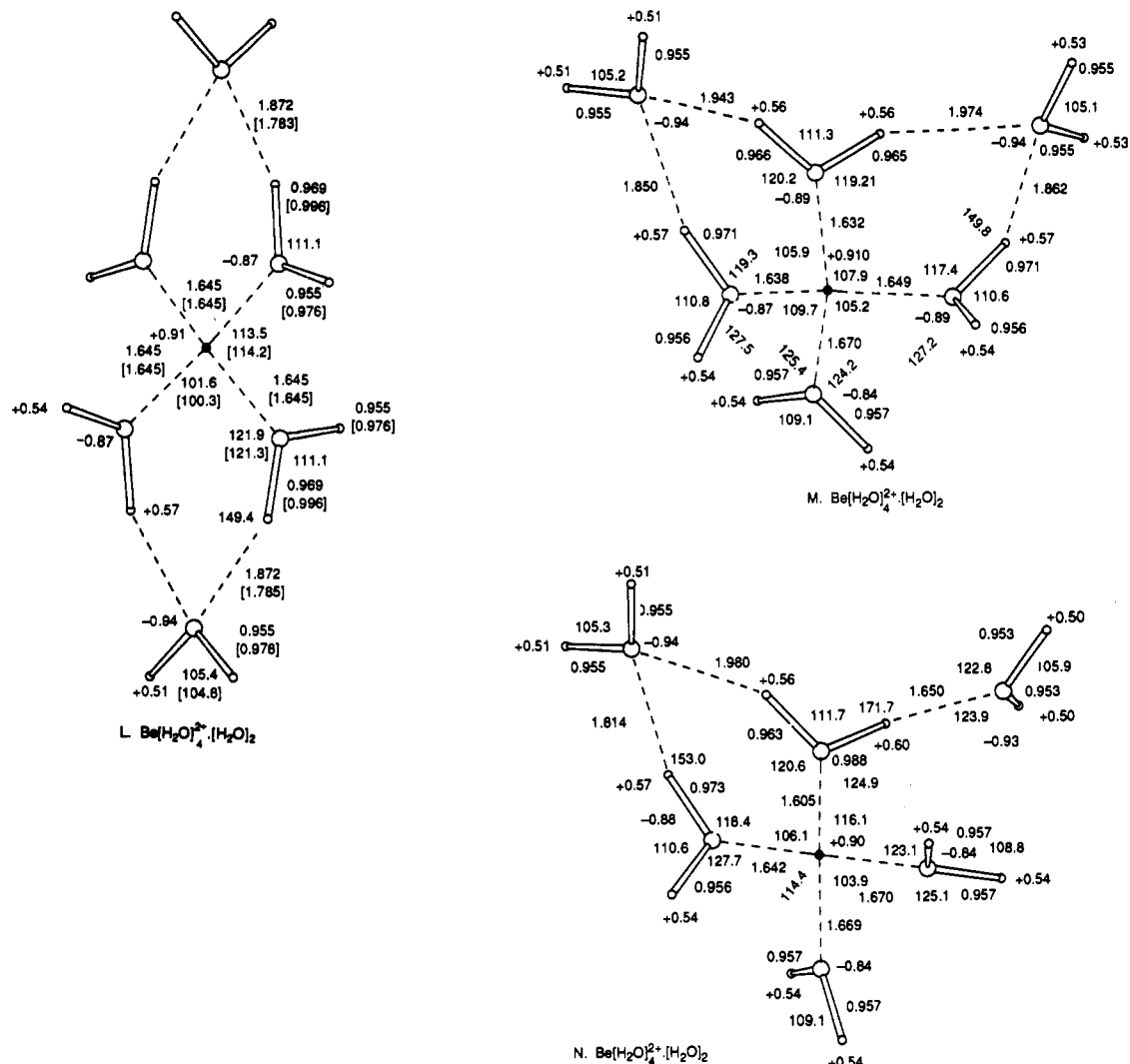
Be[H₂O]₃²⁺·H₂O and Be[H₂O]₄²⁺·H₂O. Stable structures were found with either three or four water molecules bound to beryllium in the first coordination shell, and with a single water molecule in the second coordination shell, hydrogen-bonded to two water molecules in the first shell, see Figure 1G,K, which we designate as $Be[H_2O]_3^{2+}·H_2O$ and $Be[H_2O]_4^{2+}·H_2O$, respectively. In each case, a symmetrical six-membered ring is formed. Attempts to find stable configurations with the water molecule in the second shell hydrogen bonded to only one water molecule in the first shell always reverted to the ring systems in Figure 1G,K. In accord with expectations,[8] the O–H bonds of the water molecules in the inner shell that participate in the hydrogen bonding lengthen approximately 0.01–0.02 Å, the Be–O bonds which become part of the ring shorten approximately 0.01 Å, and the O–Be–O angles which become interior angles in the ring are reduced by some 7°–9°, compared to their corresponding values in $Be[H_2O]_3^{2+}$ and $Be[H_2O]_4^{2+}$. The computed lengths of the $H_{1st \, shell}···O_{2nd \, shell}$ hydrogen bonds are rather sensitive to the inclusion of the effects of electron correlation in the optimization, e.g. $H_{1st \, shell}···O_{2nd \, shell}$ distances are found to be approximately 0.1 Å *shorter* at the MP2/6-31G*//MP2/6-31G* level than at the RHF/6-31G*//RHF/6-31G* level. The binding energies of the water molecules in the outer shells of $Be[H_2O]_3^{2+}·H_2O$ and $Be[H_2O]_4^{2+}·H_2O$ are 37.6 and 32.5 kcal/mol respectively, at the MP4SDQ/6-31G*//RHF/6-31G* level, see Table II. The lower value for $Be[H_2O]_4^{2+}·H_2O$ correlates well with the $H_{1st \, shell}···O_{2nd \, shell}$ distance which is 0.021 Å longer in $Be[H_2O]_4^{2+}·H_2O$ at the RHF/6-31G*//RHF/6-31G* level.

