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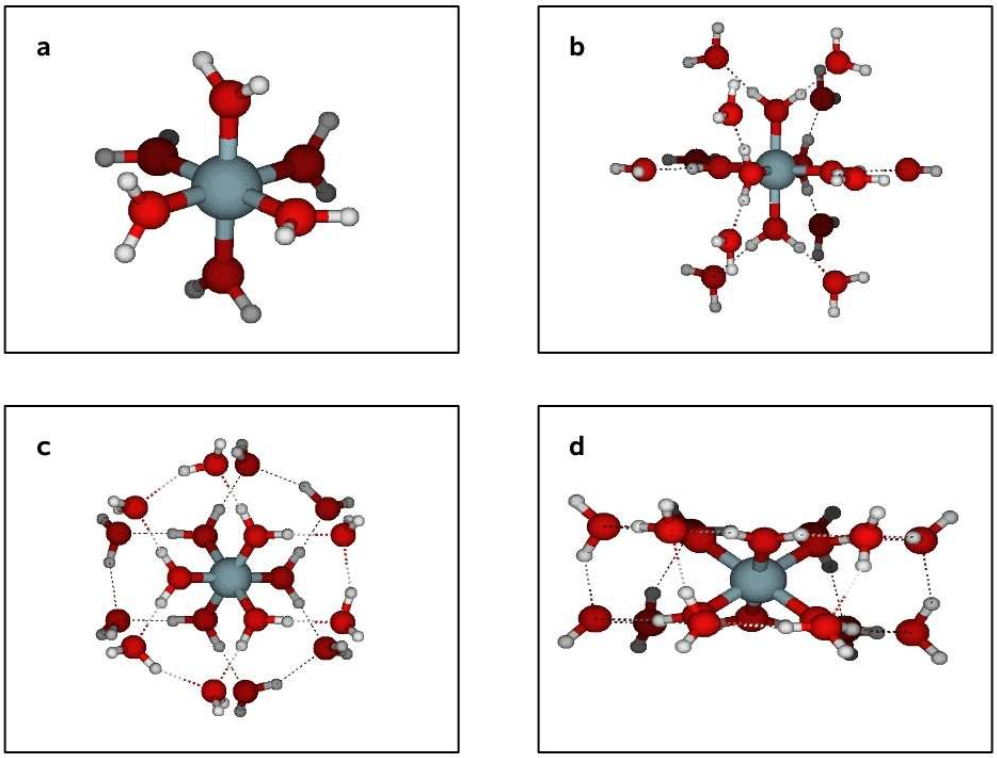

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Opposite effects of successive hydration shells on the aqua ion structure of metal cations

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Abstract

The conformation adopted by water molecules around a metal ion in aqueous solution can be approached from a discrete representation of the solvent by studying the structure and stability of microsolvation clusters including a different number of water molecules. In this contribution we present a Quantum Mechanics and ab initio Molecular Dynamics study on how the arrangement of water molecules around Mg^{2+} and Al^{3+} shows preferentially a T_h or S_6 symmetry depending on the number of hydration shells explicitly included in the calculation. The behavior observed for both cases is the following: a) For a cluster composed of the metal ion plus a first hydration shell the preferred geometry shows a T_h symmetry. b) When a second hydration shell is added, a minimum can be found with a S_6 disposition of water molecules around the metal center. c) However, if a third hydration shell is considered a T_h arrangement of water molecules around the central ion is strongly favored. The structures of the different solvation complexes studied in this work are characterized. The preference for a T_h or S_6 distribution of water ligands is rationalized in terms of total energies, interaction energies and the hydrogen bond network.

1 Introduction

Aqua ions, of general formula $[M(H_2O)_n]^{m+}$, are the most common structures adopted by metal cations, M^{m+}, in water when chemical conditions inhibit the formation of hydrolyzed and polymerized derivatives.[1] The implicit net charge, m+, and the polar and polarizable character of water lead to electrostatic effects so strong that the perturbation exerted on the solvent goes beyond the formation of these coordination complexes or aqua ions, defining different solvation shells which surround the central metal cation. This picture of the hydration structure was firstly proposed by Frank and Evans and is regarded as the *concentric shells model*.[2] In a global sense the formation of the aqua ion is not enough to describe the behavior of an ion in solution, and the condensed medium effect has to be taken into account through different solvation shells and/or the bulk.

The structural information derived from experimental techniques for metal ions in aqueous solutions is restricted to one or two hydration shells solved by X–ray and neutron diffraction methods as well as X–ray absorption spectroscopies.[1,3–6] NMR, Raman, IR and vis–UV techniques may also help in determining particular structural and dynamic properties.[1,3,5] More recently, studies of small multivalent ion–water clusters in gas phase have been possible by a variety of techniques which supply both thermochemical and structural information.[7–12] The characterization of increasingly large metal–water clusters is an important source of information not only for gas–phase ion chemistry, but it also allows the splitting of the solvent effects into specific and long-range contributions. Key structural parameters as coordination numbers vary from gas phase to solution, being a function of the cluster size.[12]

Theoretical methods may also provide a molecular description of the environment of a metal ion in water. From a quantum–mechanical point of view, there are three ways to represent the solvation of an ion in solution. In the discrete approach, a certain number of solvent molecules are explicitly included in the calculation in order to represent the intermolecular interactions between the ion and its closest solvent environment.[13] In the

continuum approach, the solvent is represented in an averaged manner by a polarizable dielectric continuum, generally characterized by macroscopic properties of the pure liquid solvent.[14,15] In the semi-continuum approach, the closest environment of the ion is represented by discrete water molecules, while the rest of the solvent is described by a continuum.[16,17] The molecular description of the solvent has been tackled at two levels. On one hand, the use of force fields in order to perform computer simulations and molecular mechanics allows the inclusion of a significant number of solvent molecules, but representing the inter- and intramolecular interactions in a simplified form. On the other hand, a more refined description of the interactions can be achieved by the use of static quantum–mechanical calculations, although in this case the computational requirements are high and only a limited number of solvent molecules can be treated, typically up to two solvation shells. If more solvation shells are to be considered, the statistical factors become important in order to describe the solvent, and then it seems more appropriate to perform ab initio Molecular Dynamics (MD) simulations such as Born-Oppenheimer[18] or Car-Parrinello MD.[19]

In the present study we aim to analyze the effect of successively increasing the number of hydration shells around two metal ions, Mg^{2+} and Al^{3+}, whose aqua ion structure in solution has been determined experimentally.[1,3,20,21] It is well known that the first coordination shell of both Mg^{2+} and Al^{3+} is sixfold, the aqua ion exhibiting an average T_h symmetry in solution.

There are also theoretical studies on these metal ions within the discrete representation of the solvent. When the structure of the hexahydrate is quantum–mechanically optimized, i.e. only the metal ion and its first hydration shell are considered, in the absence of hydrolysis effects the resulting configurational minimum has a T_h symmetry[22,23] (see Fig. 1a). Although at this level we are excluding a large amount of solvent effects, the structure of the aqua ion is already coherent with the known T_h structure that is found in solution.

Several configurational minima have been reported when two hydration shells are included in the calculation. First of all, a minimum with T_h symmetry can be found, in which the overall shape of the system is roughly spherical[22,24] (Fig. 1b). Pye and Rudolph[25] find another minimum in which the second–shell water molecules are distributed into three interacting clusters (see Fig. 12 of Ref. 25). This structure has a lower energy than the T_h minimum. Bock *et al.*[26] find yet another minimum with S_6 symmetry, and lower in energy that the other two configurations (Fig. 1c,d). In this structure, the second–shell water molecules are arranged into the form of a crown surrounding the core hexahydrate, i.e. the overall shape of the system is no longer spherical. This result is striking since it does not fit the behavior expected for a metal hexahydrate in liquid water, as summarized by the concentric shells model of Frank and Evans. It is neither consistent with the description obtained from MD simulations of the ions in liquid water. In the present contribution we reexamine the evolution of the stability of the T_h and S_6 aqua ion conformers by successively increasing the number of hydration shells around the metal ion, combining static QM calculations and ab initio MD simulations. A careful analysis of their structures, relative energies and of their inter–shell interactions is needed to get insight into this problem.

2 Methods

Gas-phase quantum-mechanical (QM) optimizations have been performed for the structures of Mg^{2+} and Al^{3+} aqua ions including one and two hydration shells ($[M(H_2O)_6]^{m+}$ and $[M(H_2O)_{18}]^{m+}$, respectively). For each case the optimization started from two configurations, one with T_h and the other one with S_6 arrangement of ligands, and no symmetry restrictions were applied during the minimization process. In the one–shell complexes a single minimum was found, showing T_h symmetry. Inclusion of a second hydration shell allows the finding of two minima, having T_h and S_6 symmetry respectively.

