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Stabilization of a Cl^- – Cl^- Anion Pair in the Gas Phase: Ab Initio Microsolvation Study

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ABSTRACT: Despite the confirmation of Cl^- – Cl^- association in aqueous solution and crystalline state, there have been no reports about the existence of stable dichloride anion pair in the gas phase. In the current work we performed a systematic ab initio study of microsolvation of dichloride anion pair. The stepwise solvation mechanism observed for free gaseous $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2$ – 10) clusters was found to be quite interesting. The lowest structure for dichloride hexahydrate closely resembles cubic water octamer W8 in which two water molecules in the corners of the cube are substituted by two chloride anions. We have also shown that Cl^- – Cl^- pair may be completely stabilized by about 36 water molecules in the gas phase. Stabilization of the pair leads to the formation of cyclic H_2O structures that bridge the Cl^- ions. It has been predicted that the large clusters of $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ may exhibit properties analogous to bulk aqueous solutions, therefore they could become good molecular models for understanding complicated processes of solvation of Cl^- in the bulk.



INTRODUCTION

The understanding of many physical and chemical processes that involve fluids in the Earth's crust and reactions in oceanic and atmospheric environments requires a detailed knowledge of the mechanisms in which ions and molecules are solvated. Particularly, the hydrated chloride anions are of great significance in a variety of processes since they are the most common anions in nature playing an important role in numerous chemical, environmental, and biological systems.^{1–3} Therefore, the systematic study of the structures of chloride–water clusters at the molecular level can provide valuable insight into solvation phenomena,⁴ electrical phenomena in the troposphere and ionosphere, ion selectivity of ion channels in biological membranes, and processes on different water/membrane interfaces.⁵ Indeed, there are a lot of experimental and theoretical works on halide–water clusters, where most of these studies are devoted to hydrated monochloride anions $[\text{Cl}(\text{H}_2\text{O})_n]^-$. These hydrated anions have been characterized within lattices of organic hosts and metal complexes.^{6–9} For $[\text{Cl}(\text{H}_2\text{O})_n]^-$ ($n = 1$ – 7) clusters in the gas phase experimental photoelectron spectra have been recorded.¹⁰ Thus, properties such as coordination numbers, the stability and structures of the complexes, and their infrared spectra have been thoroughly investigated. However, theoretical and experimental studies on like-charged ion dihalide hydrates are rare and only recently became an attractive area of research. To the best of our knowledge, only five dichloride water clusters of $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$,¹¹ $[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$,^{12,13} $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$,^{14,15} $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$,¹⁶ and $[\text{Cl}_2(\text{H}_2\text{O})_{14}]^{2-}$ ¹⁷ have been obtained in the solid state as discrete units. Their salts were structurally characterized by low-temperature X-ray and neutron diffraction

studies, and the corresponding clusters $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2, 4, 6, 10, 14$) were also investigated by single crystal infrared spectroscopy. Gao et al.¹⁸ conducted a combined study of crystallographic analyses and ab initio calculations providing strong support of the possible existence of dichloride ion pair in water. It was also found that the bridging effect of water between the two anions can stabilize these clusters. X-ray diffraction¹⁹ and neutron scattering experiments²⁰ provided further evidence for the existence of halide ion pairs in high salt concentration solution.

As one can see, despite some advances being achieved for the preparation of solids with dichloride hydrate clusters and confirmation of the stable Cl^- – Cl^- anion pairs in solution, reports of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ in the gas phase are scarce. We were not able to find any experimental work on such systems in the gas phase. As for theoretical studies of stable Cl^- – Cl^- , there is only one paper, published in 1996, that is devoted to molecular dynamic simulations of dichloride anion pair in steam.²¹ Therefore it seems that gaseous dihalide hydrates have been almost completely ignored, probably because of the expectation that the electrostatic repulsion between the two anions would make the formation of dihalide hydrates in the gas phase unfavorable. This would mean that such species would be of little relevance to natural systems. However, many widely spread ions such as SO_4^{2-} or CO_3^{2-} are not stable in the gas phase²² (like Cl^- – Cl^-) due to the tremendous intramolecular

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Coulomb repulsion. However, they are stabilized in solution by the solvent. For example, it was found that both SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ require a minimum of three water molecules to be stabilized and observed by means of photoelectron spectroscopy in the gas phase.^{23,24} The study of such multiply charged ions is of great importance, since solvated clusters can provide molecular models to understand complicated processes of solvation in the bulk.²⁵

In this work we present a systematic study of microsolvation of dichloride anion pair. Although the term “like-charged ion pair” usually refers to aqueous solutions in order to emphasize nearly contact distance between the two ions, here we use the term “stable Cl^- – Cl^- pair” meaning that two chlorides do not repel each other and may coexist in a stable $\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$ cluster. Various experiments have confirmed Cl^- – Cl^- association in aqueous solution, however, an experimental and theoretical understanding of stabilization of Cl^- – Cl^- in the gas phase has not been established. The main goal of the current study is to trace microsolvation of dichloride pair and find the number of water molecules that would be sufficient to make like-charged Cl^- – Cl^- pair stable and assessable for the experimental photoelectron spectroscopy studies.

■ COMPUTATIONAL AND THEORETICAL METHODS

Finding the global minimum structure on potential energy surface (PES) was one of the main goals of our study, because the experimental conditions of thermodynamic equilibrium allow detecting only the global minimum structure or isomers that are very close in energy to their ground state.²⁶ A computational search for the lowest lying structures of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$), $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$, and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ systems was performed using the Coalescence Kick (CK) program written by Averkiev.²⁷ In the CK method, a random structure is first checked for connectivity: if all atoms in the structure belong to one fragment, then the structure is considered connected, and the Berny algorithm²⁸ for geometry optimization procedure is applied to it. However, in most cases, a randomly generated structure is fragmented; that is, the structure contains several fragments not bonded with each other, including cases with just one atom not being connected. In these cases, the coalescence procedure is applied to the fragmented structure: all of the fragments are pushed to the center of mass simultaneously. The magnitude of shift should be small enough so that atoms or molecules do not approach each other too closely but large enough so that the procedure converges in a reasonable amount of time. The obtained structure is checked for connectivity again, and the procedure repeats. When two fragments approach each other close enough, they “coalesce” to form a new fragment, which will be pushed as a whole in the following steps. Obviously, at some point, all fragments are coalesced. This method does not deal with cases when, in a randomly generated structure, two atoms are too close to each other. To avoid this problem, the initial structures are generated in a very large box with all three linear dimensions being 4^* (the sum of atomic covalent radii). Hence, usually an initially generated random structure consists of separated atoms as initial fragments. The current version of the program is designed for the global minimum searches of both single molecules of desired composition and complexes of molecules like solvated anions (e.g., $\text{SO}_4^{2-}\cdot 4\text{H}_2\text{O}$),²⁹ where the initial geometry of each molecular unit is specified in the input file. In the latter case, the two molecular units of the complex are considered as connected in a fragment if the distances

between two of their atoms are less than the sum of the corresponding van der Waals radii. In the current study, the CK method for solvated Cl^- – Cl^- anion pair (with the initial setup distance of 5.0 Å between two chloride ions) was used. The CK calculations for $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ systems become extremely computationally expensive. For the large $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ systems, we generated a large number (~ 1000) of reasonable cluster structures within a box to avoid the generation of unnecessary structures. In the first step, the single-point energy calculations of the generated structures have been performed exclusively. The lowest structures (100 structures) were then optimized to the nearest local minima to reveal the lowest energy isomers. Taking into account the fact that the number of lowest isomers, which are different in energy by only 1–2 kcal/mol, is growing exponentially with increasing number of water molecules in the system, it is difficult to explore the PES thoroughly. Therefore, we do not insist that the found lowest structures of the large chloride hydrate clusters can be represented solely by a global minimum structure. In fact, a large number of structures will contribute to the average geometry, which should be treated by statistical mechanical methods.