Comparing the total molecular energies of $Be[H_2O]_3^{2+}·H_2O$ and $Be[H_2O]_4^{2+}$, we find $Be[H_2O]_4^{2+}$ to be 16.5 kcal/mol (15.4 kcal/mol) *lower* in energy than $Be[H_2O]_3^{2+}·H_2O$ at the MP4SDTQ/6-31G*//RHF/6-31G* (MP2/6-31G*//MP2/6-32G*) level. Although the SCF charge density suggests more charge has been transferred to the central beryllium atom in $Be[H_2O]_3^{2+}·H_2O$, the second order MP2/6-31G*//RHF/6-31G* charge density with all orbitals active finds more charge transferred to beryllium in $Be[H_2O]_4^{2+}$. In any event, it is clear that there is a significant lowering of the energy when four water molecules are directly bound to the beryllium ion, compared to the case in which three water molecules are bound to the beryllium ion and one water molecule is hydrogen-bonded to two water molecules in the first shell.

(17) Bock, C. W.; Glusker, J. P. Unpublished results.
(18) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

A. H₂O

B. Be[H₂O]²⁺

C. Be[H₂O]₂²⁺

D. Be[H₂O]₃²⁺

E. Be[H₂O]₄²⁺

F. Be[H₂O]₆²⁺

G. Be[H₂O]₃²⁺·[H₂O]

H. Be[H₂O]₃²⁺·[H₂O]₂

I. Be[H₂O]₃²⁺·[H₂O]₃ "Dangling"

J. Be[H₂O]₃²⁺·[H₂O]₃ "Tile"

K. Be[H₂O]₄²⁺·[H₂O]
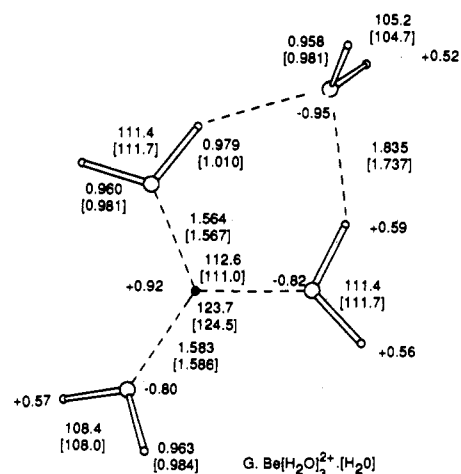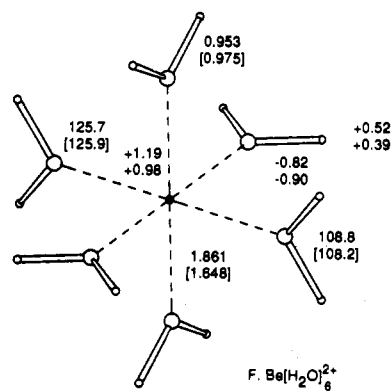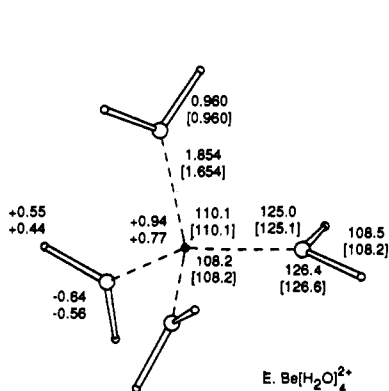
Figure 1. Structures (bond lengths, three decimal places, in Å and bond angles, one decimal place in deg) of H_2O and hydrated Be^{2+} ions computed at the RHF/6-31G*//RHF/6-31G* level. The values in brackets, braces, and parentheses are the structural parameters computed at the MP2/6-31G*//MP2/6-31G*, RHF/6-311G**//RHF/6-311g**, and MP2/6-311g**//MP2/6-311G** levels, respectively. Atomic charges (given to two decimal places) from the SCF density (top values) and, where available, from the second order density (lower values) are also shown. Key: Solid circles, Be; open circles, O; small circles, H.
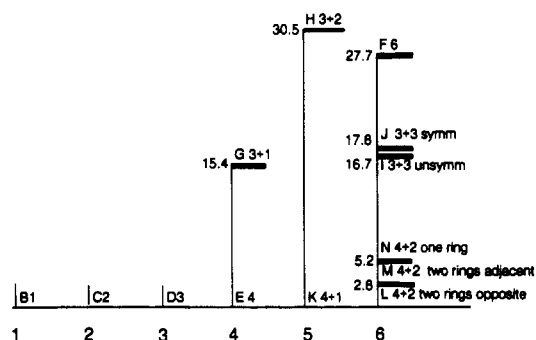
Figure 2. Energy levels of the various ways of arranging 1–6 water molecules around a beryllium cation.