When a third solvation shell is explicitly taken into account, the number of degrees

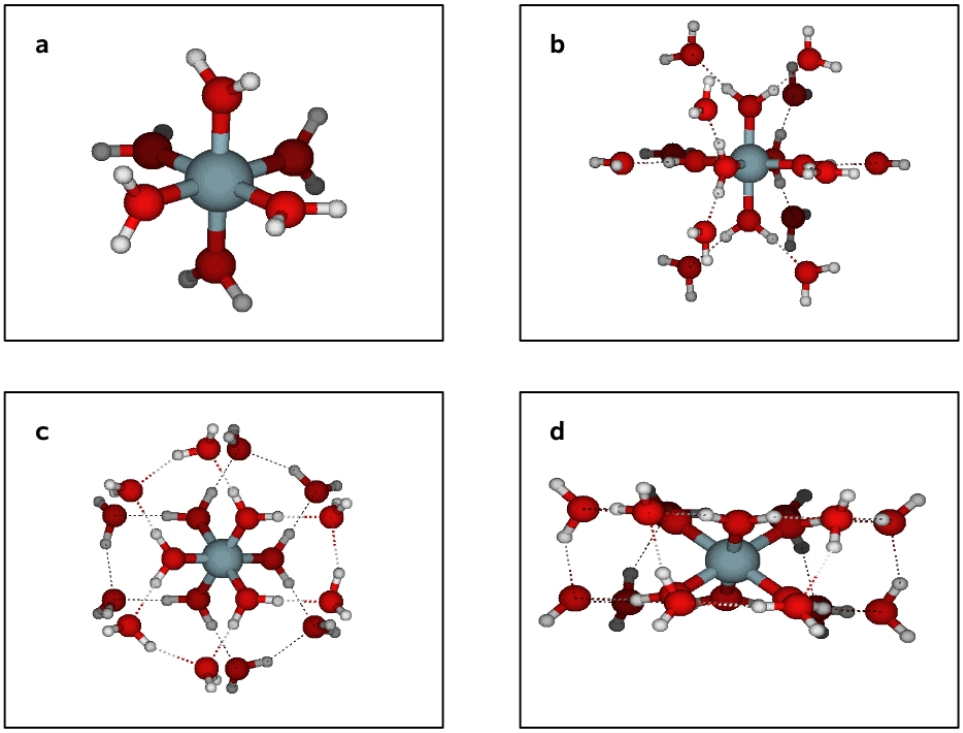

Figure 1: Representative configurations of the QM optimized structures of: a) $[M(H_2O)_6]^{m+}$ b) $[M(H_2O)_{18}]^{m+}$, T_h conformer c) and d) $[M(H_2O)_{18}]^{m+}$, S_6 conformer.

of freedom in the system increases to make a QM optimization of the structure hardly affordable in terms of computational costs. Furthermore, the shape of the potential energy surface (PES) includes a large number of local minima with similar energies, and it is difficult to reach a global minimum. Therefore we have employed an alternative strategy using ab initio Car-Parrinello Molecular Dynamics simulations[19] (CP-MD) to obtain a configuration that, while being only a local minimum on the PES is representative of a T_h or S_6 arrangement of ligands in the second hydration shell of the aqua ion.

For each metal cation, Mg^{2+} and Al^{3+}, $[M(H_2O)_{42}]^{m+}$ initial configurations have been built by addition of 24 extra water molecules around the T_h and S_6 $[M(H_2O)_{18}]^{m+}$ minima using the Packmol code.[27,28] The coordination number of 24 water molecules for the third shell was chosen in order to provide the minimum number of water molecules which may coordinate to the 12 second–shell water molecules by hydrogen bonding. An initial relaxation of the system has been performed by equilibration of the nuclei to a

low temperature (50 K) and during a short period of time ($\sim$ 0.4 ps) in order to avoid strong deviations from the initial symmetry (T_h or S_6) within the $[M(H_2O)_{18}]^{m+}$ unit. Afterwards an annealing procedure is applied, slowly diminishing the temperature of the system by applying a reducing factor on the nuclei velocities at each MD simulation step, until the temperature is below 5 K. Due to the thermal agitation experienced by the system during this process, in the final conformation the inner $[M(H_2O)_{18}]^{m+}$ core does neither maintain the initial symmetry nor is a minimum on the PES. However it is close enough to be qualitatively representative of the T_h or S_6 coordination modes (see Fig. 2).

Gas–phase QM calculations and CP-MD simulations were performed using the CPMD program package.[29] Norm–conserving Gaussian pseudopotentials of the Troullier–Martins type[30] and a plane wave (*p.w.*) cutoff of 80 Ry were employed, applying cluster boundary conditions[31] to avoid spurious electrostatic coupling of periodic images of the charged clusters. During the simulations the equations of motion were integrated using a time step of 4 a.u. together with a fictitious electron mass parameter of 400 a.u. and the hydrogen mass for H. All calculations were carried out with the PBE exchange and correlation GGA functional.[32,33]

3 Results and discussion

3.1 Comparison between plane waves and Gaussian functions

Previous QM calculations cited in the literature used Gaussian functions (*g.f.*) as basis sets.[22–26] In order to check the influence of *p.w.* or *g.f.* as a basis set, the gas–phase QM optimizations of the structures containing one or two hydration shells were also performed using the 6–311++G(2d2p) basis sets[34,35] with the Gaussian03 code[36] using the same PBE exchange and correlation GGA functional[32,33] as for the *p.w.* calculations. The interatomic distances using *p.w.* are larger than those obtained with *g.f.* (see Supporting Information). The maximum differences are of circa 0.1 Å within the first hydration shell,

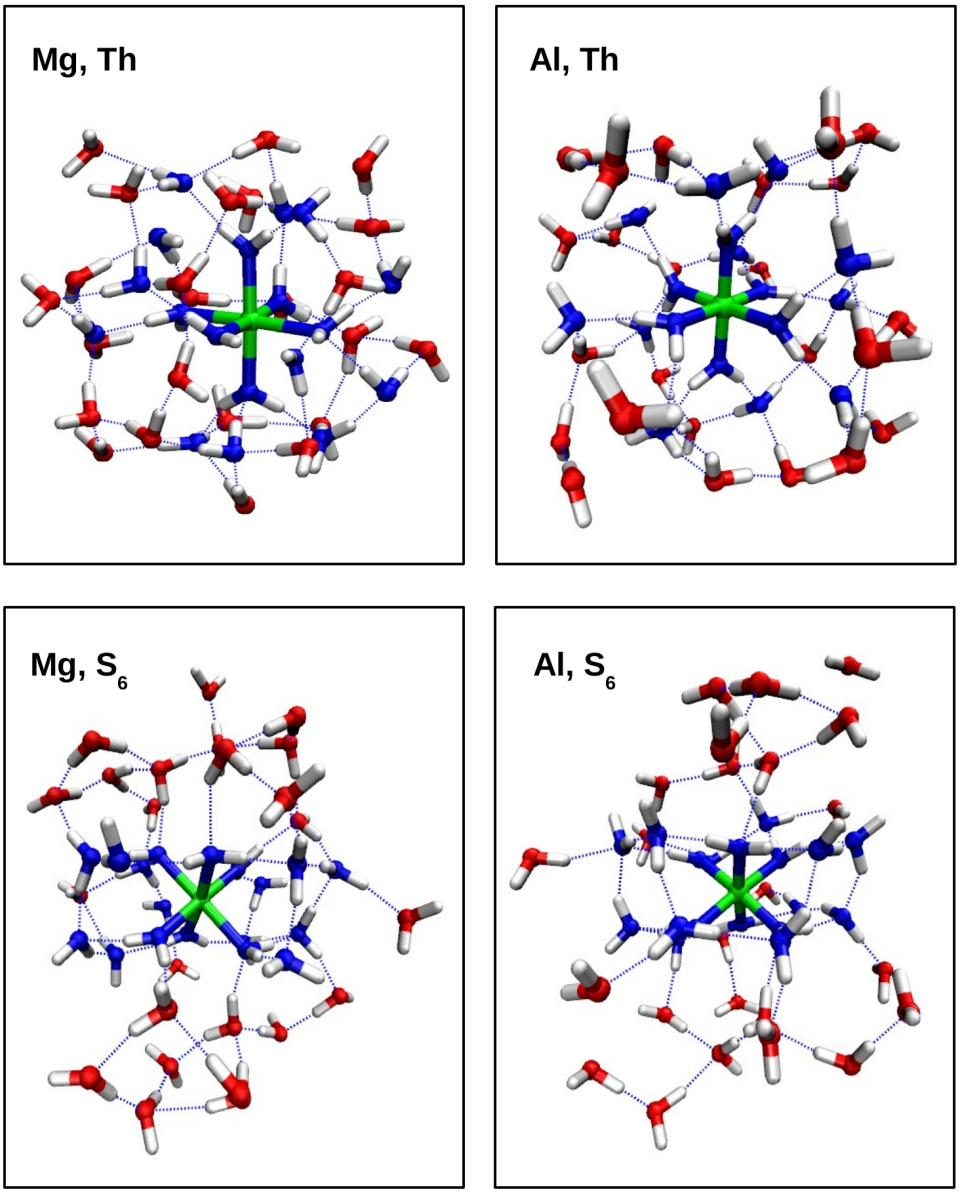

Figure 2: Final structures resulting from the annealing process for the $[Mg(H_2O)_{42}]^{2+}$ and $[Al(H_2O)_{42}]^{3+}$ clusters.

and somewhat larger in the second shell for the T_h structures. At least some hundredths of Å within this difference can be ascribed to the fact that *g.f.* are intrinsically affected of basis set superposition error while *p.w.* are not.[31] However the inner description of H_2O in the first and second shells is not affected by the use of *p.w.* or *g.f.* Furthermore, the energy difference between the T_h and S_6 structures including the metal ion plus two solvation shells is the same, within 0.3 kcal/mol, if computed with *p.w.* or *g.f.* for both

Mg^{2+} and Al^{3+}. Therefore *p.w.* provide a description equivalent to that obtained with *g.f.*, at least concerning the issues studied in this contribution, and only results obtained with the *p.w.* will be discussed in the rest of the paper.

3.2 Structural analysis

The $[M(H_2O)_6]^{m+}$ and $[M(H_2O)_{18}]^{m+}$ optimized structures for Mg^{2+} and Al^{3+} aqua ions (Fig. 1) and the final $[M(H_2O)_{42}]^{m+}$ structures obtained from the annealing process (Fig. 2) are described in Table 1 by means of selected structural data. Overall, the resulting structures are in good agreement with the data available in the bibliography for these hydration complexes.[1,3,22–26] In order to facilitate the visualization of the different T_h and S_6 structures, the cartesian coordinates of the $[M(H_2O)_{18}]^{m+}$ and $[M(H_2O)_{42}]^{m+}$ clusters described in Table 1 have been included as Supporting Information.