The CK calculations were performed at the M06-2X level of theory using the aug-cc-pvDZ basis set for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) and the 3-21G basis set for $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$, $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ cluster systems.^{30,31} Low-lying isomers were reoptimized with follow up frequency calculations at the M06-2X level of theory using the aug-cc-pvTZ ($[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$)) and the aug-cc-pvDZ ($[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$) basis sets.³²⁻³⁴ The final relative energies of the found low-lying isomers were calculated at the CCSD(T)/aug-cc-pvDZ level. The global minim geometrical structures for monochloride hydrates $[\text{Cl}(\text{H}_2\text{O})_n]^-$ ($n = 1-10, 18, 20$) have been obtained from previous experimental and theoretical reports,³⁵⁻³⁸ and optimized with follow-up frequency calculations using the same methods as for the studied $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ systems in order to trace the change in dissociation energies of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ at different numbers of water molecules (n).

The vertical detachment electron energies (VDEs) of the lowest isomers were calculated using the electron propagator method, outer-valence Green’s function (OVGF).^{39,40} The adiabatic detachment energies calculations were performed using the M06-2X level of theory. The 6-311++G** basis was used in the electron propagator calculations and aug-cc-pvDZ basis for M06-2X calculations.⁴¹⁻⁴³ All pole strengths (OVGF) exceeded 0.90.

The atomic charges on chloride anions were calculated using natural population analysis (NPA)⁴⁴ at the M06-2X/aug-cc-pvTZ level. All ab initio calculations were done using the Gaussian 09 program.⁴⁵ Molecular structure visualization was performed with the Chemcraft program.⁴⁶

■ RESULTS AND DISCUSSION

It is obvious that the two like-charged ions of Cl^- with eight electrons in the outer shell (a complete octet) repel each other. However, it is possible to overcome such repulsion between two chlorides by sequentially adding water molecules. We first performed an ab initio random search for the lowest lying structures of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$), using the M06-2X/aug-cc-pvDZ level of theory. Then low-lying isomers were reoptimized at higher level of theory (M06-2X/aug-cc-pvTZ) and single-point CCSD(T)/aug-cc-pvDZ calculations were

made in order to compare their final relative energies. By adding one water molecule to the chlorides, we did not find any isomer on the potential energy surface, because $\text{Cl}^-(\text{H}_2\text{O})\text{Cl}^-$ complex immediately dissociates into Cl^- and $\text{Cl}^-(\text{H}_2\text{O})$ anions. However, starting from $\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$, all the chloride anion pair clusters considered in the current work were found to be local minima, in spite of the strong electrostatic repulsion between the two Cl^- ions. This was confirmed by frequency calculations which yielded all positive vibrational frequencies for these structures. The calculated stabilization energies of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 1-10$) and $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) clusters relative to the infinitely separate species were determined by the following processes (eqs 1, 2) and are given in Table 1 and Table 2, respectively.

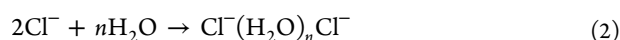


Table 1. Calculated Stabilization Energies of $\text{Cl}^-(\text{H}_2\text{O})_n$ Clusters (kcal/mol) at Different Levels of Theory

$\text{Cl}^-(\text{H}_2\text{O})_n$	M062X/ aug-cc- pvDZ	M062X/ aug-cc- pvTZ	CCSD(T)/ aug-cc- pvDZ	exp. ⁴⁷
$\text{Cl}^-(\text{H}_2\text{O})$	-15.2	-15.3	-14.6	-17.5/-13.1 ⁴⁸
$\text{Cl}^-(\text{H}_2\text{O})_2$	-31.1	-31.4	-29.7	-31.4
$\text{Cl}^-(\text{H}_2\text{O})_3$	-49.1	-49.5	-46.3	-43.6
$\text{Cl}^-(\text{H}_2\text{O})_4$	-64.2	-64.2	-61.2	-
$\text{Cl}^-(\text{H}_2\text{O})_5$	-75.4	-75.8	-72.1	-
$\text{Cl}^-(\text{H}_2\text{O})_6$	-91.6	-91.6	-88.5	-
$\text{Cl}^-(\text{H}_2\text{O})_7$	-103.0	-103.2	-100.1	-
$\text{Cl}^-(\text{H}_2\text{O})_8$	-116.5	-116.3	-113.3	-
$\text{Cl}^-(\text{H}_2\text{O})_9$	-127.1	-127.0	-123.9	-
$\text{Cl}^-(\text{H}_2\text{O})_{10}$	-140.6	-140.4	-139.2	-

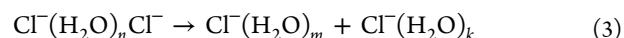
Table 2. Calculated Stabilization Energies of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) Clusters (kcal/mol) at Different Levels of Theory

$\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$	symm	M062X/aug- cc-pvDZ	M062X/aug- cc-pvTZ	CCSD(T)/aug- cc-pvDZ
$\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$	D_{2h}	15.5	14.8	15.4
$\text{Cl}^-(\text{H}_2\text{O})_3\text{Cl}^-$	C_1	-4.3	-5.1	-3.7
$\text{Cl}^-(\text{H}_2\text{O})_4\text{Cl}^-$	C_1	-27.7	-28.0	-26.3
$\text{Cl}^-(\text{H}_2\text{O})_5\text{Cl}^-$	C_1	-43.6	-44.1	-41.6
$\text{Cl}^-(\text{H}_2\text{O})_6\text{Cl}^-$	S_6	-62.9	-63.7	-61.8
$\text{Cl}^-(\text{H}_2\text{O})_7\text{Cl}^-$	C_1	-79.4	-80.1	-78.1
$\text{Cl}^-(\text{H}_2\text{O})_8\text{Cl}^-$	S_2	-95.2	-96.0	-94.3
$\text{Cl}^-(\text{H}_2\text{O})_9\text{Cl}^-$	C_1	-109.8	-110.5	-108.5
$\text{Cl}^-(\text{H}_2\text{O})_{10}\text{Cl}^-$	S_2	-123.8	-124.5	-122.3

As one can see from Table 1, Cl^- already forms a stable complex with water: $\text{Cl}^-(\text{H}_2\text{O})_n$ at $n = 1$. The computed stabilization energies are generally in agreement with experimental data (column 5 in Table 1), thus confirming the choice of the theoretical methods and basis sets employed for the current study of water–chloride systems.

