

for the nonhydrogen atoms and important bond lengths and angles are given in Tables I and III, respectively.

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125615-90-9; 13, 137039-46-4; (Z)-dbb, 57788-53-1; (E)-dbb, 62444-32-0; HC≡C'Bu, 917-92-0; Ru(CO)(PPh₃)₃(H)(C≡CPh), 125615-95-4; Ru(CO)(PPh₃)₃(H)(C≡CSiMe₃), 125615-96-5; HC≡CSiMe₃, 1066-54-2; Ru(CO)(PPh₃)₃(C≡CSiMe₃)₂, 137039-47-5; Ru(CO)(PPh₃)₃(C≡CPh)₂, 137039-48-6; RuCl(CO)(PPh₃)₃H, 16971-33-8; RuCl₂(PPh₃)₃, 15529-49-4; RuBr₂(PPh₃)₃, 15709-75-8; C(C≡C'Bu)≡C'Bu, 6130-98-9; Ru(cod)(cot), 42516-72-3.

Supplementary Material Available: Tables of positional and thermal parameters for 12 and a full tabulation of bond distances and angles (5 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Ab Initio and Crystal Structure Analysis of Like-Charged Ion Pairs

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Abstract: A combined approach of crystallographic analyses and ab initio molecular orbital computations provides strong support to the previous theoretical finding of the possible existence of a stable Cl₂²⁻ aggregate in water. Consistent with previous explanations, the stabilization of like-charged ion pairs in aqueous solution was rationalized by the Born model of solvation and the solvent-bridged hydrogen-bonding interactions that offset Coulombic repulsion between the two anions. Analysis of the Cambridge Structural Database revealed correlation patterns in hydrogen-bonding interaction. Further, the ab initio results were compared with those predicted using empirical potential functions and good agreement was obtained.

Introduction

Electrostatic interactions play a key role in determining the function and reactivity of biological molecules in aqueous solution.² Consequently, the study of ionic solvation has been a central theme in physical chemistry.³ An important phenomenon of electrolytic solution is the formation of ion pairs consisting of oppositely charged species proposed in the Bjerrum theory.^{3b,4} This has now been supported by many experimental investigations including neutron and X-ray diffraction studies.⁵⁻⁷ However, more detailed understanding of the molecular interactions in solution was aided through computer simulations of ion pairs in water. These computations revealed an oscillatory behavior in the potential of mean force (pmf) for cation-anion interactions, corresponding to contact and solvent separated ion pairs.⁸⁻¹² Moreover, a striking finding in both integral equation computations and simulation studies is the observation of a stable, like-charged ion pair in aqueous so-

lution near contact distance between two chloride ions.^{9,10,13,14} Stabilization of the anion pairing has been attributed to the formation of several bridging hydrogen bonds between water molecules and the two Cl⁻ ions.^{13,14}

Experimental evidence for the possible existence of halide ion pairs in solution was provided by NMR and diffraction measurements. The NMR relaxation data for aqueous alkali halide indicated long-lived anion pairing with strong stabilization for F⁻...F⁻.¹⁵ Further, X-ray diffraction patterns obtained by Smith and Wertz for aqueous lanthanum(III) chloride supported a Cl⁻...Cl⁻ distance of 4.7 Å at high concentrations.¹⁶ Similar results were obtained by neutron diffraction studies.^{5,6} However, these experiments were typically performed at high salt concentrations, making comparison with the computed pmf difficult. Convincing evidence is now provided from the analysis of X-ray crystal structures containing halide ions. A survey of the Cambridge Structural Database (CSD) revealed that contact chloride pairs are common in the crystalline state.