The QM optimization of the $[M(H_2O)_6]^{m+}$ structure yields a T_h arrangement of water molecules around the metal ion for both Mg^{2+} and Al^{3+}. However, when a second hydration shell of water molecules is considered in the calculation, two minima can be found, with T_h and S_6 symmetries, respectively. These two conformations are remarkably distinct from the geometrical point of view: in the T_h case, the water molecules in the first and second shells have a strong ion–dipole orientation towards the central cation (Fig. 1b) while for the S_6 conformer the H atoms in the first shell are tilted from their ion–dipole orientation, allowing second–shell water molecules to arrange into the shape of a crown around the metal ion (Fig. 1c,d). Due to such an arrangement of water molecules, the distance from the metal to H atoms in the first shell is slightly shorter in the S_6 conformer. This variation in the $M{-}H_I$ distance translates into a more important difference concerning oxygen atoms in the second shell of the S_6 arrangement: their distance to the central ion is circa 0.4 Å shorter in the case of Mg^{2+} and 0.2 Å for Al^{3+}. Accordingly, the $M{-}H_{II}$ distances are also shorter in the S_6 than in the T_h conformers. The rest of structural parameters reported in Supporting Information are not influenced

Table 1: Selected interatomic distances (Å) for the solvation complexes of Mg^{2+} and Al^{3+} including a different number of hydration shells. Average distances are given in the case of the $[M(H_2O)_{42}]^{n+}$ clusters. Reference data from the literature (Refs. 1,3,22–26) are given in parenthesis.

System	Symmetry	$d_{(M-O)_I}$	$d_{(M-H)_I}$	$d_{(M-O)_{II}}$	$d_{(M-H)_{II}}$
$[Mg(H_2O)_6]^{2+}$	T_h	2.21	2.90	–	–
		(2.00–2.15)			
$[Mg(H_2O)_{18}]^{2+}$	T_h	2.19	2.89	4.50	4.78, 5.39
		(2.07–2.10)			
	S_6	2.19	2.87	4.13	4.07, 5.04
		(2.10)	(2.78)	(4.13)	(5.02)
$[Mg(H_2O)_{42}]^{2+}$	T_h	2.20	2.85	4.39	4.61
	S_6	2.22	2.83	4.29	4.40

System	Symmetry	$d_{(M-O)_I}$	$d_{(M-H)_I}$	$d_{(M-O)_{II}}$	$d_{(M-H)_{II}}$
$[Al(H_2O)_6]^{3+}$	T_h	2.00	2.71	–	–
		(1.87–1.95)			
$[Al(H_2O)_{18}]^{3+}$	T_h	1.98	2.69	4.22	4.61, 5.07
	S_6	1.98	2.68	4.01	4.10, 4.87
		(1.92)		(3.99)	
$[Al(H_2O)_{42}]^{3+}$	T_h	1.98	2.68	4.28	4.78
	S_6	1.99	2.64	3.93	4.36

by one or the other symmetry type.

The distance between the metal center and the oxygen atoms in the first hydration shell (M−O_I) is shortened in the $[M(H_2O)_{18}]^{m+}$ clusters with respect to the $[M(H_2O)_6]^{m+}$ structures, since the interaction between water molecules in the first shell with outer water molecules enhances the transfer of electron density towards the metal center.[22,37] However, further inclusion of a third solvation shell translates into a slight elongation of the M−O_I distances, showing that the water–water interactions between the first and second shells are hampered by the presence of a third shell of water molecules.

The M−O and M−H interatomic distances in a $[M(H_2O)_n]^{m+}$ structure are always shorter for Al^{3+} than for Mg^{2+}, since the higher net charge on the metal center in the case of Al makes the metal–water interactions stronger. However, the difference between the M−O distances in the first and second solvation shells ($d_{(M-O)_{II}} - d_{(M-O)_I}$) is very similar for the T_h or S_6 $[M(H_2O)_{18}]^{m+}$ clusters of both Mg^{2+} and Al^{3+}. The polarization experienced by water molecules in the first shell of Al^{3+} is of greater magnitude than for water molecules in the first shell of Mg^{2+}, but this difference does not affect to a great extent the interactions between water molecules in the first and second hydration shells of the ion. Once the first hydration shell of a metal ion is defined, its interaction with the water molecules in the second shell and in the bulk is unspecific with respect to the chemical identity of the ion, but is dominated by the conformation adopted by the first shell.

3.3 Energy analysis

In order to assess the relative stabilities of the microsolvated clusters considered in this study, we have computed the energy differences between the T_h and S_6 conformers including two and three hydration shells, which are reported in Table 2. For the case of the two–shell structures, the S_6 conformer is energetically more stable than the T_h one, for both Mg^{2+} and Al^{3+}. The resulting energy differences are in agreement with the values

previously reported by Markham et al[24] for Mg^{2+} (34–41 kcal/mol). However, when a third solvation shell is included in the calculation, the tendency is reversed and the T_h arrangement is clearly favored, recovering the behavior observed for these metal ions in aqueous solution. The energy difference is so large that one would not expect to observe the S_6 conformer even at room temperature.

Table 2: Energy difference (kcal/mol) between the T_h and S_6 conformers with two and three hydration shells, including the metal hexahydrate (ΔE) or excluding it in the calculation of the total energy (ΔE^W).

	$\Delta E(T_h - S_6)$	$\Delta E^W(T_h - S_6)$		$\Delta E(T_h - S_6)$	$\Delta E^W(T_h - S_6)$
$[Mg(H_2O)_{18}]^{2+}$	+44.6	+88.4	$[Al(H_2O)_{18}]^{3+}$	+25.4	+74.3
$[Mg(H_2O)_{42}]^{2+}$	−64.8	−63.2	$[Al(H_2O)_{42}]^{3+}$	−63.6	−39.5

This behavior can be understood in terms of different interaction energy contributions. When the metal is surrounded by only the first hydration shell, the orientation of water molecules is driven by electrostatic interactions with the cation. The most stable arrangement is the one that maximizes the metal–water electrostatic interaction, but minimizes the water–water repulsion. Therefore the T_h conformer is preferred.

When a second shell of water molecules is considered, the S_6 arrangement favors attractive water–water interactions within the second shell, yielding the crown–shaped structure shown in Fig. 1c,d. The energetic gain in terms of water–water interaction is enough to modify the geometrical arrangement of the inner hexahydrate by tilting the water molecules in the first hydration shell. If a third solvation shell is added, the T_h configuration is recovered since this conformation allows a maximum interaction of the $[M(H_2O)_{18}]^{m+}$ unit with the remaining solvent molecules.

In order to illustrate these ideas, we have computed the total energy for the $(H_2O)_{12}$ and $(H_2O)_{36}$ arrangements of water molecules corresponding to the second or second–and–third solvation shells in the $[M(H_2O)_{18}]^{m+}$ and $[M(H_2O)_{42}]^{m+}$ clusters obtained from QM–optimization and annealing, respectively. To this aim the structures and spatial distribution of water molecules in the $(H_2O)_{12}$ and $(H_2O)_{36}$ systems are kept frozen with

respect to the structures of the clusters including the metal hexahydrate. The energy differences between the T_h and S_6 arrangements of second–shell $(H_2O)_{12}$ or second– and third–shell $(H_2O)_{36}$ water molecules, $\Delta E^W(T_h - S_6)$, are included in Table 2. In the clusters containing a cation surrounded by two solvation shells, $[M(H_2O)_{18}]^{m+}$, the water–water interactions are enough to stabilize the S_6 versus the T_h conformers. When a third hydration shell is included, the water–water interactions favor the T_h arrangement of water molecules around the metal ion. This result is in agreement with our picture of a S_6–crown–shaped second hydration shell in which water molecules interact with each other rather than with water molecules in some outer shell. The presence of a third solvation shell favors the maximization of the water–water interaction through adoption of a T_h–like distribution of water molecules around the metal ion.

An alternative way to consider the solvation effects is via the use of a continuum model instead of explicit water molecules to represent the solvent. In such an approximation one really deals with a cation in solution, whereas in the case of the cluster including three hydration shells the system consists of a multiply–hydrated cation in gas phase, or a drop. We have used the PCM model within the IEFPCM formalism[38] to optimize the structures of the $[M(H_2O)_{18}]^{m+}$ clusters in the T_h and S_6 arrangements. Contrarily to the results obtained using three explicit hydration shells, the preference for the T_h arrangement is not recovered using the continuum model. A detailed comparative analysis of the importance of using a molecular description of the solvent instead of a continuum representation in order to study the relative stabilities of different conformers is currently being developed in our group for a series of metal cations, and will be the topic of another publication.

3.4 Analysis of hydrogen bonds

An additional way to quantify the water–water interactions within the different hydration complexes consists in taking into account the number of hydrogen bonds (HB) established between adjacent hydration shells. We have adopted the criteria used by Chandra[39] to

define a hydrogen bond between water molecules: the distance between the two oxygen atoms is shorter than 3.5 Å, the distance between the accepting oxygen atom O* and the hydrogen atom is less than 2.45 Å, and the $\widehat{\mathrm{OO^*H}}$ angle is less that 30°. Then we define three indexes: W_1 is the number of HB per water molecule in which a first–shell water molecule takes part. W_{21} is the number of HB per water molecule established between water molecules in the second shell and water molecules in the first shell. W_{22} is the number of HB per water molecule formed between second–shell water molecules. Table 3 shows the values of these indexes obtained for the optimized $[\mathrm{M(H_2O)_{18}}]^{\mathrm{m+}}$ structures and for the final $[\mathrm{M(H_2O)_{42}}]^{\mathrm{m+}}$ structures obtained from the annealing process. In this sense, the two–shell structures serve as a reference in order to quantify the distortion from the original T_h or S_6 symmetry in the disordered $[\mathrm{M(H_2O)_{42}}]^{\mathrm{m+}}$ structures.

Table 3: Number of hydrogen bonds per water molecule in the microsolvated complexes of Mg and Al including two and three hydration shells.