The results from Table 2 demonstrate that the hydrogen-bonding interaction involving two water molecules was not sufficient to compensate the Coulombic repulsion between two chloride ions. However, we found small negative complexation energy of -3.7 kcal/mol (CCSD(T)/aug-cc-pvDZ level of theory) for $\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$ complex at $n = 3$. The complex is

further stabilized by -22.6 kcal/mol (Table 2) by adding another water molecule. Addition of more waters makes the stabilization energies of dichloride clusters comparable to those of monochloride complexes. In spite of this fact, it is necessary to evaluate the dissociation energies of dichloride hydrate clusters in order to make a conclusion about their stability in the gas phase. Therefore, we calculated the reaction energy for the dissociation process defined by eq 3:



The results of our calculations at different levels of theory are shown in Table 3. The dissociation energies for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) systems were found to be 27–45 kcal/mol exothermic. Consequently, small $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ clusters are highly unstable and would not exist in the gas phase due to more energetically favorable decomposition of $\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$ into two negatively charged monochloride hydrates. The calculated barrier (M06-2X/aug-cc-pvTZ) for the smallest $\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$ cluster appeared to be only 1.1 kcal/mol, further confirming instability of the $\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$ ($n = 2-10$) complexes.

First, we will describe local minima structures of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) clusters in order to obtain a more qualitative picture about how Cl^- – Cl^- pair is solvated by H_2O leading to the stabilization of dichloride anion pair in the gas phase, and then move on to the determination of the number of water molecules needed for the dissociation process (eq 3) to become endothermic.

$[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ Clusters. Our CK search found only one D_{2h} structure, I.1 (Figure 1A), to be a local minimum for $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ stoichiometry. Structure I.1 represents two chloride ions connected through two bridged water molecules. The Cl^- – Cl^- distance was found to be 5.77 Å at M06-2X/aug-cc-pvTZ. Despite this structure having positive stabilization energy of 15.4 kcal/mol (Table 2), it is interesting that already two water molecules are able to hold two negative chloride anions together. Moreover, structure I.1 is vertically and adiabatically electronically stable, which has been confirmed by vertical detachment electron energy (VDE) and adiabatic detachment electron energy (ADE) calculations (Table 4). The VDE and ADE for $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ cluster I.1 are 1.62 and 1.43 eV, respectively. It is also worth noting that Basu et al.¹¹ has recently shown the encapsulation of an analogous D_{2h} planar cyclic tetrameric chloride water cluster $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ within the dimeric capsular assembly of a conformationally flexible tripodal amide receptor, where $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ has acted as a template in the formation of the dimeric capsular complexes.

$[\text{Cl}_2(\text{H}_2\text{O})_3]^{2-}$ Clusters. According to the results of the CK search for $[\text{Cl}_2(\text{H}_2\text{O})_3]^{2-}$, stoichiometry structure II.1 (Figure 1B) is 0.9 kcal/mol (CCSD(T)/aug-cc-pvDZ) lower than the three-water-bridged D_{3h} structure II.2. The separation distance between two chloride anions is now 5.67 Å, which is only 0.1 Å shorter than the corresponding distance in the $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$ cluster. The results show that the two-water-bridged structure II.1 is slightly more energetically favorable than the three-water-bridged structure II.2 and structure II.3, in which two water molecules connect two chlorides and the third water forms hydrogen bonds with the other water molecules (Figure 1B). As it was mentioned above, the stabilization energy for $[\text{Cl}_2(\text{H}_2\text{O})_3]^{2-}$ is -3.7 kcal/mol, so addition of three water molecules is sufficient to offset Coulombic repulsion between the two anions and to observe the $\text{Cl}^- \cdots \text{Cl}^-$ aggregate in

Table 3. Calculated Dissociation Energies for Different Dissociation Channels $\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^- \rightarrow \text{Cl}^-(\text{H}_2\text{O})_m + \text{Cl}^-(\text{H}_2\text{O})_k$, where $m + k = n$ (kcal/mol)

method/ basis	$m = 1,$ $k = 1$	$m = 1,$ $k = 2$	$m = 1, k = 3$			$m = 1, k = 4$			$m = 1, k = 5$			$m = 1, k = 6$			$m = 1, k = 7$			$m = 1, k = 8$			$m = 2, k = 2$			$m = 2, k = 3$			$m = 2, k = 4$			$m = 2, k = 5$			$m = 2, k = 6$			$m = 2, k = 7$			$m = 2, k = 8$			$m = 3, k = 3$			$m = 3, k = 4$			$m = 3, k = 5$			$m = 3, k = 6$			$m = 3, k = 7$			$m = 3, k = 8$			$m = 4, k = 4$			$m = 4, k = 5$			$m = 4, k = 6$			$m = 4, k = 7$			$m = 4, k = 8$			$m = 5, k = 5$			$m = 5, k = 6$			$m = 5, k = 7$			$m = 5, k = 8$																																																																																																																																																																																																																																																																																																																																																																																												
			$m = 1,$ $k = 3$	$m = 1,$ $k = 4$	$m = 1,$ $k = 5$	$m = 1,$ $k = 6$	$m = 1,$ $k = 7$	$m = 1,$ $k = 8$	$m = 2,$ $k = 2$	$m = 2,$ $k = 3$	$m = 2,$ $k = 4$	$m = 2,$ $k = 5$	$m = 2,$ $k = 6$	$m = 2,$ $k = 7$	$m = 2,$ $k = 8$	$m = 3,$ $k = 3$	$m = 3,$ $k = 4$	$m = 3,$ $k = 5$	$m = 3,$ $k = 6$	$m = 3,$ $k = 7$	$m = 3,$ $k = 8$	$m = 4,$ $k = 4$	$m = 4,$ $k = 5$	$m = 4,$ $k = 6$	$m = 4,$ $k = 7$	$m = 4,$ $k = 8$	$m = 5,$ $k = 5$	$m = 5,$ $k = 6$	$m = 5,$ $k = 7$	$m = 5,$ $k = 8$	$m = 6,$ $k = 6$	$m = 6,$ $k = 7$	$m = 6,$ $k = 8$	$m = 7,$ $k = 7$	$m = 7,$ $k = 8$	$m = 8,$ $k = 8$	$m = 9,$ $k = 9$	$m = 10,$ $k = 10$	$m = 11,$ $k = 11$	$m = 12,$ $k = 12$	$m = 13,$ $k = 13$	$m = 14,$ $k = 14$	$m = 15,$ $k = 15$	$m = 16,$ $k = 16$	$m = 17,$ $k = 17$	$m = 18,$ $k = 18$	$m = 19,$ $k = 19$	$m = 20,$ $k = 20$	$m = 21,$ $k = 21$	$m = 22,$ $k = 22$	$m = 23,$ $k = 23$	$m = 24,$ $k = 24$	$m = 25,$ $k = 25$	$m = 26,$ $k = 26$	$m = 27,$ $k = 27$	$m = 28,$ $k = 28$	$m = 29,$ $k = 29$	$m = 30,$ $k = 30$	$m = 31,$ $k = 31$	$m = 32,$ $k = 32$	$m = 33,$ $k = 33$	$m = 34,$ $k = 34$	$m = 35,$ $k = 35$	$m = 36,$ $k = 36$	$m = 37,$ $k = 37$	$m = 38,$ $k = 38$	$m = 39,$ $k = 39$	$m = 40,$ $k = 40$	$m = 41,$ $k = 41$	$m = 42,$ $k = 42$	$m = 43,$ $k = 43$	$m = 44,$ $k = 44$	$m = 45,$ $k = 45$	$m = 46,$ $k = 46$	$m = 47,$ $k = 47$	$m = 48,$ $k = 48$	$m = 49,$ $k = 49$	$m = 50,$ $k = 50$	$m = 51,$ $k = 51$	$m = 52,$ $k = 52$	$m = 53,$ $k = 53$	$m = 54,$ $k = 54$	$m = 55,$ $k = 55$	$m = 56,$ $k = 56$	$m = 57,$ $k = 57$	$m = 58,$ $k = 58$	$m = 59,$ $k = 59$	$m = 60,$ $k = 60$	$m = 61,$ $k = 61$	$m = 62,$ $k = 62$	$m = 63,$ $k = 63$	$m = 64,$ $k = 64$	$m = 65,$ $k = 65$	$m = 66,$ $k = 66$	$m = 67,$ $k = 67$	$m = 68,$ $k = 68$	$m = 69,$ $k = 69$	$m = 70,$ $k = 70$	$m = 71,$ $k = 71$	$m = 72,$ $k = 72$	$m = 73,$ $k = 73$	$m = 74,$ $k = 74$	$m = 75,$ $k = 75$	$m = 76,$ $k = 76$	$m = 77,$ $k = 77$	$m = 78,$ $k = 78$	$m = 79,$ $k = 79$	$m = 80,$ $k = 80$	$m = 81,$ $k = 81$	$m = 82,$ $k = 82$	$m = 83,$ $k = 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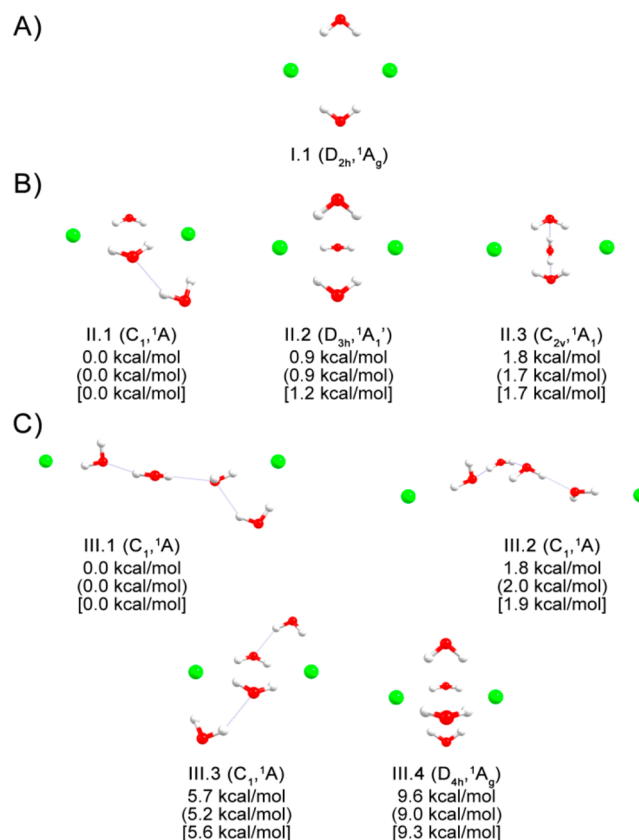