Questions concerning the accuracy of the theoretical results still remain in computer simulation studies of ion pair in solution because pair-wise, effective potential functions are typically

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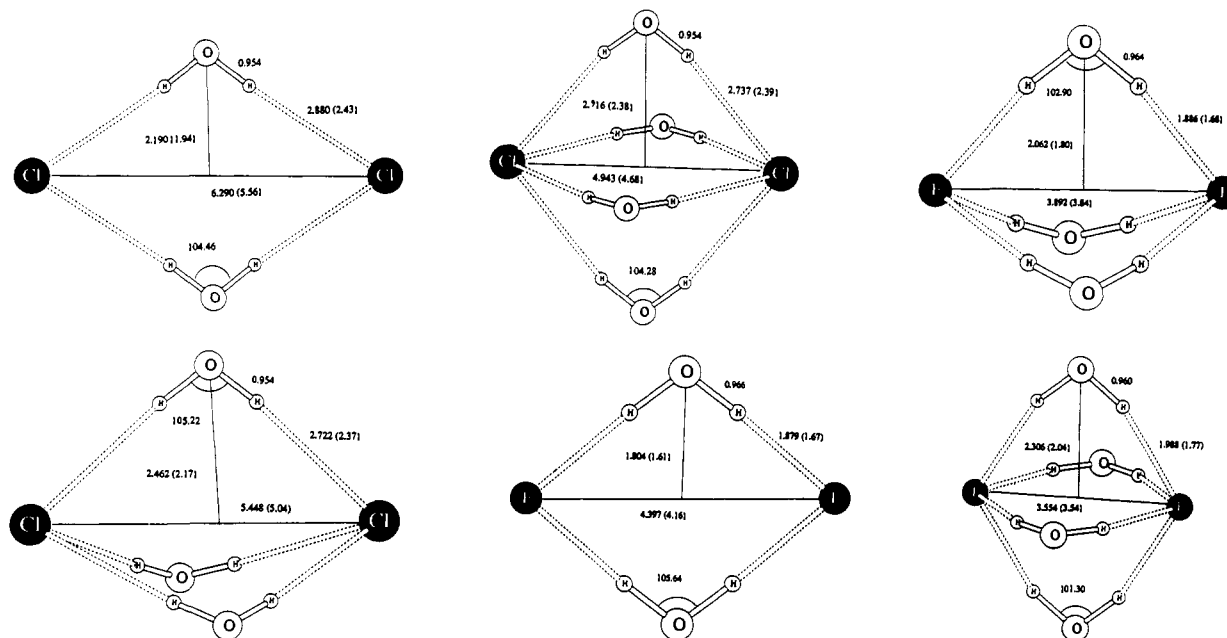


Figure 1. Optimized structure using 6-31+G(d) basis set and empirical potential function (number in parentheses). Bond length in angstroms.

used.⁸⁻¹⁴ Zhong and Friedman, applying integral equation methods, found that the distinct diffusion coefficient was inconsistent with the formation of like-charged ion pairs in water.¹⁷ Additionally, calculations based on a continuum electrostatic theory failed to produce the contact ion pair minimum on the potential of mean force.¹⁸ On the other hand, it has also been suggested that long-range Born polarization energy might be responsible for the stabilization of paired ions with the same charge.^{19,20} Recently, Jarque and Buckingham evaluated the polarization energy for a model polarizable lattice consisting of two point charges.²⁰ They found that the attraction due to the polarization effect could exceed the Coulombic repulsion between two like-charged ions with large effective polarizability. To address these questions, we have carried out ab initio molecular orbital (MO) calculations on like-charged ion pair/water clusters for the $F^- \cdots F^-$ and $Cl^- \cdots Cl^-$ systems. Energetic and geometrical results are compared to findings of the Cambridge Structural Database analysis. Below, computational details are first given followed by results and discussion.

Computational Details

Ab initio SCF calculations of fluoride and chloride ion pair water clusters were executed with the GAUSSIAN 88 program²¹ on IBM 3090 and Stardent 3000 computers. Geometry optimizations were carried out by energy gradient methods for all structures with the 6-31G(d) and 6-31+G(d) basis functions,²² which are a split valence type consisting of a set of d orbitals on all non-hydrogen atoms. In addition, the 6-31+G(d) basis set includes s and p type diffuse functions for all heavy atoms.^{22b} The diffuse functions are known to be important for study of electronic structures of anionic systems.^{22,23} To incorporate electron correlation effects, the 6-31+G(d) geometries and basis set were subsequently uti-

lized in the third-order Moller-Plesset perturbation computations.²⁴ Thus, the standard notation is MP3/6-31+G(d)//6-31+G(d). In the MP3 calculations, frozen-core approximation was adopted.