	T_h			S_6		
	W_1	W_{21}	W_{22}	W_1	W_{21}	W_{22}
$[\mathrm{Mg(H_2O)_{18}}]^{2+}$	2.00	1.00	0.00	2.00	1.00	1.00
$[\mathrm{Mg(H_2O)_{42}}]^{2+}$	2.00	0.92	0.23	2.17	0.93	0.57
$[\mathrm{Al(H_2O)_{18}}]^{3+}$	2.00	1.00	0.00	2.00	1.00	1.00
$[\mathrm{Al(H_2O)_{42}}]^{3+}$	2.00	1.00	0.00	2.33	1.00	0.71

The W_1 index equals 2.00 for the two–shell structures, since in the symmetric clusters each water molecule in the first shell forms two hydrogen bonds with accepting water molecules in the second–shell. When the water molecules form the crown–shaped S_6 structure, they are distributed within a restricted volume around the metal center, and void regions are defined above and below such crown allowing for water molecules in the second shell to donate HB to first–shell water molecules, W_1 becoming greater than 2.00. This can also happen in the T_h conformer if the M−O distance is long enough, as in the case of Mg^{2+}. However in the present case there is a fortuitous cancellation: the second

shell of Mg^{2+} is not so strongly structured as in Al^{3+}, not all first–shell water molecules give 2 HB towards the second shell, and there are also first–shell water molecules accepting HB from the second shell, resulting in W_1 equals 2.00.

W_{21} equals 1.00 for the four two–shells optimized structures, since each second–shell water molecules accepts a HB from a water molecule in the first shell. In the case of the three–shell structures, for Mg^{2+} the second shell is more diffuse, less defined, there are more than 12 water molecules in the second shell and not all of them form HB with first–shell water molecules, resulting in a W_{21} value of less than 1.00. For Al^{3+} the second shell is much better defined and we do not observe a value smaller than 1.00.

The W_{22} index provides a useful and simple way to distinguish between the T_h and S_6 coordination modes. In a strictly defined, highly symmetrical T_h arrangement of water molecules, water molecules in the second shell cannot form HB with other second–shell water molecules (see Fig. 1b) and W_{22} is zero. Likewise, in a highly symmetrical S_6 arrangement, each second–shell water molecules forms a HB with another water molecules, and W_{22} is 1.00 (see Fig. 1c,d). According to this definition we can observe that in the final structures from the annealing, the symmetry of the starting configuration has remained quite unaffected in spite of the thermal fluctuations. However, the crown–like arrangement of second–shell water molecules in the S_6 conformers at the end of the annealing is slightly distorted towards the much more stable T_h conformation. The distortions from the initial symmetry are higher for Mg^{2+}, given its less defined second hydration shell. The value of W_{22} greater than zero in the T_h Mg^{2+} conformer responds to the fact that there are more than 12 water molecules in the second solvation shell of the metal, and thus there is certain degree on hydrogen bonding within the second shell.

In the absence of thermal agitation, in an ideal hydrogen–bonded structured water, each water molecule in the second shell would ideally form 4 HB in total, one of each would bind it to a water molecule in the first shell, and the other three remaining available for interaction with other water molecules. In a two–shell structure, the second–shell water

molecules achieve a higher saturation of their interaction sites by establishing HB with other second–shell water molecules, and the S_6 conformer is more stable. When a third solvation shell is considered, the more stable arrangement is the one that allows a maximum occupation of space through a maximum interaction of second–shell water molecules with other solvent water molecules. That is achieved by adopting a T_h arrangement.

4 Concluding remarks

When an aqua ion composed of a hexahydrated metal cation plus a certain number of additional water molecules distributed within different hydration shells is considered, the energetic enhancement of a T_h versus a S_6 structure, and vice-versa, is intrinsic to the arrangement of water molecules within the second shell and is a function of the degree of hydration, i.e. the number of hydration shells surrounding the metal cation determines the preferred arrangement. There are two contributions taking part: metal cation–water and water–water interactions, the water–water contribution becoming determinant when there are two or more hydration shells included to describe the system. In a structure containing two hydration shells, the key point for the appearance of the S_6 arrangement is joined to the ability of second–shell water molecules to combine their coordination with water molecules in the first shell and water–water interactions within the second shell. This can be achieved if the octahedral disposition of the hexahydrated aqua ion is distorted leading to the S_6 conformer. When a third hydration shell is added, the water molecules in the second shell form new hydrogen bonds with water molecules in the third shell, and the second–shell network is partially lost. Then the T_h conformer is recovered as the preferred conformer. The use of a molecular description of the solvent in the third solvation shell is mandatory in order to recover the T_h arrangement of water molecules, given that a continuum representation of the solvent is not sufficient to provide the solvent–solvent interactions that reverse the relative stabilities between the S_6 and T_h conformers including only two hydration shells. Furthermore, the present results show that the use of only

two hydration shells are useful to characterize gas–phase microsolvated clusters, but does not warrant a proper description of metal aqua ions in solution. The results presented in this contribution concern isolated molecular aggregates at temperatures close to 0 K. The inclusion of temperature effects and outer solvations shells to achieve the description of a condensed medium will be undertaken in the future.

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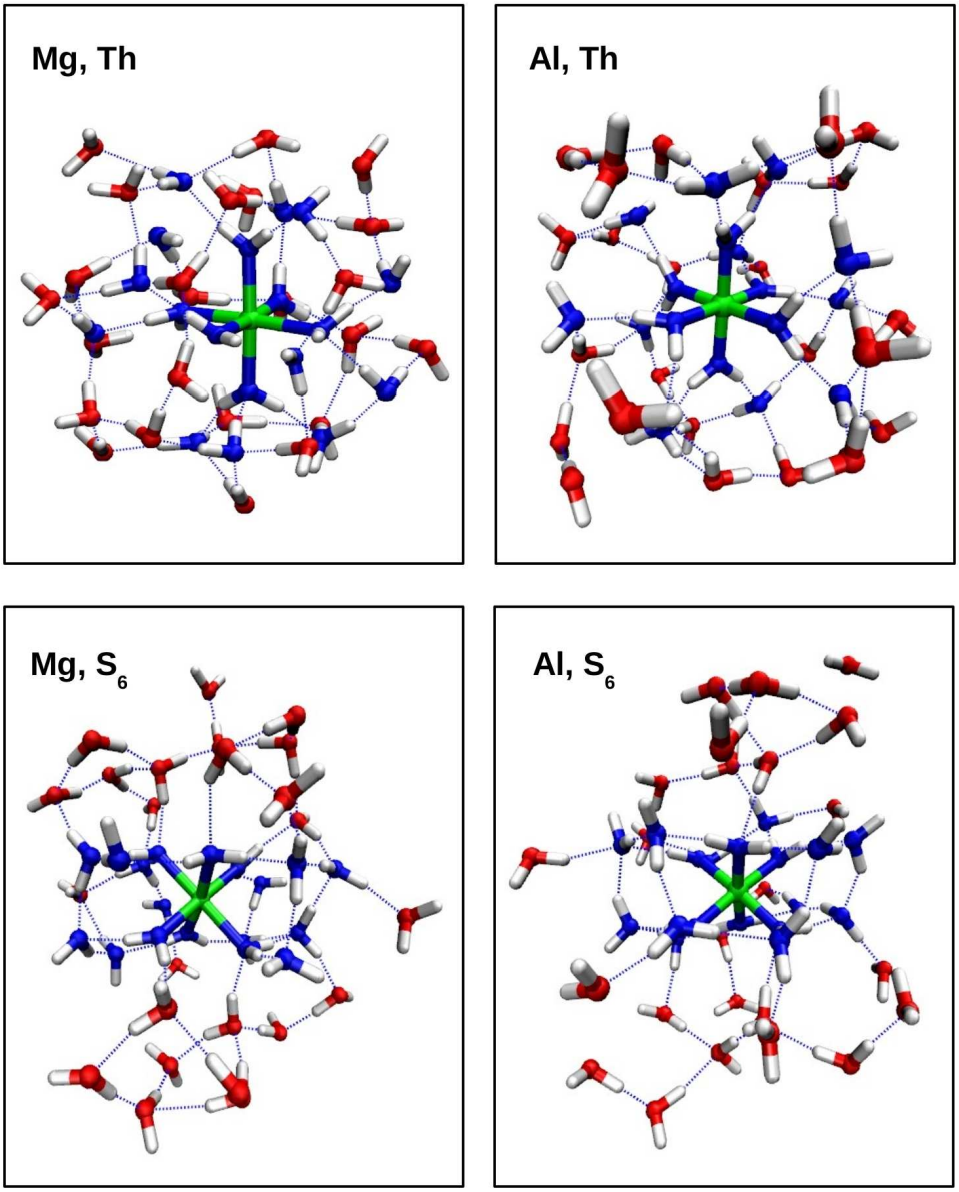

187x232mm (200 x 200 DPI)

Opposite effects of successive hydration shells on the aqua ion structure of metal cations

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Supporting Information

Comparison between the structures obtained with plane waves and with Gaussian functions.

Table 1: Comparison between the structures obtained with plane waves ($p.w.$) and Gaussian functions ($g.f.$) for the solvation complexes of Mg^{2+} and Al^{3+} including a different number of hydration shells (distances in Å and angles in sexagesimal degrees).

System	Symmetry	$d_{(M-O)_I}$		$d_{(M-H)_I}$		$d_{(O-H)_I}$		$\alpha_{(H-O-H)_I}$		$\alpha_{(O-M-O)_I}$		$d_{(M-O)_{II}}$		$d_{(M-H)_{II}}$		$d_{(O-H)_{II}}$		$\alpha_{(H-O-H)_{II}}$	
		$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$
$[Mg(H_2O)_6]^{2+}$	T_h	2.11	2.21	2.81	2.90	0.97	0.98	106.4	105.5	90.0	90.0								
$[Mg(H_2O)_{18}]^{2+}$	T_h	2.09	2.19	2.79	2.89	0.98	0.99	108.1	106.2	90.0	90.0	4.34	4.50	4.55, 5.26	4.78, 5.39	0.97	0.97	105.7	105.1
	S_6	2.10	2.19	2.78	2.87	0.98	0.99	109.6	109.0	89.0, 91.0	89.9, 90.1	4.11	4.13	4.08, 5.00	4.07, 5.04	0.97, 0.99	0.98, 1.00	106.4	105.9

System	Symmetry	$d_{(M-O)_I}$		$d_{(M-H)_I}$		$d_{(O-H)_I}$		$\alpha_{(H-O-H)_I}$		$\alpha_{(O-M-O)_I}$		$d_{(M-O)_{II}}$		$d_{(M-H)_{II}}$		$d_{(O-H)_{II}}$		$\alpha_{(H-O-H)_{II}}$	
		$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$	$g.f.$	$p.w.$
$[Al(H_2O)_6]^{3+}$	T_h	1.94	2.00	2.64	2.71	0.98	0.99	107.5	106.9	90.0	90.0								
$[Al(H_2O)_{18}]^{3+}$	T_h	1.92	1.98	2.63	2.69	1.00	1.01	109.1	108.6	90.0	90.0	4.15	4.22	4.50, 4.53	4.61, 5.07	0.97	0.98	105.5	105.1
	S_6	1.92	1.98	2.62	2.67	1.00	1.01	110.0	110.3	89.4, 90.6	89.2, 90.8	3.97	4.01	4.08, 4.83	4.10, 4.87	0.97, 0.99	0.98, 0.99	105.9	106.1

Coordinates of the optimized $[Mg(H_2O)_{18}]^{2+}$ cluster in T_h symmetry.