Be[H₂O]₃²⁺·[H₂O]₂ and Be[H₂O]₄²⁺·[H₂O]₂. If another water molecule is added to the outer coordination shell of Be-$[H_2O]_3^{2+}$·H_2O, a structure with two identical, but unsymmetrical, six-membered, hydrogen-bonded rings with a common Be–O bond is found to be stable, see Figure 1H. The two $H_{1st\ shell}\cdots O_{2nd\ shell}$ distances differ in length by nearly 0.25 Å at the RHF/6-31G*//RHF/6-31G* computational level. Interestingly, the smaller of the two O···H bonds is more than 0.04 Å shorter, and the other is nearly 0.2 Å longer than the two symmetrical O···H bonds in Be[H₂O]₃²⁺·H₂O.

Comparing the two hydrates containing five water molecules, Be[H₂O]₄²⁺·H₂O is found to be 15.3 kcal/mol lower in energy than Be[H₂O]₃²⁺·[H₂O]₂ at the MP4SDQ/6-31G*//RHF/6-31G* level. Interestingly, this energy difference is nearly the same as that found between Be[H₂O]₄²⁺ and Be[H₂O]₃²⁺·H₂O, i.e. 16.5 kcal/mol at the same computational level. Thus, it seems clear that a divalent beryllium cation finds configurations with four water molecules in the inner shell energetically preferable to configurations with three water molecules in the inner shell.

Another water molecule can be added to the second coordination shell of Be[H₂O]₄²⁺·[H₂O] in several ways, see Figure 1L–N. The most stable form, see Figure 1L, contains two equivalent, symmetrical, hydrogen-bonded, six-membered rings with no bonds in common to the two rings. The $H_{1st\ shell}\cdots O_{2nd\ shell}$ distances are 0.04 Å–0.05 Å longer than the corresponding distances in Be-$[H_2O]_3^{2+}$·H_2O which also contains a symmetrical six-membered ring, see Figure 1G. The next most stable form, see Figure 1M, also contains two six-membered, hydrogen-bonded rings, but they are neither equivalent nor symmetric and contain a common Be–O bond. In the two rings, the $H_{1st\ shell}\cdots O_{2nd\ shell}$ distances differ by 0.11 and 0.09 Å, less than half the difference found in the unsymmetrical rings in Be[H₂O]₃²⁺[H₂O]₂, see Figure 1H. In the highest energy form of Be[H₂O]₄²⁺·[H₂O]₂ we found, see Figure 1N, one of the water molecules in the outer shell is hydrogen-bonded to two adjacent water molecules in the first