In most cases, geometry optimization was performed with constraints of the highest symmetry in the system (Figure 1). A separate computation for the $F^-(H_2O)_2F^-$ complex without imposing any geometrical restrictions resulted in the same D_{2h} structure. Apparently, the D_{nh} geometry in $X^-(H_2O)_nX^-$ ($X = F, Cl$; $n = 2, 3$, and 4) minimizes electrostatic interactions between the bridging water monomers. The $X^-(H_2O)_n$ ($n = 1, 2$, and 3) complexes were investigated for comparison with the ion pair clusters, also using the D_{nh} symmetry.

To evaluate the validity of empirical potential functions for condensed phase simulations, molecular mechanics calculations were performed on these systems. The OPLS parameters for the ions were tested in conjunction with the TIP4P water model.²⁵ These parameters are similar to those used in the pmf computations for $Cl^- \cdots Cl^-$ in water.^{13,14}

Results and Discussion

Analysis of Crystallographic Data. A connectivity search of the Cambridge Structural Database (CSD)²⁶ for the $Cl^-(H_2O)-Cl^-$ fragment, without applying any geometrical restrictions, was first enacted and yielded 900 structure hits. These structures, excluding metal complexes with chloride ligands, were then used for further analysis. When distance constraints of 6 Å between two chloride ions and 3.75 Å for the O_w-Cl^- separations were added, a total of 33 structures were found, in which at least one water molecule is simultaneously hydrogen bonded to two chloride ions with both hydrogen atoms. Of course, the anion pairs were also stabilized through interactions with countercations in the crystal. The average Cl-Cl distance for these structures is 5.1 ± 0.5 Å. Figure 2 illustrates two structure fragments near the contact chloride pairs found in the crystals.²⁷ It should be mentioned, however, that the geometry analysis was limited to the primary unit cell only. Obviously, inclusion of interactions

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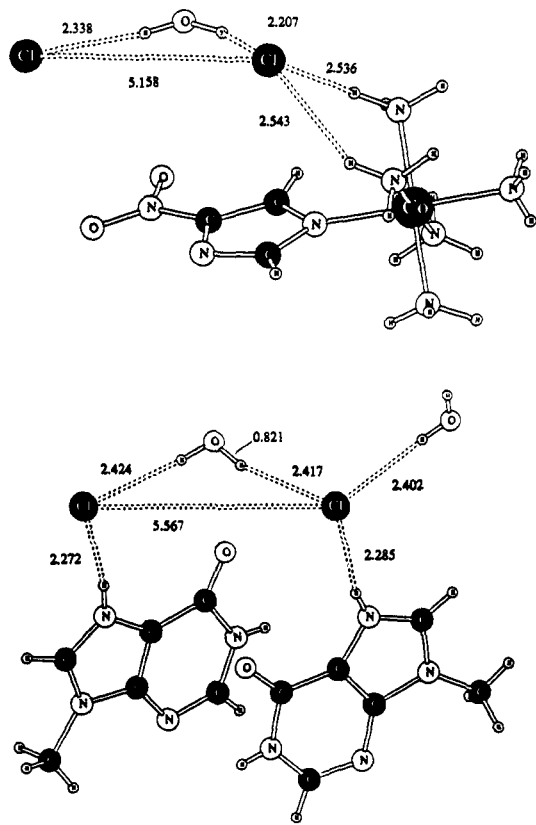


Figure 2. Crystal structures containing the Cl_2^{2-} aggregate stabilized by solvent-bridged hydrogen bonds (ref 24).