55

Mg	0.000000	0.000000	0.000000
O	0.000000	0.000000	-2.093442
O	0.000000	2.093442	0.000000
O	0.000000	-2.093442	0.000000
O	-2.093442	0.000000	0.000000
O	2.093442	0.000000	0.000000
O	0.000000	0.000000	2.093442
H	0.796496	0.000000	-2.670690
H	-0.796496	0.000000	-2.670690
H	0.796496	0.000000	2.670690
H	0.000000	2.670690	0.796496
H	0.000000	-2.670690	-0.796496
H	0.000000	-2.670690	0.796496
H	0.000000	2.670690	-0.796496
H	-2.670690	0.796496	0.000000
H	2.670690	-0.796496	0.000000
H	2.670690	0.796496	0.000000
H	-2.670690	-0.796496	0.000000
H	-0.796496	0.000000	2.670690
O	0.000000	3.706130	2.261862
O	0.000000	-3.706130	2.261862
O	0.000000	-3.706130	-2.261862
O	-3.706130	-2.261862	0.000000
O	-3.706130	2.261862	0.000000
O	3.706130	2.261862	0.000000
O	3.706130	-2.261862	0.000000
O	2.261862	0.000000	3.706130
O	-2.261862	0.000000	3.706130
O	-2.261862	0.000000	-3.706130
O	2.261862	0.000000	-3.706130
O	0.000000	3.706130	-2.261862
H	0.000000	3.290752	3.137853
H	0.000000	-3.290752	3.137853
H	0.000000	-3.290752	-3.137853
H	-3.290752	-3.137853	0.000000
H	-3.290752	3.137853	0.000000
H	3.290752	3.137853	0.000000
H	3.290752	-3.137853	0.000000
H	3.137853	0.000000	3.290752
H	-3.137853	0.000000	3.290752
H	-3.137853	0.000000	-3.290752
H	3.137853	0.000000	-3.290752
H	0.000000	3.290752	-3.137853
H	0.000000	4.661980	2.424881
H	0.000000	-4.661980	2.424881
H	0.000000	-4.661980	-2.424881
H	-4.661980	-2.424881	0.000000

```
H      -4.661980    2.424881    0.000000
H       4.661980    2.424881    0.000000
H       4.661980   -2.424881    0.000000
H       2.424881    0.000000    4.661980
H      -2.424881    0.000000    4.661980
H      -2.424881    0.000000   -4.661980
H       2.424881    0.000000   -4.661980
H       0.000000    4.661980   -2.424881
```

Coordinates of the optimized $[Mg(H_2O)_{18}]^{2+}$ cluster in S_6 symmetry.

```
55

Mg      0.000000    0.000000    0.000000
O      -1.091370    1.341721    1.191305
O      -0.616279   -1.616015    1.191305
O       0.616279    1.616015   -1.191305
O      -1.707650   -0.274294   -1.191305
O       1.091370   -1.341721   -1.191305
O       1.707650    0.274294    1.191305
H      -0.794481    2.246247    1.434661
H      -1.548067   -1.811164    1.434661
H       1.548067    1.811164   -1.434661
H      -2.342548    0.435083   -1.434661
H       0.794481   -2.246247   -1.434661
H       2.342548   -0.435083    1.434661
H      -2.044444    1.245917    1.413311
H      -0.056773   -2.393499    1.413311
H       0.056773    2.393499   -1.413311
H      -2.101218   -1.147582   -1.413311
H       2.044444   -1.245917   -1.413311
H       2.101218    1.147582    1.413311
O      -3.835701    0.807990    1.251012
O       1.218111   -3.725810    1.251012
O      -1.218111    3.725810   -1.251012
O      -2.617591   -2.917820   -1.251012
O       3.835701   -0.807990   -1.251012
O       2.617591    2.917820    1.251012
H      -3.829665   -0.183631    1.235513
H       2.073862   -3.224771    1.235513
H      -2.073862    3.224771   -1.235513
H      -1.755803   -3.408402   -1.235513
H       3.829665    0.183631   -1.235513
H       1.755803    3.408402    1.235513
H      -4.494373    1.067727    1.915847
H       1.322508   -4.426105    1.915847
H      -1.322508    4.426105   -1.915847
H      -3.171865   -3.358378   -1.915847
H       4.494373   -1.067727   -1.915847
H       3.171865    3.358378    1.915847
O       0.000000    3.922236    1.227865
```

O	-3.396756	-1.961118	1.227865
O	3.396756	1.961118	-1.227865
O	-3.396756	1.961118	-1.227865
O	0.000000	-3.922236	-1.227865
O	3.396756	-1.961118	1.227865
H	-0.438140	4.082511	0.353422
H	-3.316488	-2.420696	0.353422
H	3.316488	2.420696	-0.353422
H	-3.754628	1.661815	-0.353422
H	0.438140	-4.082511	-0.353422
H	3.754628	-1.661815	0.353422
H	-0.241028	4.671012	1.798031
H	-3.924701	-2.544242	1.798031
H	3.924701	2.544242	-1.798031
H	-4.165729	2.126769	-1.798031
H	0.241028	-4.671012	-1.798031
H	4.165729	-2.126769	1.798031

Coordinates of the optimized $[Al(H_2O)_{18}]^{3+}$ cluster in T_h symmetry.

55

Al	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.915848
O	0.000000	1.915848	0.000000
O	0.000000	-1.915848	0.000000
O	-1.915848	0.000000	0.000000
O	1.915848	0.000000	0.000000
O	0.000000	0.000000	1.915848
H	0.815740	0.000000	-2.496533
H	-0.815740	0.000000	-2.496533
H	0.815740	0.000000	2.496533
H	0.000000	2.496533	0.815740
H	0.000000	-2.496533	-0.815740
H	0.000000	-2.496533	0.815740
H	0.000000	2.496533	-0.815740
H	-2.496533	0.815740	0.000000
H	2.496533	-0.815740	0.000000
H	2.496533	0.815740	0.000000
H	-2.496533	-0.815740	0.000000
H	-0.815740	0.000000	2.496533
O	0.000000	3.595497	2.071728
O	0.000000	-3.595497	2.071728
O	0.000000	-3.595497	-2.071728
O	-3.595497	-2.071728	0.000000
O	-3.595497	2.071728	0.000000
O	3.595497	2.071728	0.000000
O	3.595497	-2.071728	0.000000
O	2.071728	0.000000	3.595497
O	-2.071728	0.000000	3.595497
O	-2.071728	0.000000	-3.595497

O	2.071728	0.000000	-3.595497
O	0.000000	3.595497	-2.071728
H	0.000000	3.380682	3.017778
H	0.000000	-3.380682	3.017778
H	0.000000	-3.380682	-3.017778
H	-3.380682	-3.017778	0.000000
H	-3.380682	3.017778	0.000000
H	3.380682	3.017778	0.000000
H	3.380682	-3.017778	0.000000
H	3.017778	0.000000	3.380682
H	-3.017778	0.000000	3.380682
H	-3.017778	0.000000	-3.380682
H	3.017778	0.000000	-3.380682
H	0.000000	3.380682	-3.017778
H	0.000000	4.565566	2.025984
H	0.000000	-4.565566	2.025984
H	0.000000	-4.565566	-2.025984
H	-4.565566	-2.025984	0.000000
H	-4.565566	2.025984	0.000000
H	4.565566	2.025984	0.000000
H	4.565566	-2.025984	0.000000
H	2.025984	0.000000	4.565566
H	-2.025984	0.000000	4.565566
H	-2.025984	0.000000	-4.565566
H	2.025984	0.000000	-4.565566
H	0.000000	4.565566	-2.025984

Coordinates of the optimized $[Al(H_2O)_{18}]^{3+}$ cluster in S_6 symmetry.

55

Al	0.000000	0.000000	0.000000
O	-1.367729	-0.789658	1.098471
O	1.367729	-0.789658	1.098471
O	-1.367729	0.789658	-1.098471
O	0.000000	-1.579317	-1.098471
O	1.367729	0.789658	-1.098471
O	0.000000	1.579317	1.098471
H	-2.234175	-0.339993	1.319899
H	1.411531	-1.764856	1.319899
H	-1.411531	1.764856	-1.319899
H	-0.822645	-2.104849	-1.319899
H	2.234175	0.339993	-1.319899
H	0.822645	2.104849	1.319899
H	-1.431563	-1.771702	1.294514
H	2.250121	-0.353919	1.294514
H	-2.250121	0.353919	-1.294514
H	0.818557	-2.125621	-1.294514
H	1.431563	1.771702	-1.294514
H	-0.818557	2.125621	1.294514
O	-1.454095	-3.456185	1.306924

O	3.720191	0.468809	1.306924
O	-3.720191	-0.468809	-1.306924
O	2.266096	-2.987375	-1.306924
O	1.454095	3.456185	-1.306924
O	-2.266096	2.987375	1.306924
H	-0.508404	-3.732017	1.370503
H	3.486223	1.425718	1.370503
H	-3.486223	-1.425718	-1.370503
H	2.977819	-2.306299	-1.370503
H	0.508404	3.732017	-1.370503
H	-2.977819	2.306299	1.370503
H	-1.927569	-3.943114	2.005239
H	4.378621	0.302233	2.005239
H	-4.378621	-0.302233	-2.005239
H	2.451052	-3.640881	-2.005239
H	1.927569	3.943114	-2.005239
H	-2.451052	3.640881	2.005239
O	-3.700792	0.525371	1.342533
O	1.395411	-3.467665	1.342533
O	-1.395411	3.467665	-1.342533
O	-2.305381	-2.942294	-1.342533
O	3.700792	-0.525371	-1.342533
O	2.305381	2.942294	1.342533
H	-4.102257	0.220145	0.496191
H	1.860478	-3.662731	0.496191
H	-1.860478	3.662731	-0.496191
H	-2.241779	-3.442586	-0.496191
H	4.102257	-0.220145	-0.496191
H	2.241779	3.442586	0.496191
H	-4.364646	0.365466	2.037783
H	1.865820	-3.962627	2.037783
H	-1.865820	3.962627	-2.037783
H	-2.498826	-3.597161	-2.037783
H	4.364646	-0.365466	-2.037783
H	2.498826	3.597161	2.037783

Coordinates of the $[Mg(H_2O)_{42}]^{2+}$ cluster in T_h symmetry after annealing.