Table II. Hydration Energies (kcal/mol)[a]

n	m	RHF/6-31G*// RHF/6-31G*	MP2/6-31G*// RHF/6-31G*	MP3/6-31G*// RHF/6-31G*	MP4SDQ/6-31G*// RHF/6-31G*	MP4SDTQ/6-31G*// RHF/6-31G*	MP2/6-31G*// MP2/6-31G*
		(A) Reaction Energies for $Be[H_2O]_n{}^{2+} + H_2O \rightarrow Be[H_2O]_{n+1}{}^{2+}$					
0		−144.68	−149.28	−148.41	−148.67	−149.29	−149.97
1		−119.25	−123.64	−123.54	−123.36	−123.98	−124.19
2		−78.96	−83.20	−82.98	−82.86	−83.39	−83.63
3		−50.85	−55.27	−54.79	−54.70	−55.30	−55.56
		(B) $Be[H_2O]_n{}^{2+} + 2H_2O \rightarrow Be[H_2O]_{n+2}{}^{2+}$					
4		−29.17	−39.69	−37.70	−37.98		−40.06
		(C) $Be[H_2O]_n{}^{2+} \cdot [H_2O]_m + H_2O \rightarrow Be[H_2O]_n{}^{2+}[H_2O]_{m+1}$					
3	0	−33.43	−38.79	−37.52	−37.57	−38.24	−39.57
3	1	−30.68	−35.09	−34.07	−34.12		
3	2[b]	−29.27	−32.69	−31.80	−31.77		
4	0	−28.58	−33.66	−32.50	−32.53		−34.39
4	1[c]	−27.41	−31.66	−30.68	−30.67		−32.10

[a] Corrected for zero point vibrational energy differences. [b] The structure in Figure 1I was used for $Be[H_2O]_3{}^{2+}\cdot[H_2O]_3$. [c] The structure in Figure 1L was used for $Be[H_2O]_4{}^{2+}\cdot[H_2O]_2$.
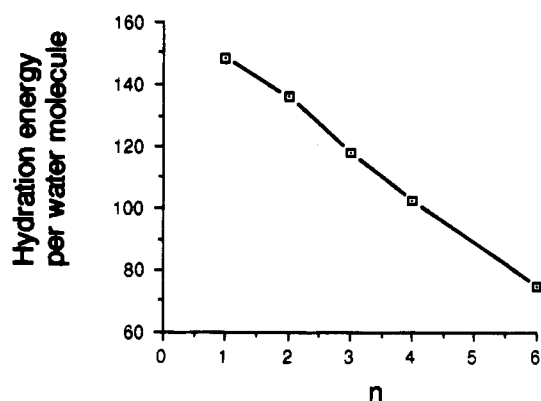
Figure 3. Hydration energy per water molecule computed at the MP4SDQ/6-31G*//RHF/6-31G* level and corrected for zero-point vibrational energy differences according to eq 2.
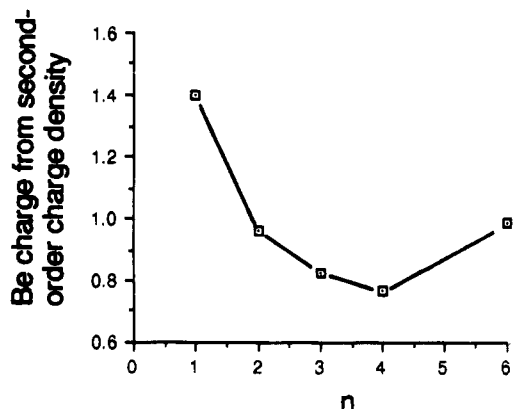
Figure 4. Net charge on the beryllium cations in the structures $Be[(H_2O)_n]^{2+}$ ($n = 1$–4, 6), computed from the MP2/6-31G**/MP2/6-31G* charge density.

shell forming an unsymmetrical six-membered ring. The other water molecule in the second shell hydrogen-bonds to a single water molecule in the inner shell, producing what we shall call a "dangling" configuration. We were unable to form a stable "dangling" configuration to water molecules in the inner shell unless that water molecule was part of the six-membered ring. We cannot, of course, rule out the possibility that there may be other stable configurations of $Be[H_2O]_4{}^{2+}\cdot[H_2O]_2$, which we have not yet been able to locate.

The energy required to remove one of the water molecules in the outer shells of $Be[H_2O]_3{}^{2+}[H_2O]_2$ and $Be[H_2O]_4{}^{2+}[H_2O]_2$, Figure 1I, are 34.1 and 30.7 kcal/mol, respectively, at the MP4SDQ/6-31G*//RHF/6-31G* level, see Table II, a few kcal/mol less than that required to remove a water molecule from the outer shells of $Be[H_2O]_3{}^{2+}\cdot[H_2O]$ and $Be[H_2O]_4{}^{2+}\cdot[H_2O]$.

Comparing the energies of $Be[H_2O]_4{}^{2+}[H_2O]_2$ and $Be[H_2O]_6{}^{2+}$, we find that all three forms of $Be[H_2O]_4{}^{2+}[H_2O]_2$ which we were able to locate are more than 20.0 kcal/mol *lower* in energy than $Be[H_2O]_6{}^{2+}$, where all six water molecules are crowded into the first coordination shell. Furthermore, for all three structures of $Be[H_2O]_4{}^{2+}[H_2O]_2$, calculations using the SCF or second order density show significantly more charge transferred to the central beryllium atom from the surrounding water than for $Be[H_2O]_6{}^{2+}$.