Figure 1. Representative optimized structures of (A) $[\text{Cl}_2(\text{H}_2\text{O})_2]^{2-}$, (B) $[\text{Cl}_2(\text{H}_2\text{O})_3]^{2-}$, and (C) $[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$, their point group symmetries, spectroscopic states and ZPE (M06-2X/aug-cc-pvTZ) corrected relative energies. The energies are given at CCSD(T)/aug-cc-pvDZ (bold), M06-2X/aug-cc-pvTZ (in brackets), and M06-2X/aug-cc-pvDZ (square brackets). Here and elsewhere hydrogen bonds between adjacent water molecules are marked with tiny blue lines.

Table 4. Calculated Adiabatic (ADE) and Vertical (VDE) Electron Binding Energies for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) in eV

$\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$	VDE (OVGF/6-311++G**)	VDE (M062X/aug-cc-pvDZ)	ADE (M062X/aug-cc-pvDZ)
$\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$	1.62	1.49	1.43
$\text{Cl}^-(\text{H}_2\text{O})_3\text{Cl}^-$	1.89	1.88	1.00
$\text{Cl}^-(\text{H}_2\text{O})_4\text{Cl}^-$	2.89	2.77	1.17
$\text{Cl}^-(\text{H}_2\text{O})_5\text{Cl}^-$	2.60	2.72	1.22
$\text{Cl}^-(\text{H}_2\text{O})_6\text{Cl}^-$	2.86	2.79	1.83
$\text{Cl}^-(\text{H}_2\text{O})_7\text{Cl}^-$	3.09	3.01	2.27
$\text{Cl}^-(\text{H}_2\text{O})_8\text{Cl}^-$	3.56	3.42	2.44
$\text{Cl}^-(\text{H}_2\text{O})_9\text{Cl}^-$	3.78	3.74	2.59
$\text{Cl}^-(\text{H}_2\text{O})_{10}\text{Cl}^-$	4.42	4.38	2.76

aqueous solution.¹⁸ The VDE and ADE values for the lowest structure II.1 are 1.89 and 1.00 eV, respectively.

$[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$ Clusters. From the CK search for $[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$, we found that structure III.1 (Figure 1C) without bridged water molecules and the highest Cl^- – Cl^- separation distance (11.69 Å) is the lowest energy dichloride tetrahydrate. D_{4h} symmetric four-water-bridged structure III.4 is 9.6 kcal/mol higher in energy. Therefore, although Gao et al.¹⁸ revealed that water-bridged hydrogen bonds with two chloride ions, in addition to interactions with counterions, play a major role in the stabilization of the Cl^- – Cl^- pair in the crystalline