127

Mg	11.915601507325	12.005157068593	11.416553119413
O	9.144492569943	13.806969884367	8.422768025689
O	12.379249673023	6.662285029345	9.703556823750
O	9.216093859130	9.385016712044	7.739896683975
O	10.296483153976	16.815602747779	14.487812770594
O	10.346273782535	7.478369663059	14.088450230459
O	13.667541152015	13.395817327791	15.546616947150
O	8.861714870999	9.179914300881	10.456477782115
O	10.584370681898	11.995122842653	17.546216993107
O	13.916168097596	11.426280419463	6.928454969181
O	13.290540826192	16.363369566140	10.050719310688

O	14.137878256586	7.391318557198	14.640403535543
O	17.051015043486	12.052530882899	16.113404806590
O	16.768425246608	9.840062691980	13.101142241874
O	16.525668523235	14.944854349391	12.098057772826
O	9.413024390269	16.397544610390	8.948322440113
O	13.091812813217	11.062497373608	16.910505246342
O	16.797832569722	9.979744792158	9.405169148754
O	14.996961190207	7.776089991077	9.833932280613
O	6.614795480582	10.309931366844	11.484285183590
O	15.701166935502	15.529962424766	9.187041799867
O	7.152553706812	15.049846097669	12.348379655855
O	8.455269418323	9.066454286639	15.343093045910
O	13.522870782043	16.997360031908	14.978864993741
O	7.545979076727	13.842709367144	14.795980964708
O	11.567142558127	12.463919140676	9.262680841826
O	14.025787421511	12.507093675328	11.377766582325
O	9.765297573409	11.566933986625	11.619454358281
O	11.595876456238	14.074786369008	12.087082107049
O	12.317523759811	9.922706367832	10.864913187350
O	12.148449089305	11.534914128342	13.541972714472
O	16.009389952604	12.474396280508	13.376567084845
O	8.034940128295	11.262299549442	13.709941883011
O	7.759770445621	13.028393087911	10.535782715902
O	9.543070065178	16.488693595163	11.791468804145
O	13.800768935561	15.628767980521	12.600256493720
O	14.402532469230	8.665584002566	12.251534585095
O	10.138783380960	6.914481007115	11.415875235197
O	12.247395896137	9.263765786558	14.939204323980
O	11.206681227425	14.515622005487	15.848026353886
O	12.318912445949	14.656138895204	8.194941931519
O	12.026295861728	9.600805257955	7.841424507325
O	15.468692249419	12.462370669953	9.031027643550
H	9.981268999754	13.318476208501	8.625463812787
H	9.345837661202	14.785802810443	8.592291488629
H	13.206431284080	7.189244789010	9.554995372090
H	11.913108355207	6.575651319240	8.824573166354
H	8.818619400612	8.539328911224	7.396446243568
H	9.062880339899	9.320268583244	8.731856763168
H	10.112600813868	16.633660223784	13.523709427583
H	9.392496657550	16.948711095126	14.879223198505
H	10.515325056868	6.555716233362	14.402870891496
H	11.052628754625	8.069425905348	14.479787179211
H	13.722470896489	13.091416820933	14.616508835054
H	12.789465618409	13.885192503237	15.602403800456
H	9.399485213873	9.914362399565	10.855654616370
H	9.282532589542	8.329828370513	10.784428992704
H	9.984330645429	12.587982312732	18.093567872202
H	10.661334233331	12.523577569476	16.722911712968
H	13.517139020881	12.030459283538	6.273343722783
H	13.182825704900	10.789533337384	7.177303210226
H	13.393857071435	16.208902128664	11.033945025120
H	12.992925181001	17.316643565713	9.944892429160
H	13.853476967229	6.435682173533	14.705859090837

H	14.677086139401	7.525418849376	15.475289224426
H	16.504702124652	11.393759883355	16.641336316648
H	17.728437185293	11.500474352045	15.675688453422
H	17.569557209060	9.794792724535	12.496337426455
H	17.005693245475	9.345100767610	13.908925443181
H	16.452980743808	13.998564254757	12.395013715870
H	16.375052499629	14.957094731517	11.121914312337
H	9.559713335790	16.426198636364	9.930074409834
H	8.459465297423	16.699898585723	8.817202904212
H	13.336733541596	11.896440375675	16.407634221706
H	12.335908609347	11.357021333492	17.480662312454
H	16.426705444837	10.884968577076	9.234205323662
H	17.461925083324	10.110379256435	10.122968425815
H	14.814191366474	7.939828004183	10.811572290558
H	15.514188414372	8.586891810037	9.596160967488
H	7.043279118476	10.743282567740	12.276280279446
H	7.347281522179	9.726163968969	11.119605589805
H	14.814572386910	15.863381544122	9.536873453534
H	16.190635436116	16.385021553905	9.033904709571
H	7.318441021450	14.334875375846	11.671241278141
H	6.171017928047	15.203906209151	12.287121268480
H	9.030771765826	8.431594534573	14.830479767605
H	8.967714203855	9.228032146097	16.190013726688
H	12.623428392986	16.816914742399	15.318575850837
H	14.169557722048	16.524831434051	15.591689654589
H	7.428663998024	14.310775346822	13.909986416558
H	8.434601969644	14.108402446537	15.107223956513
H	11.749318838874	11.705185259014	8.671785700805
H	11.998581719276	13.299198393327	8.816840477773
H	12.225216727163	10.615762629961	13.961196905904
H	14.641044481121	12.465335946813	12.150740753321
H	9.092270853721	12.151255910326	11.150722848688
H	9.323626823637	11.431389946377	12.508401896412
H	14.575691179150	12.465009974052	10.549056355402
H	12.430692931211	14.595545304608	12.273842572971
H	12.342335404221	9.604398262796	9.934070044650
H	13.054307419787	9.461556749512	11.354744142491
H	10.906894927021	14.738351956913	11.875011206128
H	11.493618389034	12.010860699089	14.085567800020
H	16.170982704906	12.607660053668	14.342454368274
H	7.837197453110	12.109668570315	14.194681004594
H	8.132785739625	13.305838728642	9.635782549574
H	8.591357919319	16.245207678655	11.948397809860
H	14.765362815017	15.393455879371	12.521611812468
H	15.227097682557	9.179019832798	12.466870995371
H	10.356165256014	7.211944912696	12.345683951675
H	12.992252781593	8.590549695623	14.834852110658
H	10.897622578939	15.196763690556	15.191406235117
H	12.573752880362	15.282688680115	8.935911743627
H	12.440811976263	8.844341507049	7.353883978109
H	14.855294202962	12.251874860496	8.277733162276
H	16.333445518977	11.539649671330	13.242977855641
H	8.192280242640	10.534389089951	14.380751402607

H	7.114956160941	12.302572990380	10.401182050890
H	9.617722443672	17.484450926806	11.659397135140
H	13.712903172834	16.171717568536	13.433894368508
H	14.291226308182	8.093584030580	13.063736787866
H	10.998587967501	6.910995393927	10.912426663160
H	12.463284062174	9.768707582984	15.771380722987
H	11.123479904995	15.022818573680	16.703913818914
H	13.089081902582	14.709032987427	7.565729777054
H	11.039667823180	9.497808364549	7.691346744497
H	15.735166240446	13.404111354404	8.920126915425

Coordinates of the $[Mg(H_2O)_{42}]^{2+}$ cluster in S_6 symmetry after annealing.

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Mg	11.875472988238	12.042543535400	12.114052818261
O	10.325715439646	10.528773617097	17.588379974518
O	15.599004724176	12.714374165387	7.287385715682
O	12.396962611582	15.701100938136	8.469400283590
O	11.184445394734	7.873798704809	7.768912994317
O	14.840807959566	15.215951223970	7.456145944900
O	7.723446246474	14.747220818835	16.474890637340
O	10.971031534090	12.083573075101	7.676693034955
O	13.599804019454	10.177237616932	4.204650101056
O	12.088052037421	13.601178674475	18.133818827083
O	7.382504116480	11.563494664589	8.148838776874
O	18.229714651685	14.058207539338	13.602878880354
O	14.704048321568	10.158284551957	17.246416332692
O	9.149634533140	12.953200343876	18.132919714441
O	8.802159756555	13.831878795346	7.287062868086
O	11.624318983098	5.747452987635	14.454670132574
O	11.449113623626	16.084644569405	17.204235182436
O	7.738612175051	8.624679525980	11.188967426503
O	13.232947515592	17.422501717670	10.356129778345
O	9.369290724349	9.960275896169	7.077040640021
O	12.585623837625	11.602969787048	16.449593044133
O	11.306057356716	6.402090075232	11.827060353380
O	16.739266584648	11.424651732597	16.048850804632
O	15.896094798994	11.773871711427	9.760848874989
O	13.469946989106	11.160849281076	6.757867811162
O	11.550484779827	10.161922326578	13.147721126964
O	13.062719083809	12.692893642465	13.919416026322
O	10.687333696404	11.359334753499	10.368422471881
O	13.605755730331	11.098255407445	11.118958198767
O	11.973926052810	13.993020842356	10.989286915151
O	10.190048034425	13.044762224490	13.136764228948
O	14.031511578762	9.096091320207	13.775794713512
O	13.380306778623	15.455023712880	14.207446409301
O	10.343984926242	8.599272817575	10.288420584026
O	16.280140691530	13.429928560158	11.768186821021
O	9.137608376307	15.322346259214	11.080510751314