$Be[H_2O]_3{}^{2+}\cdot[H_2O]_3$. Adding three water molecules to the second coordination shell of $Be[H_2O]_3{}^{2+}$ to form $Be[H_2O]_3{}^{2+}\cdot[H_2O]_3$ can be accomplished in two ways. The higher-energy form has three equivalent symmetrical hydrogen-bonded six-membered rings with relatively long $H_{1st\ shell}\cdots O_{2nd\ shell}$ bonds, see Figure 1J. We shall refer to this form as the "tile" configuration. Interestingly, the magnesium equivalent of this hydrate is not stable, but rather a third order transition state. Removing a water molecule from the outer shell of the "tile" structure requires ~31.8 kcal/mol, less than that required to remove a water molecule from the outer shells of either $Be[H_2O]_3{}^{2+}\cdot2H_2O$ or $Be[H_2O]_3{}^{2+}\cdot H_2O$, see Table II. The lowest-energy form of $Be[H_2O]_3{}^{2+}[H_2O]_3$ has two inequivalent unsymmetrical hydrogen bonded rings and one "dangling" water molecule, see Figure 1I, and is approximately 0.5 kcal/mol lower in energy than the "tile" form.

Both forms of $Be[H_2O]_3{}^{2+}\cdot[H_2O]_3$ are at least 9.6 kcal/mol *lower* in energy at the MP4SDQ/6-31G* level than $Be[H_2O]_6{}^{2+}$. However, the structures with four water molecules in the inner shell, $Be[H_2O]_4{}^{2+}\cdot[H_2O]_2$, are at least 12.1 kcal/mol lower in energy than either of the $Be[H_2O]_3{}^{2+}\cdot[H_2O]_3$ structures. Thus, for beryllium ions surrounded by six water molecules, the lowest-energy forms have four water molecules in the inner shell, followed by those with three in the inner shell, and the highest energy form has six water molecules in the inner shell.

Structural Studies

We reviewed the structural data on crystal structures containing aquated beryllium ions in order to compare the geometry of the water coordination with that found in the ab initio calculations. The coordination number of beryllium cations appears to be 4.0 in the crystalline state. For example, a review of cation coordination numbers in crystal structures by Brown[19] lists 4.0 as the average coordination of beryllium ion inorganic structures. A search of the crystal structure data contained in the Cambridge Structural Database (1992 version)[20] (containing organic crystal structures) showed that the maximum coordination number of

(19) Brown, I. D. *Acta Crystallogr.* **1988**, *B44*, 545.
(20) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, G. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331.

(a)

(b)

(c)

Chemical formulas.

(a)

(b)

(c)
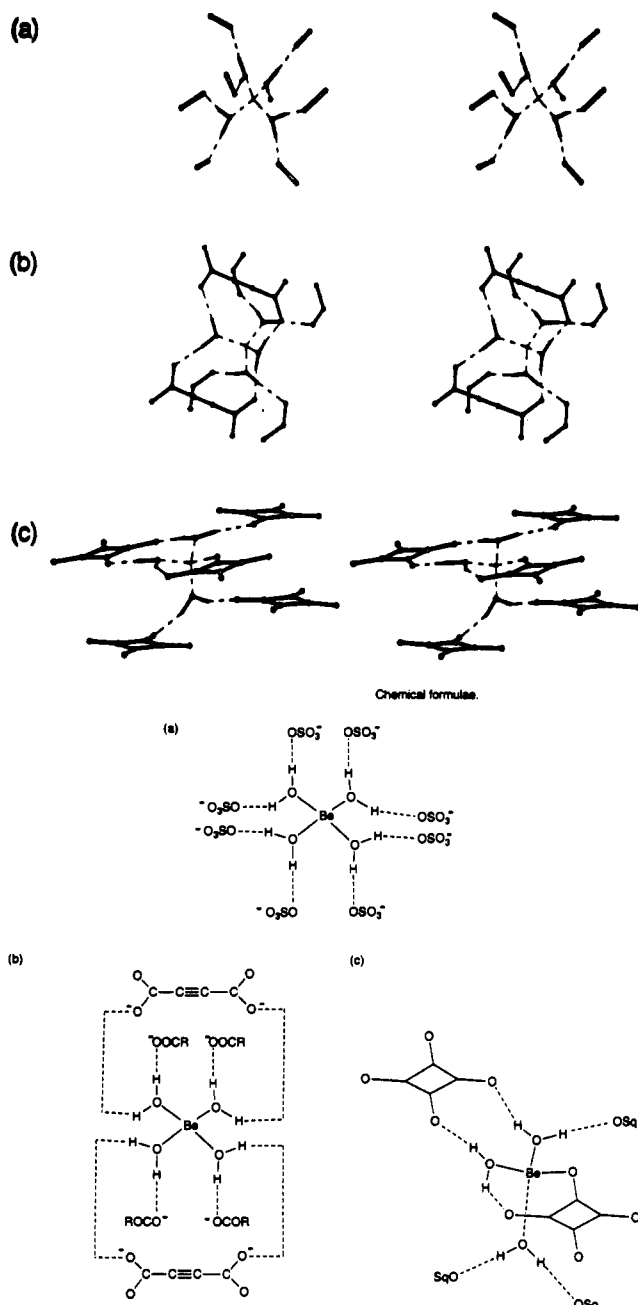
Figure 5. Stereoviews of the surroundings of beryllium cations in the crystal structures of sulfate tetrahydrate[21,22] and (b) and (c) two carboxylate complexes of beryllium (Sq = squarate) [(b) tetraaquaberyllium acetylene dicarboxylate, Refcode KIDREU[24] and (c) triaqua(squarato-O-)beryllium, Refcode TACZQY[25] in the Cambridge Structural Database]. Chemical formulas are also shown.