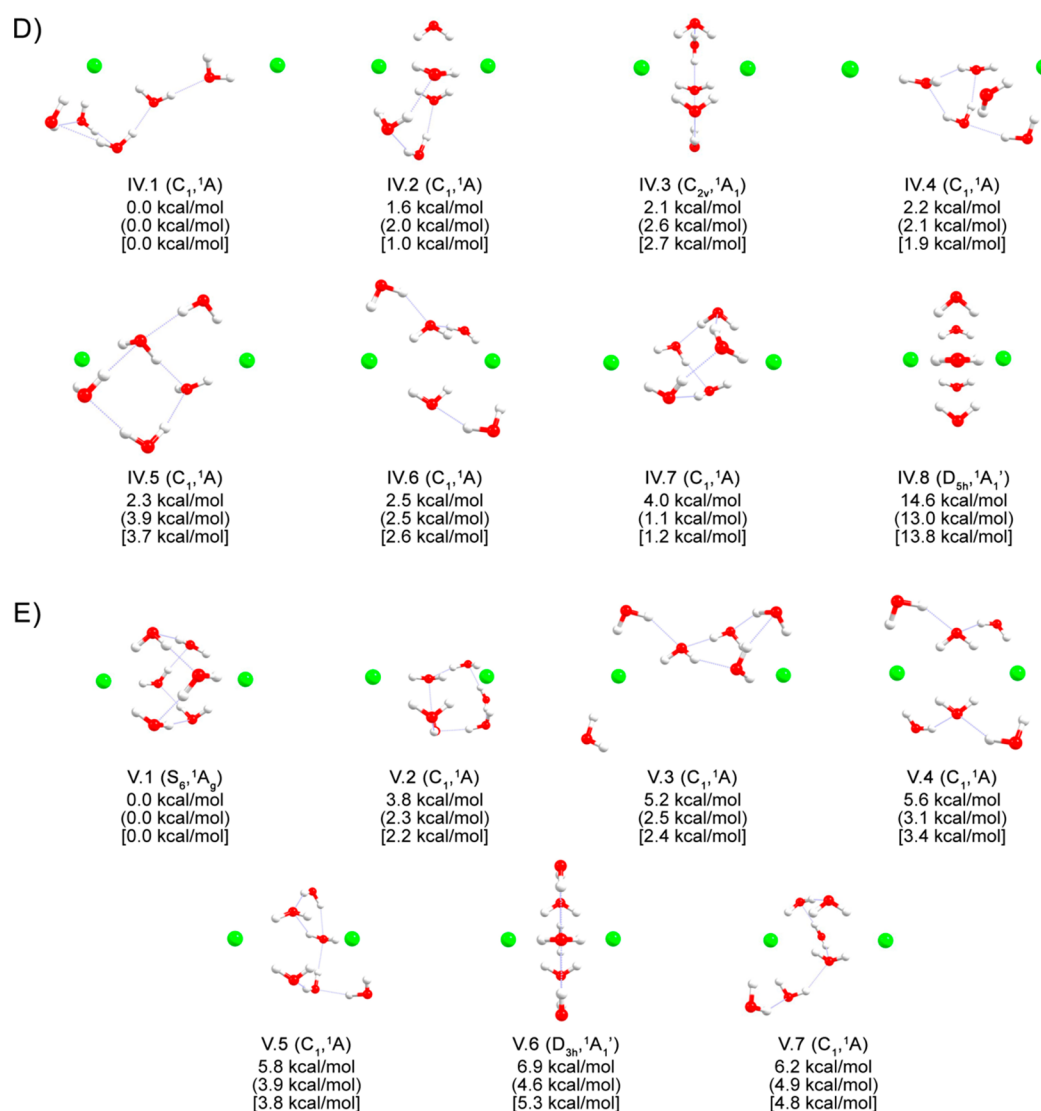


Figure 2. Representative optimized structures of (D) $[\text{Cl}_2(\text{H}_2\text{O})_5]^{2-}$ and (E) $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$, their point group symmetries, spectroscopic states, and ZPE (M06-2X/aug-cc-pvTZ) corrected relative energies. The energies are given at CCSD(T)/aug-cc-pvDZ (bold), M06-2X/aug-cc-pvTZ (in brackets), and M06-2X/aug-cc-pvDZ (in square brackets).

state, it is not the case for the gas phase. The VDE and ADE values (2.89 and 1.17 eV) for $[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$ are becoming higher compared to the smaller dichloride hydrate clusters.

Our results for the three structures of water bridged chloride clusters (structures I.1, II.2, and III.4 (Figure 1)) are in agreement with previous calculations performed by Gao et al.,¹⁸ where the corresponding like-ion chloride clusters were optimized in order to support the theoretical finding of the possible existence of a stable Cl_2^{2-} aggregate in water.

$[\text{Cl}_2(\text{H}_2\text{O})_5]^{2-}$ Clusters. The CK search of the $[\text{Cl}_2(\text{H}_2\text{O})_5]^{2-}$ species revealed that the potential energy surface has more low-lying structures than that of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-4$) (Figure 2, D). In the lowest structure IV.1, water molecules again avoid the formation of bridges between two negatively charged chloride ions. However, three-water-bridged structure IV.2 with the $\text{Cl}^- - \text{Cl}^-$ distance of 5.02 Å is higher than the lowest structure IV.1 on just 1.6 kcal/mol. The maximum number (5) of bridged waters and the smallest separation distance between two Cl^- (4.19 Å) is observed for D_{3h} structure IV.8 (Figure 2, D), which is 14.6 kcal/mol less energetically favorable than structure IV.1.

$[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ Clusters. For $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ stoichiometry, we unexpectedly found that structure V.1 (Figure 2E) of S_6 symmetry is the lowest one among other dichloride hexahydrates. Thus, for $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ we observe a new type of coordination of water molecules between the chloride anions, where the water molecules tend to adopt a cubic arrangement in the space between two Cl^- . The $\text{Cl}^- - \text{Cl}^-$ distance in structure V.1 is now balanced (6.52 Å), which is contrary to what we saw for structure III.1 of $[\text{Cl}_2(\text{H}_2\text{O})_4]^{2-}$ and structure IV.1 of $[\text{Cl}_2(\text{H}_2\text{O})_5]^{2-}$ clusters, in which the largest separation between two Cl^- was the most preferable. Interestingly, in 1991 Jordan using ab initio and model-potential calculations predicted⁴⁹ and later characterized by spectroscopic studies⁵⁰ the lowest energy structure for $(\text{H}_2\text{O})_8$ —the cubic water octamer (W8)—with the eight tricoordinated water molecules taking up positions at the corners of the cube. Therefore, the lowest structure V.1 depicted in Figure 2E can be viewed as water octamer W8, where two water molecules in the corners of the cube are substituted by two chloride anions. The structure of such dichloride hexahydrate cube, $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$, as a salt with the