O	7.686367038832	11.976666145011	12.896255934832
O	8.859912868089	9.686316616105	13.563384438462
O	15.443306086804	11.494582084090	13.672028735069
O	8.376724876721	12.671883732965	10.460164408797
O	15.265284954664	8.475490820662	11.523965694255
O	14.197041222069	15.279722758313	11.663011384554
O	9.966986942081	15.164309073557	15.029686041638
H	9.702053145879	9.962800394383	17.005600916413
H	10.564759301068	9.938172401529	18.328338850956
H	15.762878780467	12.432592263906	8.244392695058
H	14.792561422960	12.164104640560	7.037754295746
H	12.669892710227	16.348082626935	9.193129375406
H	12.035733617413	14.930212489004	8.962460368810
H	10.913780228160	8.105542373198	8.707834075843
H	10.975903344386	6.887748740152	7.682969381931
H	13.901483502701	15.284064653053	7.809167791964
H	15.105307512901	14.234100663065	7.439403859176
H	8.205292658422	14.180260822482	17.130542236717
H	6.797354494562	14.372119564644	16.433374141894
H	11.031102811607	11.875879757380	8.651463826363
H	11.875112617947	11.895854885257	7.304721736681
H	14.279656013166	9.807671393993	3.524993128187
H	13.018693003010	10.764906619293	3.685190691733
H	11.133429927288	13.394072185307	18.260524858360
H	12.393675873434	12.903532199090	17.468806402372
H	8.095170117426	10.906682043686	7.915758260982
H	6.563128001309	10.987041957622	8.300647771788
H	18.764875811795	14.870350399160	13.379882878636
H	17.847355408825	14.218486081384	14.495067741581
H	13.869930649346	10.626198602795	16.938329587410
H	14.729729299144	9.271347453860	16.789444305327
H	9.590073052552	12.056945481311	18.070217238742
H	9.226600321402	13.361177167383	19.047522351540
H	9.684592510653	13.370802228668	7.327324097918
H	8.164243944452	13.135898657273	7.584255920824
H	12.393166788391	5.970106092629	15.025202314286
H	10.833424903192	6.080760668461	14.984274535992
H	11.782090118579	15.189563576539	17.509587222698
H	10.915010792370	15.853122242201	16.390328316482
H	7.423455328503	9.547220827090	11.129340522807
H	7.071813383989	8.101381557643	10.655412588086
H	12.541501547501	17.904814797700	10.900288747455
H	13.833235750497	18.121002713835	9.978373415465
H	10.018884145937	10.724158470529	7.145465897129
H	9.895284449168	9.150793524377	7.307763656790
H	11.731194922929	11.131545122152	16.660603661378
H	12.575591160611	11.893719383824	15.495306130686
H	10.529767615251	5.833149860954	11.657335626078
H	11.492884952184	6.272673956606	12.808653332515
H	17.443813549465	10.756141637132	16.273050190510
H	15.940897518732	11.044839755184	16.536421607971
H	16.548020829137	11.053543426130	9.547197909518
H	16.276764732108	12.384983960791	10.458089985085

H	13.595053009170	10.349903676547	7.321617118082
H	13.536326171653	10.825591089407	5.822128461186
H	10.639317561702	9.843819244898	13.386431844463
H	14.003858184629	12.325562689240	13.886269351652
H	9.765424660229	11.774760219901	10.400824476506
H	13.797898906385	10.143668591854	11.232799111458
H	12.791030009656	14.535490526561	11.240066878631
H	10.212055538898	13.731081853467	13.849842860898
H	12.257983886591	9.592080931739	13.538005882469
H	13.143330179493	13.668571684883	14.107692663094
H	10.575785547142	10.364547694062	10.365743415155
H	14.374078152511	11.409089292584	10.562340835070
H	11.176184886177	14.527259916267	11.212705769510
H	9.259656899048	12.685684100301	13.134733852710
H	14.549190370745	9.946950773720	13.794538763170
H	12.662957422856	16.111209432054	14.354913586195
H	10.792912682607	8.025655467034	10.960551003982
H	15.588045795320	14.145474992491	11.708274842224
H	8.844009794253	14.386473540529	10.894479108841
H	7.917497122280	11.100570881532	13.325624725340
H	14.370195069221	8.549392962316	14.542143559901
H	14.166833378017	15.751403495852	14.758415455038
H	9.373865880027	8.535853246366	10.521291693886
H	17.009698557357	13.774714308400	12.356372189856
H	8.929452221875	15.782716190442	10.212817611656
H	7.017256028086	12.507532013548	13.396211203356
H	8.459383129662	8.984662908992	13.001573806773
H	15.813998086910	12.078863306745	12.956454542690
H	7.933139404909	12.355445762465	11.301240798501
H	14.798722921338	8.531070635157	12.418275726845
H	13.965447294121	15.454312532686	12.624795299934
H	9.796033683190	15.913555228387	14.426285224540
H	8.738632624129	9.415403718005	14.532957991351
H	16.066922722061	11.514323663894	14.456459044099
H	7.858627617800	12.328070510242	9.680688122306
H	16.062657969282	9.025036847339	11.636086930213
H	14.034921395727	16.153781958136	11.202860577766
H	9.072192497148	14.951375007902	15.433393068284

Coordinates of the $[Al(H_2O)_{42}]^{3+}$ cluster in T_h symmetry after annealing.

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Al	12.011878405780	12.142974248187	12.093336669141
O	8.766204523131	16.431585098525	9.805095014554
O	12.332343179370	6.862749862701	10.517116930038
O	11.031953465084	13.329944996934	6.132319968374
O	11.054813360007	16.960562534926	15.486586710840
O	9.869144891451	10.626519766611	17.261762818107
O	14.406674280840	12.087667624453	16.587401036169
O	9.480989605798	10.289924298158	8.270461318282

O	9.381732977335	8.420789144978	13.799237804116
O	13.618961702006	12.617857017499	5.365124625241
O	17.923609711085	15.049855812613	12.954930062282
O	11.846626838482	7.289226232496	14.845828198161
O	15.944166184332	9.096494069087	13.233537730882
O	14.088898539559	8.427186326733	16.775137874801
O	16.118205776513	15.053164999708	10.822160929770
O	11.396251255057	16.558650282770	10.440882186056
O	9.750086253329	13.329273611487	17.309928646402
O	14.693915755104	11.592040861800	7.667070788387
O	13.130500702955	7.614097096285	8.059950797867
O	7.840337096383	8.312940340622	9.039862026733
O	18.053358685815	11.158057625769	9.685363759834
O	7.904707887761	16.504246964038	12.374631582211
O	6.650879298254	9.026995777020	11.335307778008
O	16.131265413363	16.857258086767	14.306526353074
O	6.101798813752	12.585837649368	14.258460857456
O	12.121521708163	12.163478813831	10.118916763591
O	13.994832496961	12.008300564983	12.186526799237
O	10.018526178865	12.296475673664	11.942912915074
O	12.120901957088	14.095170854783	12.116558242968
O	11.881303642130	10.197563030644	12.044759325830
O	11.865038779351	12.171102312649	14.057633189207
O	15.737574876059	11.578758944865	14.220778271777
O	8.112607440722	10.885530879008	13.279969387976
O	8.415405827447	12.297994553612	9.688921392597
O	10.467440566760	15.918943767832	12.929329632975
O	14.192461793535	15.828669046273	12.462366846179
O	13.397096066917	8.139719194089	12.717409943501
O	10.111061216071	8.367050924906	11.169752660101
O	12.240845899380	10.464300337081	15.961323591126
O	11.799615540623	14.297084803310	15.878647383493
O	12.097664205857	14.238795295220	8.512659769909
O	12.373850606897	10.117811016793	8.182347409355
O	15.650299227451	12.484760242934	10.099205364672
H	9.751817874976	16.461421805524	9.984882920631
H	8.334408862660	16.500291872664	10.712948409056
H	12.070363182226	5.900170467879	10.453651146480
H	11.473534288258	7.335534634200	10.711677445611
H	10.565679849461	12.464172117424	5.945641923647
H	10.598716382555	14.013156299922	5.543333918493
H	11.419561500728	17.849967563290	15.202834921733
H	10.116716724963	17.157183727582	15.792821181993
H	9.813578301232	11.630821384521	17.349164970641
H	9.139261685646	10.399545262810	16.654598532601
H	13.517780628136	11.692867537677	16.377163073267
H	14.691389534218	11.491227771192	17.352134100210
H	9.135725038645	11.094794766768	8.775590714533
H	10.409958738310	10.145906413087	8.566719195296
H	10.223921318566	8.248714450498	14.296070101168
H	9.110451609137	9.368558211284	13.903329874368
H	12.707595447012	12.968577400488	5.572450076099
H	14.240267824756	13.395676551348	5.274575923715