beryllium ions for 41 entries is also 4. Of these, there were 6 crystal structure determinations in which the beryllium was bonded to oxygen atoms. All of these structures contained beryllium coordinated precisely with four oxygen atoms. Three crystal structures were chosen for comparison since they contained aquated beryllium ions. These were beryllium sulfate tetrahydrate,[21,22] from the Inorganic Crystal Structure Database[23] and two beryllium carboxylates[24,25] from the Cambridge Structural Database.[20] Stereoviews of these three structures, together with the chemical formulae, are shown in Figure 5. The Be⋯O distance

in crystal structures appears to lie between 1.60 and 1.63 Å when the coordination number is 4 and all ligands are oxygen atoms. The average O–Be–O angle is 109.5°, as expected for a regular tetrahedron, but the angles range from 87° to 122°.

In order to study the geometry of the water molecules in hydrated beryllium salts, we have concentrated on the only relevant neutron diffraction study available, that of beryllium sulfate tetrahydrate.[21] Hydrogen atoms, it should be noted, are located much more precisely in neutron diffraction analyses than in X-ray diffraction analyses. The geometries of the heavier atoms were very similar in both the neutron and X-ray structure determinations. In the X-ray study[22] the Be–O distance is found to be 1.610(4) Å, while in the neutron study it is 1.618(4) Å. Similarly, the O–Be–O angles were 117.5(3)° and 105.6(3)° in the X-ray diffraction study and 117.0(2)° and 105.8(2)° in the neutron diffraction study. The neutron diffraction study also provided information on the water geometry. It showed that the water O–H distances are 0.967(6) Å and 0.971(8) Å, the H–O–H angle is 112.7(8)°, the hydrogen bonds to sulfate oxygen atoms have H⋯O distances of 1.656(8) Å and 1.719(6) Å with O–H⋯O angles of 171.7(8)° and 172.3(6)°, respectively, and the Be⋯O–H angles are 118.2(5)° and 126.2(5)°.

A comparison of these experimental results with the various $Be[H_2O]_4[H_2O]_m$ ($m = 0, 1, 2$) structures in Figure 1, computed at the RHF/6-31G* or MP2/6-31G* levels, shows good overall agreement, see deposited Table 2S. The computed Be–O bond lengths at the RHF/6-31G* and MP2/6-31G* level are, however, somewhat longer than the experimental values. This is probably a result of the truncated basis set we are using. Specifically, the computed Be–O bond length in $Be[H_2O]_4^{2+}$ is 1.645 Å at the MP2/6-31G* level, and as noted above, we expect this to be approximately 0.02 Å too long, which would suggest a Be–O bond length of 1.625 Å in reasonable agreement with the average Be–O distance from X-ray diffraction studies listed in the Cambridge Structural Database.[20]

Some trends in water geometry become evident in the structures calculated by ab initio methods. We will report here the MP2/6-31G*//MP2/6-31G* levels only. The H–O–H angle in water in the absence of a beryllium cation is 104.0°. This is expanded to approximately 108.2° on binding to a beryllium cation and the O–H bond length is lengthened as it is bound to this charged cation. The value for this length, 0.968 Å in a single water molecule in vacuo, is increased approximately 0.008 Å when six water molecules bind to Be^{2+}. As water molecules are removed from $Be[H_2O]_6^{2+}$, the oxygen atoms experience more charge and the O–H bond length increases (0.008 Å for each water removed) to 1.005 Å for $Be[H_2O]^{2+}$.