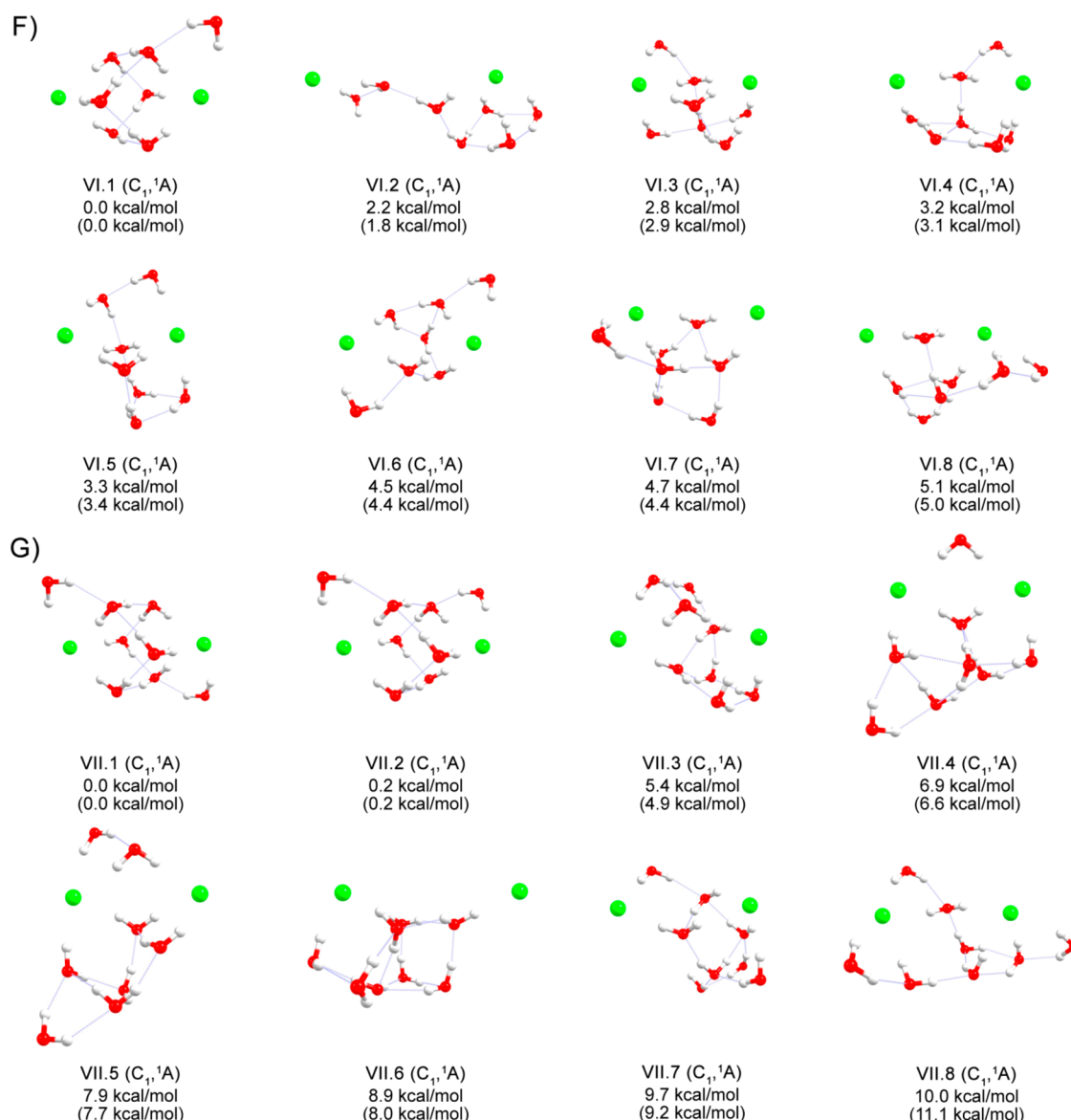


Figure 3. Representative optimized structures of (F) $[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$ and (G) $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$, their point group symmetries, spectroscopic states and ZPE corrected relative energies. The energies are given at M06-2X/aug-cc-pvTZ (bold) and M06-2X/aug-cc-pvDZ (in brackets).

tris(diisopropylamino)-cyclopropenium cation, $[\text{C}_3(\text{NiPr}_2)_3]^+$, has been determined and well characterized by low-temperature X-ray and neutron diffraction studies by Butchard et al.^{14,15} Our calculations of VDE and ADE for cubic hexahydrate V.1 also confirmed its vertical and adiabatic electronic stability (Table 4). However, despite the negative stabilization energy (Table 2) $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ clusters are still far from being able to be detected in the gas phase (the computed dissociation energy (eq 3) remains highly exothermic (-34.1 kcal/mol for $m = 3$, $k = 3$ dissociation channel (Table 3)).

$[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$, $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$ clusters. The low-lying structures for $[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$, $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$ clusters identified by the CK search are shown in Figure 3. The number of isomers grows very fast with the cluster size. Almost all of the local minimum structures now have isomers (not shown) that differ only by relative orientations of the dangling H atoms on water molecules. These isomers are all found within 0.5–1 kcal/mol from one another. However, the barriers to the interconversion of structures of each type achieved through the flipping motion of dangling hydrogen atoms appeared to be

smaller than 1 kcal/mol (M06-2X/aug-cc-pvTZ), which is below the zero-point energy of these clusters. Hence, such hydrogen flips are thermally allowed at room temperature, and these clusters would be indistinguishable. Importantly, however, the nature of the coordination of water molecules and the relative energies of typical isomers are preserved for $[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$ clusters. Since the M062x/aug-cc-pvTZ level of theory results for the energy sequence of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 3-6$) structures are generally in agreement with CCSD(T)/aug-cc-pvDZ, we did not perform single-point CCSD(T)/aug-cc-pvDZ calculations for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 7-10$) systems. The lowest structures found by our search are structure VI.1 of $[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$ and structure VII.1 of $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$ (Figure 3F,G) with a cubic arrangement between two Cl^- similarly to the structure of the lowest dichloride hexahydrate. The addition of one ($[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$) or two water molecules ($[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$) does not destruct the cubic pattern of the corresponding clusters. In structure VI.1 (Figure 3F) the water molecule forms a hydrogen bond with one of the chloride anions, and in structure VII.1 (Figure 3G)