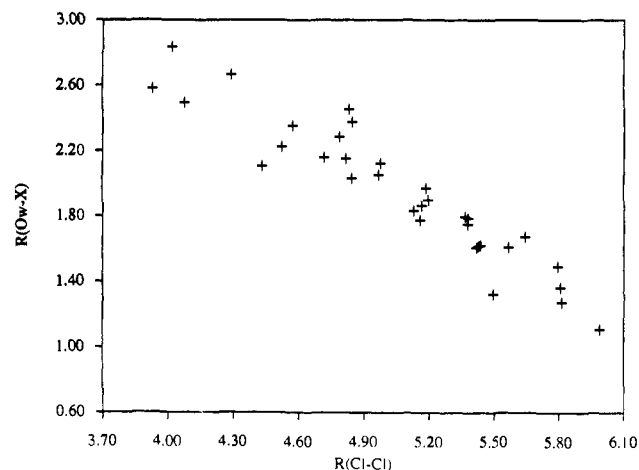


Figure 3. Correlation of the distance of O_w from the $\text{Cl}-\text{Cl}$ axis and $\text{Cl}-\text{Cl}$ separation. Data from the Cambridge Structural Database. A list of references and CSD refiles is given in the supplementary material.

with the neighboring unit cells would produce many more structures. Nevertheless, the existence of the chloride ion pair near the contact distance in the crystalline state is evident and provides strong support to the simulation results.

In Figure 3, the distance of water oxygen from the $\text{Cl}-\text{Cl}$ axis is plotted versus the chloride ion separation ($R_{\text{Cl}-\text{Cl}}$), while Figure 4 shows the sum of the two $\text{Cl}-\text{O}$ distances (R_i) in the bridged structures as a function of $R_{\text{Cl}-\text{Cl}}$. Clearly, a qualitative correlation exists in Figure 3 (with a correlation coefficient of -0.94); as the $\text{Cl}-\text{Cl}$ distance decreases, the bridging water molecule is pushed farther out from the central axis. Although the dependence in Figure 4 is less apparent ($r = -0.37$), there is a somewhat more populated distribution of R_i between 6.2 and 6.6 Å along the entire abscissa. This would translate to a distance of ca. 3.1–3.3 Å between the water oxygen and Cl^- atoms, close to the optimal distance for a linear Cl^- -water hydrogen bond. Thus, it seems that water molecules in the bridged structures tend to keep the

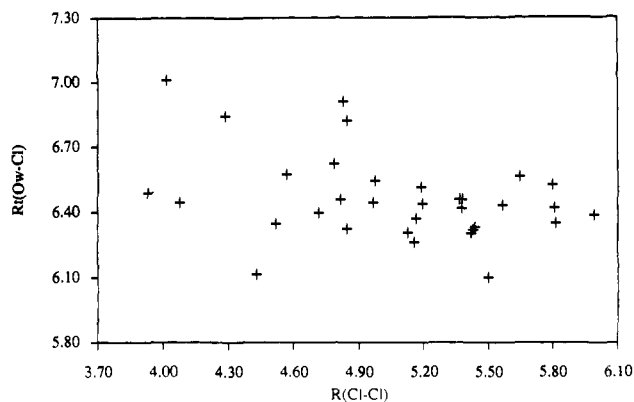


Figure 4. Correlation of the sum of O_w-Cl distances and $\text{Cl}-\text{Cl}$ separation. Data correspond to the same structures shown in Figure 3.

hydrogen bonding interaction with Cl^- optimal as the interionic distance varies. Consequently, at a short $\text{Cl}-\text{Cl}$ separation, the $\text{Cl}-\text{O}-\text{Cl}$ angle becomes smaller, leading to a longer distance between the water oxygen and the $\text{Cl}-\text{Cl}$ axis (Figure 3). This trend also mirrors the structural features obtained from the ab initio optimizations (see below).

$\text{X}^-(\text{H}_2\text{O})_n\text{X}^-$ Clusters. The optimized structures at the 6-31+G(d) level for the $\text{F}^-\cdots\text{F}^-$ and $\text{Cl}^-\cdots\text{Cl}^-$ ion pairs with 2–4 bridging water molecules considered in the present work are shown in Figure 1 along with key geometrical variables. Details for the \mathbf{Z} matrix and total energies are provided in the supplementary material. Structural and energetic results are discussed below.