The H–O–H angle is also sensitive to the number of hydrogen bonds in which its atoms partake. In the inner sphere, coordinated to the beryllium cation, it is found that water molecules that have one hydrogen bond generally have an angle of 110–113°, while if they take part in two hydrogen bonds this angle may be further expanded to as much as 116°. In the outer shells we have only considered water molecules that receive, but do not donate, to hydrogen bonds. The H–O–H angles in these outer-shell water molecules vary from 104.7° to 106.5° and the O–H distances vary from 0.953 Å to 0.979 Å. This shows that two major factors affect the H–O–H angle: coordination to a cation and donation of a hydrogen atom to a hydrogen bond. Acceptance of a hydrogen bond has very little effect on this angle. Details of the results are given in deposited Table 3S.

We had assumed that the beryllium ion would lie in the plane of each of the water molecules surrounding it, but this does not turn out to be the case, as shown in Table III. Deviations as high as 0.78 Å are found (in case M). A comparison with values in crystalline beryllium hydrates shows similar distances. Since the beryllium does lie in the plane of the water molecules in the case of the lowest-energy form (L), this would appear to be a

(21) Sikka, S. K.; Chidambaram, R. *Acta Crystallogr.* **1969**, *B25*, 310.
(22) Dance, I. G.; Freeman, H. C. *Acta Crystallogr.* **1969**, *B25*, 304.
(23) Bergerhoff, G.; Hundt, R.; Sievers, R.; Brown, I. D. *J. Chem. Inf. Comput. Sci.* **1983**, *23*, 66.
(24) Robl, C.; Hentschel, S. *Z. Naturforsch.* **1990**, *B45*, 1499.
(25) Robl, C.; Kinkeldey, D. *Z. Naturforsch.* **1990**, *B45*, 931.

Table III. Deviation of Beryllium from Best Plane through Water H‑ ‑O‑ ‑H

case	H1–O2–H2	H3–O2–H4	H5–O3–H6	H7–O4–H8	H9–O5–H10	H11–O6–H12
	(a) Computational Values					
C	0.00	0.00				
C	0.00	0.00				
D	0.00	0.0	0.00			
D	0.00	0.00	0.00			
E	0.06	0.06	0.05	0.05		
E	0.06	0.05	0.05	0.05		
F	0.00	0.00	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00
G	0.13	0.12	0.00			
G	0.15	0.15	0.00			
H	0.00	0.00	0.00			
I	0.00	0.00	0.00			
J	0.00	0.00	0.00			
K	0.34	0.15	0.15	0.34		
L	0.00	0.00	0.00	0.00		
L	0.00	0.00	0.00	0.00		
M	0.57	0.30	0.40	0.78		
N	0.47	0.45	0.16	0.43		
	(b) Experimental Values					
BeSO₄	0.45	0.45	0.45	0.45		
KIDREU	0.34	0.74	0.34	0.74		
TACZAY	0.75	0.32	0.63	*a*		
TACZAY	0.69	0.75	0.68	*a*		

ᵃ Coordinated to the anion, not water.

Table IV. Be‑ ‑O–H‑‑‑O Torsion Angles (deg)

(a) Experimental Values

BeSO4	19.8, 151.4
KIDREU	130.6, 20.6
TACZAY	15.8, 18.2
	34.8, 26.4
	19.0, 16.2
	2.1, 29.4
	26.9, 4.8
	2.3, 48.9

(b) Computational Values

G (3:1)	3.0, 1.9
H (3:2)	0.0, 0.1, 0.0, 0.0
I (3:3)	0.0, 0.0, 0.0, 0.1, 0.0
J (3:3)	0.0, 0.0, 0.0, 0.0, 0.0, 0.0
K (4:1)	1.1, 1.1
L (4:2)	0.0, 0.0, 0.0, 0.0
M (4:2)	0.5, 8.3, 3.0, 12.2
N (4:2)	0.4, 0.7, 1.4

favorable geometry. However, there must not be a substantial energy penalty for deviating from this plane.

This study has shown that the beryllium cation can bind four water molecules in the first shell and additional ones in a second shell. In Table IV we list experimental data on the torsion angle of binding, that is, the Be‑ ‑ ‑O–H‑ ‑ ‑ ‑O torsion angle. Values vary from 2 to 151°. In the molecular orbital study they vary from 0 to 12°. This torsion angle must be very sensitive to binding of, say, anions, in the crystalline state. Data in deposited Table 2S imply that the models we have generated are not geometrically unreasonable.