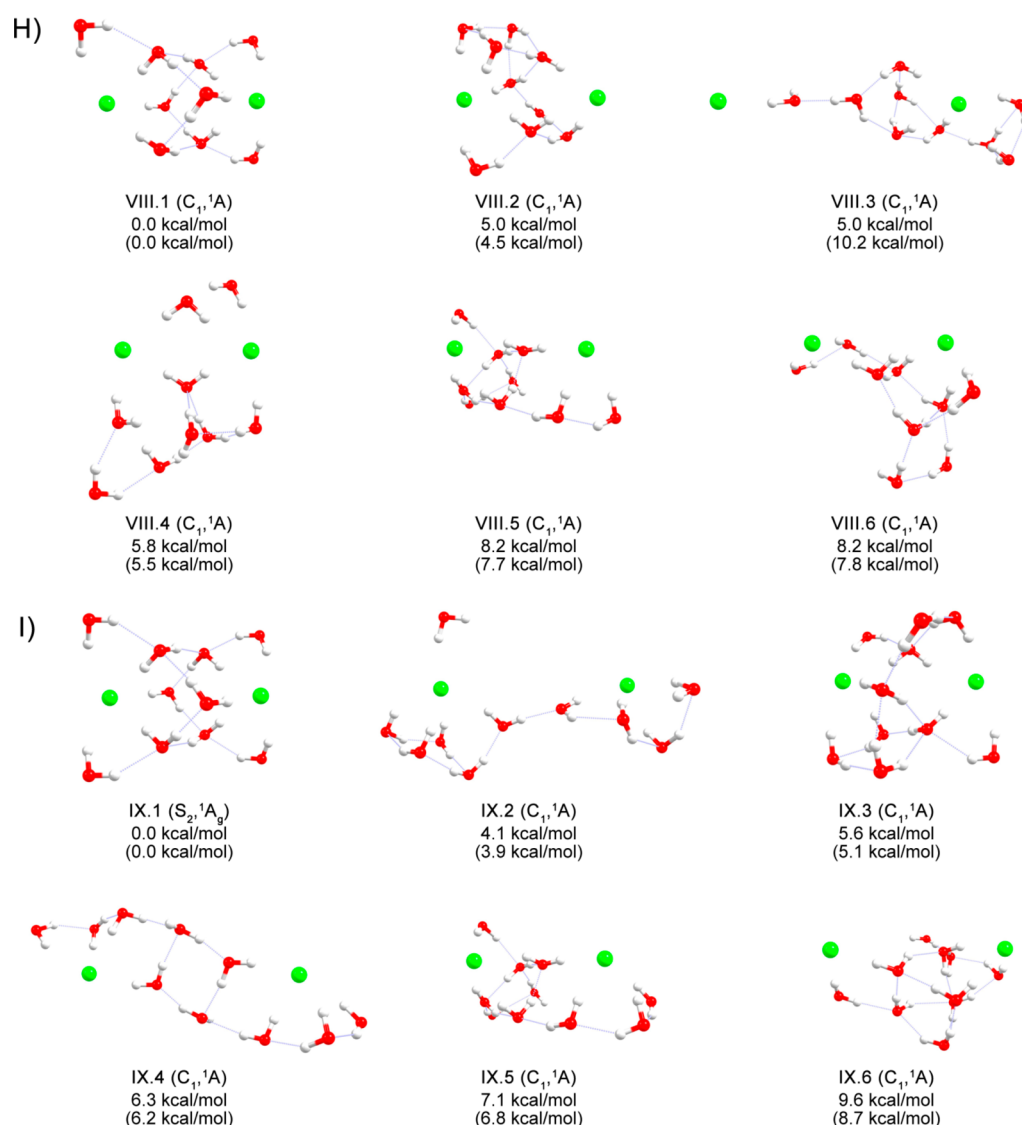


Figure 4. Representative optimized structures of (H) $[\text{Cl}_2(\text{H}_2\text{O})_9]^{2-}$ and (I) $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$, their point group symmetries, spectroscopic states and ZPE corrected relative energies. The energies are given at M06-2X/aug-cc-pvTZ (bold) and M06-2X/aug-cc-pvDZ (in brackets).

there are two water molecules that are hydrogen bonded to each of the Cl^- in trans-position. We did not find any structures with seven ($[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$) or eight ($[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$) water-bridged hydrogen bonds between chloride ions. It seems that adding more bridged waters to the chlorides causes repulsion between the adjacent water molecules, and such structures become significantly unstable.

$[\text{Cl}_2(\text{H}_2\text{O})_9]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$ Clusters. Starting with the clusters containing nine water molecules, the total number of found isomers becomes almost unmanageable. However, the lowest structures (VIII.1 and IX.1) again preserve cubic arrangement of the solvent water molecules between two Cl^- (Figure 4, H), I)). Analogous to $[\text{Cl}_2(\text{H}_2\text{O})_7]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_8]^{2-}$ clusters, the additional waters are coordinated directly to the chloride anions. It is interesting to note that the Cl^- – Cl^- separation distance (~ 6.5 Å) is almost the same for all lowest structures of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ starting from $n = 6$ until $n = 10$. Structure IX.4 of $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$, which is 6.3 kcal/mol higher than the dichloride decahydrate IX.1 (Figure 4I) has been observed in a solid-state structure of $\{[\text{Na}_2(\text{H}_2\text{O})_6(\text{H}_2\text{O}@\text{TMEQ}[6])]\cdot 2(\text{C}_6\text{H}_5\text{NO}_3)\}\text{Cl}_2(\text{H}_2\text{O})_{10}\}$, ($\text{TMEQ}[6] =$

$\alpha,\alpha',\delta,\delta'$ -tetramethylcucurbit[6]uril and can be viewed as a connection of two $[\text{Cl}(\text{H}_2\text{O})_3]^-$ clusters with a udd cyclic water tetramer through hydrogen-bonding interactions.¹⁶ One may see that for $[\text{Cl}_2(\text{H}_2\text{O})_9]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$ stoichiometries, there are many structures with cyclic water trimers and tetramers above and under the plane of chloride ions (Figure 4H,I).

The results for the dissociation energies of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2$ –10) shown in Table 3 demonstrate that the above studied cluster systems of dichloride hydrates are unstable in the gas phase. However, as the solvent H_2O number increases, the $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ clusters are gradually being stabilized. According to our calculations, the addition of the first three water molecules stabilizes the dichloride hydrate complex by as much as 10.0 kcal/mol (CCSD(T)/aug-cc-pvDZ). The complex is then further stabilized by approximately 0.5–2 kcal/mol (Table 3) by adding more and more water molecules. Consequently, the dissociation energy of our largest $[\text{Cl}_2(\text{H}_2\text{O})_{10}]^{2-}$ cluster (structure IX.1, Figure 4I) is -27.2 kcal/mol. Thus, dichloride hydrate complexes should gain additional stabilization energy of about 28 kcal/mol in order to exist as a stable gaseous Cl^- – Cl^-

pair. We believe that the repulsion between two Cl^- ions is significant since there is no sufficient dielectric screening to the electrostatic interaction between these chloride anions. Hence, to overcome such a strong electrostatic repulsion, each chloride ion in $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ cluster must be fully solvated. Kemp et al.³⁵ using the effective fragment potential (EFP) method, coupled with Monte Carlo simulations as well as HF, and MP2 calculations predicted that 18 water molecules are required to form a complete solvation shell around a Cl^- anion. Therefore, we searched for the most stable structure of $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ stoichiometry. Figure 5 (structure X) shows the global

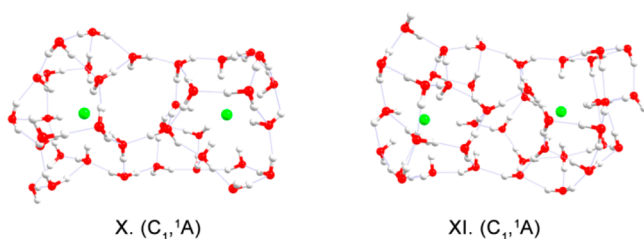
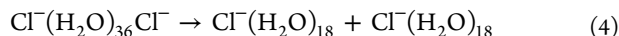


Figure 5. Optimized (M06-2X/aug-cc-pvDZ) structures of $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ (left) and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ (right) clusters, their point group symmetries, and spectroscopic states.

minimum structure optimized at the M06-2X/aug-cc-pvDZ level of theory. Interestingly, the computed dissociation energy (M06-2X/aug-cc-pvDZ), determined by the following equation:



is now +4.5 kcal/mol making reaction 4 endothermic and disadvantageous for the decomposition into two $\text{Cl}^-(\text{H}_2\text{O})_{18}$ clusters. Taking into account the fact that one of the most favorable dissociation channels for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) has been observed for $m = k$, where $m + k = n$ (Table 3 and eq 3), we think it is enough to consider only one dissociation process in order to make a conclusion about the stability of gaseous $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$. Therefore, 36 water molecules are likely needed to obtain stable Cl^- – Cl^- pair in the gas phase. Kemp et al.³⁵ also found that interior Cl^- ion of $\text{Cl}^-(\text{H}_2\text{O})_n$ is even more solvated at $n = 20$. Hence, the calculations were also performed with the Cl^- – Cl^- dianion pair and a water cluster with 40 water molecules to confirm the findings for $n = 36$. It turned out that $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ cluster (Figure 5, structure XI) is now more stabilized (+15.2 kcal/mol) than $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ with respect to the dissociation into two $\text{Cl}^-(\text{H}_2\text{O})_{20}$. The high stability of Cl^- – Cl^- pairs in the large $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters may be attributed to the delocalization of charge from the Cl^- species to the surrounding waters. To quantify the charge delocalization, the atomic charges on Cl^- ions in the clusters were calculated at the M06-2X/aug-cc-pVTZ level and are summarized in Table 5. Due to the geometric symmetries of some lowest $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ clusters, the charges on the two ions were identical within a given cluster. As one may see from Table 5, the amount of charge delocalization increased with an increasing number of water molecules for $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters: the calculated charge on Cl^- ranges from -0.98 |e| with two waters bound, to -0.85 |e| in the complex with 40 waters.