H	17.349978001595	15.642229034275	13.513717614001
H	17.401612048146	14.984660197234	12.107378554269
H	12.476958868654	7.499389910251	14.097260728742
H	12.327513650394	7.591445665167	15.645500877696
H	16.485625576145	9.253637950932	12.434433749078
H	15.872312858982	10.012800134589	13.670765649122
H	14.421544838728	9.116718981228	17.450135547545
H	14.800456237164	8.360456785720	16.106399776179
H	15.946797986437	14.133242096493	10.458769166898
H	16.152466105983	15.664522773940	10.040543198802
H	11.740811338001	15.747452595982	10.003747328868
H	11.174391801182	16.323715744389	11.389470716221
H	9.846955657490	13.708673227647	18.203457724237
H	10.513130888527	13.720402067218	16.768668085099
H	14.307530449910	12.019940988274	6.842807230347
H	13.996444109791	10.932147196281	7.921367139236
H	14.119541236429	7.533936747533	8.113384785124
H	12.812917408608	7.270849925905	8.955356790580
H	8.461574397124	9.013972250508	8.670568802686
H	8.105465734163	7.418669040323	8.639659713030
H	18.131889155231	10.342202808659	10.239423306736
H	17.885727492769	10.868896390801	8.754368610090
H	7.122065640978	15.907628340406	12.583778857107
H	7.704155040588	17.356855163492	12.847089930275
H	7.106257920205	8.662361848267	10.512763203690
H	6.461404406411	8.238229224187	11.879801431985
H	15.381691594132	16.590838854044	13.709365748040
H	15.813776656669	16.630360909343	15.227735611661
H	5.994020855192	13.434007236592	13.739010491832
H	6.375573150911	12.904082442197	15.161166056174
H	12.224349260232	11.355119696456	9.555954179128
H	12.123662542450	12.981920529727	9.515227911207
H	12.013937200755	11.389333884557	14.681581764237
H	14.585735869503	11.963862224398	13.000576857083
H	9.533155306531	12.375030472604	11.070331303909
H	9.368350336611	11.817236880176	12.547900487162
H	14.592611517072	12.140397756246	11.384494003101
H	12.971400018192	14.602232402077	12.310295193597
H	11.125073519037	9.692864118663	11.625898582396
H	12.564989134358	9.503094366955	12.332189400538
H	11.365502119455	14.647162317589	12.514147833899
H	11.897426791773	13.009315635587	14.599713130815
H	15.330143540001	11.779809384153	15.115611447465
H	7.407363410080	11.496085096903	13.654824600657
H	8.283863718937	13.123401548119	9.143002766490
H	9.470505858687	16.031475540478	12.817684650086
H	14.905155715488	15.535059594631	11.795657164424
H	14.359184527495	8.390258899194	12.802172699899
H	9.351121678275	8.327689033816	10.544653848213
H	12.792469639752	9.664642717700	16.149761618137
H	11.600373095833	15.239075267009	15.628176668028
H	13.012807252093	14.391548162621	8.208019212401
H	12.667883387786	9.132250111457	8.129872599382

H	15.240334024842	12.277126676405	9.211376785104
H	16.661686000381	11.972926880580	14.243003987144
H	7.645579309510	10.354915828923	12.589105535597
H	7.490686137152	11.950612599376	9.820256522223
H	10.700599333138	16.325802365861	13.807381205766
H	13.762520264432	16.596382184273	12.035504850751
H	13.259472478337	7.558833875581	11.916997237716
H	9.736216347032	8.250550464031	12.091580972988
H	11.396270191715	10.410147867054	16.496619658193
H	12.582556304847	14.369118780936	16.495633047040
H	11.611745235741	13.956325699828	7.679352069780
H	12.066303330076	10.338098641767	7.279652442233
H	16.536772609238	12.022773399688	10.062464529004

Coordinates of the $[Al(H_2O)_{42}]^{3+}$ cluster in S_6 symmetry after annealing.

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Al	11.888684583027	12.102526619069	12.043752294716
O	16.701945170863	10.724241867080	9.077293481958
O	12.841720617915	12.676487035984	16.161162101848
O	11.549838901656	11.652904098258	6.489653812816
O	15.092098785381	6.881247068376	10.122013327431
O	15.567115192446	10.800775177920	17.474372482806
O	6.375890146897	10.542801973891	13.723802669247
O	11.277496140022	7.307473172579	6.530563259502
O	17.209391411594	14.747384869104	9.285158961707
O	9.870750880369	5.754027487881	13.035316825566
O	10.087579351000	12.613676232781	16.321077975270
O	8.491240592597	13.765685635607	7.154508012061
O	15.499915431944	14.252523569250	7.238075894524
O	12.958677287066	10.738181542205	18.049377341304
O	9.168506222055	10.412273948105	7.253809964691
O	13.197476354866	17.468385475190	9.274209438343
O	8.249907017512	10.502635986184	15.762956959273
O	16.798795602688	9.299010910543	15.609824407800
O	7.558263337007	15.483695057676	11.720616103642
O	11.795108755882	9.280486143335	5.046750353599
O	7.290106069276	13.560879778482	9.691445194370
O	15.442487575900	13.678583708992	17.049457301630
O	13.698139367619	12.226507060927	8.118118694303
O	12.466543266263	15.861230942916	19.627467163987
O	10.876998129439	16.666782211124	15.052093342353
O	10.425359841006	11.239684823782	13.032335050077
O	13.201185903604	11.484205014779	13.453211681725
O	10.565179397911	12.874700199734	10.744648387519
O	12.152842104951	10.480912000731	10.938924998350
O	13.291639456599	12.958068714148	10.905676419190
O	11.694991567718	13.764110521679	13.072172415794
O	10.490529220078	8.498201550336	13.443705077696
O	15.404691526177	12.878404163609	13.477350935128

O	8.590702055573	11.081401562975	9.904347984973
O	14.338740259285	9.171560123590	11.365701212635
O	13.030964131260	15.589148476825	11.225869797311
O	9.615832183455	14.319929920227	14.387647024483
O	8.170174283359	12.526420700356	12.838363279623
O	13.192153603272	8.868958825982	13.785395677631
O	10.209894840604	15.602316220878	11.103250851500
O	9.987661537032	8.890451153457	10.712421749224
O	15.466307238443	11.689791869312	11.050948967171
O	13.931370928037	15.251902488882	13.774161748169
H	16.889875581404	10.756777175346	8.099379354309
H	17.398619526174	10.189215521842	9.523336393110
H	11.851012414671	12.795237191534	16.223690216774
H	12.951417943184	12.232124970534	15.286473636770
H	11.571840347706	12.345731954969	5.803205716740
H	12.317096598654	11.858980350616	7.102083881179
H	15.608055828543	6.384994535641	10.786350549846
H	14.307316064912	6.288197064277	9.897268900298
H	15.600627059972	11.790280323487	17.431872918654
H	14.581574677606	10.612129259117	17.611780080219
H	5.605874778396	10.162802518164	14.216884010345
H	6.325538376524	10.181178655225	12.798442769265
H	12.019517578190	6.676884391955	6.553958514193
H	11.593683907192	8.122689577960	5.955846864203
H	17.978380040412	14.116522928806	9.448643203737
H	16.741926850836	14.804906786508	10.140789377549
H	10.195451077577	6.684952640855	12.966558909767
H	10.186213261975	5.258671127998	12.249903858181
H	9.741857118871	12.829094388567	17.233070480700
H	9.586371549620	11.802994015064	16.037824774184
H	8.702393468764	12.841310744179	6.915239245177
H	9.355836045915	14.270839837608	7.074371970734
H	14.885496205311	13.508559395741	7.474845689236
H	16.157504262476	14.321920649352	7.994825708005
H	12.822220955528	11.478648563614	17.387986670193
H	12.248778594628	10.069779241805	17.864158861927
H	10.056187965870	10.803071550212	7.016219502077
H	9.360534589784	9.504825372728	7.592689727857
H	13.582817844143	17.117000966948	8.387647555369
H	12.329218945249	17.866941186576	9.077441015725
H	7.673817990747	10.465052119967	14.949467628401
H	8.634552821569	9.570358886798	15.856544668588
H	17.525457522476	8.907328339386	16.133881247477
H	16.355649224432	9.943934604986	16.249525457957
H	7.463436172273	14.701280574304	11.111370224755
H	7.269595763092	16.232925251093	11.140276138318
H	11.873121926159	10.138730707890	5.534133818961
H	12.533198900534	9.269809009755	4.372981435587
H	7.511448751684	12.644200976063	9.972745419200
H	7.760697108007	13.687292319567	8.821293679784
H	16.143773276669	13.557112820777	16.339822796577
H	14.550755849571	13.482160377669	16.659280696292
H	14.248155393074	11.422991974896	8.229512191329

H	13.395577434709	12.448691919988	9.037291130730
H	12.713027599723	14.919051584075	19.547588935512
H	13.232509694547	16.353564198862	19.223966370595
H	11.796478976636	16.452740404157	14.795112755769
H	10.529574975270	17.277012669527	14.316426350628
H	9.486288712983	11.657689085817	12.981951844469
H	13.256985717153	10.489213609909	13.664580776288
H	10.347400441474	13.852731091383	10.833368146777
H	11.387079595750	9.852210145995	10.785071450006
H	14.242570504579	12.538799808108	10.962132189433
H	12.460511802932	14.199533562523	13.529554326569
H	10.377016102707	10.257133121542	13.223110936407
H	14.134563322999	11.904067779533	13.482761726451
H	9.761159286170	12.360744639968	10.456933537400
H	13.002383545577	9.915980536676	11.026547934016
H	13.313174817786	13.972033457633	10.957847921064
H	10.820711329083	13.971927039851	13.619125392613
H	11.480595568593	8.505489683143	13.608711868489
H	15.007134144707	13.792493267358	13.517622253016
H	9.089130680419	10.307768758456	10.305490043262
H	14.973559163252	9.934197117839	11.279781166055
H	12.052011644414	15.586378071777	11.396662246510
H	9.718323517237	13.740647910745	15.211470348768
H	10.072589641805	8.304355245267	14.338494029750
H	16.182694331908	12.921899477236	14.108415759536
H	8.718128486714	10.949287517381	8.921347293878
H	14.662604604062	8.406508909581	10.807806705867
H	13.142365371153	16.257018942333	10.491010142740
H	9.875309466174	15.240543902299	14.678926283759
H	8.368989956290	13.324487581706	13.391753095340
H	13.733154835540	8.736659520950	12.955680138869
H	9.303313401590	15.575952685893	11.538966137089
H	9.935854117205	8.475158419802	11.606624029901
H	15.950603313733	12.109771092982	11.800770643342
H	13.821927488432	15.697857364103	12.893954479602
H	7.389084324273	12.072190026019	13.233699640980
H	13.674017469761	8.409057003141	14.531515538570
H	10.020615814627	16.087869656315	10.250008504735
H	9.760255949214	8.235232800638	9.999587083722
H	16.056817158531	11.517617063020	10.237951401553
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