Conclusions

We have shown that there exist a variety of stable structures with four, five and six water molecules partitioned between the first and second coordination shells of divalent beryllium cations. Some insight into the factors which influence the relative energies of these local minima on the various potential energy surfaces can be obtained by calculating the total energy of the neutral framework of water molecules which remains after the central

beryllium cation is removed, without reoptimizing the structure, as suggested by Hashimoto et al.[2] Consider, for example, the two cases with four water molecules surrounding the beryllium ion, e.g., $Be[H_2O]_4{}^{2+}$ and $Be[H_2O]_3{}^{2+}\cdot H_2O$. All the MP2/6‑31G*//RHF/6‑31G* level with all orbitals active, the framework $[H_2O]_3\cdot H_2O$ is 13.7 kcal/mol *lower* in energy than the framework $[H_2O]_4$. Next, *neutral* beryllium atoms were inserted into the two frameworks. This incorporates the appropriate nuclear repulsion energies into the model, but reduces the likelihood of charge transfer from the surrounding water: $Be[H_2O]_3{}^0\cdot H_2O$ is computed to be 6.0 kcal/mol higher in energy than $Be[H_2O]_4{}^0$. The second order change density shows the beryllium atoms in $Be[H_2O]_3{}^0\cdot H_2O$ and $Be[H_2O]_4{}^0$ to have charges –0.08 and +0.16, respectively. Finally, if we replace the neutral beryllium atom with a divalent beryllium cation, $Be[H_2O]_3{}^{2+}[H_2O]$ is computed to be 16.0 kcal/mol *higher* in energy than $Be[H_2O]_4{}^{2+}$, a net turnaround from the framework energies of 29.7 kcal/mol. The respective second order charges are approximately +0.79 and +0.77 respectively. Considering a few of the cases with six water molecules surrounding the beryllium, we find the framework $[H_2O]_3\cdot[H_2O]_3$ (tile) to be 10.9 kcal/mol *lower* in energy than $[H_2O]_4[H_2O]_2$ (most stable form), and 35.4 kcal/mol *lower* in energy than $[H_2O]_6$. However, $Be[H_2O]_3{}^{2+}[H_2O]_3$ is 17.7 kcal/mol *higher* in energy than $Be[H_2O]_4{}^{2+}[H_2O]_2$ and $Be[H_2O]_6{}^{2+}$ is only 10.0 kcal/mol *higher* in energy than $Be[H_2O]_3{}^{2+}[H_2O]_3$. Again the net turnaround from the framework energies is 28.6 kcal/mol between $Be[H_2O]_4{}^{2+}[H_2O]_2$ and $Be[H_2O]_3{}^{2+}[H_2O]_3$, quite similar to that found between $Be[H_2O]_4{}^{2+}$ and $Be[H_2O]_3{}^{2+}\cdot[H_2O]$. Thus, in these cases the water frameworks are lowest in energy for configurations with three water molecules in the first shell and the remaining water molecules hydrogen-bonded in the second shell, and highest if all the water molecules are crowded into the first shell. However, the interaction of Be^{2+} with the four water molecules in the first shell in some 29 kcal/mol more favorable than the interaction of Be^{2+} with three water molecules in the first shell. It is also interesting to note that the water framework $[H_2O]_4[H_2O]_2$ is 24.5 kcal/mol lower in energy than $[H_2O]_6$, and $Be[H_2O]_4{}^{2+}[H_2O]_2$ is 27.7 kcal/mol lower in energy than $Be[H_2O]_6{}^{2+}$, suggesting the interaction of Be^{2+} with six waters in the inner shell is actually slightly less favorable than with four waters in the inner shell.

Thus, the lowest energy hydration structures on the potential energy surfaces of Be^{2+} surrounded by four, five or six water molecules all have four water molecules in the inner shell with the remaining water molecules hydrogen-bonded in the second coordination shell, e.g., $Be[H_2O]_4{}^{2+}\cdot[H_2O]_m$ ($m = 0, 1, 2$). This is in agreement with the usual notion that the hydration number of beryllium is four.

Supplementary Material Available: Tables of atomic coordinates of models B–N, tables of molecular geometries (bond distances, angles, torsion angles) for models B–N [Table 1S(b)], table providing a comparison of the geometries of models B–N with the neutron diffraction study of $BeSO_4\cdot 4H_2O$ (Table 2S), and a figure showing a comparison of framework versus beryllium hydrate energies (Figure S) (23 pages). Ordering information is given on any current masthead page.