$[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters shown in Figure 5 and the structure formed by water molecules in the space between the Cl^- – Cl^- pair may not be characterized as

Table 5. Atomic Charges |e| on Ions Calculated with Natural Population Analysis (NPA)

$\text{Cl}^-(\text{H}_2\text{O})_n\text{Cl}^-$	charge on the first Cl atom	charge on the second Cl atom
$\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$	−0.9759	−0.9759
$\text{Cl}^-(\text{H}_2\text{O})_3\text{Cl}^-$	−0.9557	−0.9647
$\text{Cl}^-(\text{H}_2\text{O})_4\text{Cl}^-$	−0.9563	−0.9396
$\text{Cl}^-(\text{H}_2\text{O})_5\text{Cl}^-$	−0.9633	−0.9298
$\text{Cl}^-(\text{H}_2\text{O})_6\text{Cl}^-$	−0.9286	−0.9285
$\text{Cl}^-(\text{H}_2\text{O})_7\text{Cl}^-$	−0.9187	−0.9230
$\text{Cl}^-(\text{H}_2\text{O})_8\text{Cl}^-$	−0.9136	−0.9136
$\text{Cl}^-(\text{H}_2\text{O})_9\text{Cl}^-$	−0.9083	−0.9083
$\text{Cl}^-(\text{H}_2\text{O})_{10}\text{Cl}^-$	−0.9034	−0.9034
$\text{Cl}^-(\text{H}_2\text{O})_{36}\text{Cl}^-$	−0.8600	−0.8570
$\text{Cl}^-(\text{H}_2\text{O})_{40}\text{Cl}^-$	−0.8464	−0.8531

compact clusters. So, we do not observe two or three water bridged structures between two chlorides; instead, however, the shared waters are oriented in such a manner to create a cyclic structure that eventually bridges the Cl^- ions. Interestingly, Choi et al.⁵¹ using QM/EFP MD (quantum mechanics/effective fragment potential molecular dynamics) simulations in solution recently showed that only one-water-bridged structures were dominant at the local minimum, implying a weak dependency of ion pair structures on locally bridged waters. In $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters, the separation distance between Cl^- – Cl^- is 8.86–8.87 Å, which corresponds to 37.3 kcal/mol (M06-2X/aug-cc-pvTZ) of the Coulomb repulsion energy between bare Cl^- ions at that distance. The addition of 36 and 40 water molecules helps to overcome this high Coulomb repulsion energy. The water molecules lying in the space between the Cl^- ions are predominantly oriented in a way that the hydrogen atoms in the molecule are farther from Cl^- than the oxygen atoms due to hydrogen bonding between the shared water molecules. Also, structures formed by waters in the $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ complexes can be considered as interlacing of rings containing mostly four, five, six, and seven water molecules.

The electron binding energies VDE (Table 4) were observed to increase monotonically with the solvent number. The VDE values for $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ at $n = 36$ and $n = 40$ are as much as 6.62 and 6.86 eV, respectively. However, what is the nature of the high VDE binding energy feature in these large solvated clusters? The dimensions of our largest solvated clusters $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ are greater than 1 nm. It was observed that such water nanodroplets doped with a single solute molecule began to exhibit electronic properties similar to bulk electrolyte solutions.²⁵ Similarly to the large solvated $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ and $\text{C}_2\text{O}_4^{2-}(\text{H}_2\text{O})_n$ clusters,²⁵ the high VDE feature in $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ complexes must correspond to a new detachment channel, which may be attributed to ionization of the solvent. The ionization potentials of water clusters should be between that of gaseous water molecules at 12.6 eV and that of liquid water at 10.06 eV.⁵² Because our solvated clusters are negatively charged, the ionization potentials of water should be lowered. Indeed, it was observed that the ionization potential of a water molecule was reduced from 12.6 eV to about 6.1 eV in the $\text{F}^-(\text{H}_2\text{O})$ complex,⁵³ because of the strong Coulomb repulsion experienced by the valence electrons in H_2O from F^- ion. Therefore, stable $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ dichloride hydrates may behave analogous to bulk aqueous solutions.

However, thorough experimental photoelectron studies on gaseous $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ are needed to confirm the predicted stabilities and electronic properties of these clusters.

CONCLUSIONS

We presented a systematic ab initio study of microsolvation of dichloride anion pair by water molecules. For small $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) clusters, we obtained a clear picture of stepwise solvation and stabilization processes. We see a delicate balance between $\text{H}_2\text{O}-\text{Cl}^-$ interactions and $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions. When the solvent number is between 2 and 10 H_2O , the negative charges on Cl^- attract water strongly enough that more H-bonds are formed between Cl^- ions and waters. As the solvent number increases ($n = 36, 40$), the negative charges on chlorides are sufficiently screened that both H-bonds plus $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions, are favored. According to our results, at $n = 6$ the lowest structure of $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ represents a cube that closely resembles water octamer W8 in which two water molecules in the corners of the cube are substituted by two chloride anions. Also, adding more waters does not destruct the cubic pattern of the corresponding $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 7-10$) clusters.

It was found that the lowest structures of all studied dichloride hydrates are vertically and adiabatically electronically stable; therefore they may exist in the solid state as discrete units. However, $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ ($n = 2-10$) clusters are significantly unstable with the reaction energy for the dissociation process being highly exothermic. Thus, they would not exist in the gas phase. We predicted that the stabilization of the gaseous $[\text{Cl}_2(\text{H}_2\text{O})_n]^{2-}$ may likely be achieved at $n = 36$. The complex $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ is further stabilized by adding four water molecules. The only stable anion pairs of Cl^- are in fact hydrogen-bonded clusters of $\text{Cl}^-(\text{H}_2\text{O})_n$. Hence, they are not real dianions, but anion clusters which are large enough that the hydrogen bonds of the outer water molecules are stronger than the Coulombic repulsion between two Cl^- .

The stability of the large $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters may be attributed to the delocalization of charge from the Cl^- species to the surrounding waters. It was also found that in these large $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ clusters, stabilization of the Cl^--Cl^- pair leads to formation of cyclic H_2O structures. The water molecules formed rings or interlacing of rings depending on the size of the system. The waters in the space between two Cl^- were organized in such a way that bridged the Cl^--Cl^- pair. According to our calculations, $[\text{Cl}_2(\text{H}_2\text{O})_{36}]^{2-}$ and $[\text{Cl}_2(\text{H}_2\text{O})_{40}]^{2-}$ complexes possess the high VDE binding energies, which is the characteristic feature for bulk electrolyte solutions. We think that the association of stable gaseous Cl^--Cl^- anion pairs may play an important role in nucleation of industrial steam or geothermal steam from the Geysers wells.⁵⁴ Moreover, the studied solvated chloride clusters may be viewed as molecular models for understanding physicochemical processes in aqueous solutions containing Cl^- ions.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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