The computed stabilization energy of the ion pair clusters relative to the infinitely separate species is defined by the following process (eq 1) and given in Table I. Interestingly, all the ion pair



clusters considered here were found to be energy minima at the 6-31G(d) level, despite the strong electrostatic repulsion between the two halide ions. This was confirmed by force field calculations which yielded all positive vibrational frequencies for these structures. However, $\text{F}^-(\text{H}_2\text{O})_4\text{F}^-$ and $\text{Cl}^-(\text{H}_2\text{O})_2\text{Cl}^-$ became saddle points when the 6-31+G(d) basis set and geometries were used (one negative eigenvalue was found in the force constant matrix for each of the two structures). Not surprisingly, the D_{2h} structure in the chloride system has a large positive complexation energy, while the change in the $\text{F}^-(\text{H}_2\text{O})_4\text{F}^-$ complex may reflect a packing congestion around the smaller fluoride ions. Note that previous Monte Carlo simulations of halide ions in dilute aqueous solution yielded coordination numbers of 6.2 and 7.4 for F^- and Cl^- , respectively.

As shown in Table I, water molecules were found to be much more efficient in stabilizing the fluoride ion pair than the corresponding chloride system. For the $\text{F}^-(\text{H}_2\text{O})_n\text{F}^-$ clusters, all three structures have negative stabilization energies. At the MP3/6-31+G(d)//6-31+G(d) level, the calculated interaction energies are -2.4 , -30.8 , and -48.1 kcal/mol for $n = 2, 3$, and 4, respectively. On the other hand, the D_{2h} structure in the chloride system was predicted to be 15 kcal/mol above the isolated monomers. Apparently, the hydrogen-bonding interaction involving two bridging water molecules was not sufficient to redeem the Coulombic repulsion between two chloride ions. Although modest, the complexation energy with three water hydrogen-bonded bridges was found to be -3.0 kcal/mol at the MP3/6-31+G(d) level, whereas it is still positive without including electron correlation. The complex is further stabilized by -14.6 kcal/mol at the MP2/6-31+G(d) level (MP3 calculations failed due to disk size limitation) by adding another bridging water. It is noticed that, in the fluoride system, the larger gain in energy on going from two to three bridging waters (28.4 kcal/mol) than from three to four (17.3 kcal/mol) reflects the balancing effect between the favorable hydrogen-bonding interactions and the steric and electrostatic congestions among the water molecules. For a comparison, since the van der Waals radius of Cl^- is much larger than that of F^- , leading to a longer hydrogen bond, the Coulombic

Table I. Computed Stabilization Energies for $X^-(H_2O)_nX^-$ ($X = F$ and Cl) Complexes (kcal/mol)^a

$F^-(H_2O)_nF^-$	symm	6-31G(d)	6-31+G(d)	MP2/ 6-31+G(d)	MP3/ 6-31+G(d)
$F^-(H_2O)_2F^-$	D_{2h}	-29.0	-3.0	-2.5	-2.4
$F^-(H_2O)$			-21.5	-23.3	-23.2
F_2^{2-}			74.9	74.7	74.8
$(H_2O)_2$			4.3	1.6	1.8
$F^-(H_2O)_3F^-$	D_{3h}	-68.5	-22.3	-30.8	-30.8
$F^-(H_2O)$			-21.9	-23.6	-23.5
F_2^{2-}			84.3	84.0	84.1
$(H_2O)_2$			4.3	1.8	2.0
$F^-(H_2O)_4F^-$	D_{4h}	-91.0	-37.4	-47.8	-48.1
$F^-(H_2O)$			-21.0	-22.4	-22.3
F_2^{2-}			92.0	91.6	91.6
$(H_2O)_{2\perp}$			5.6	3.5	3.6
$(H_2O)_{2\parallel}$			2.91	1.3	1.4
$Cl^-(H_2O)_2Cl^-$	D_{2h}	16.5	19.0	14.6	15.2
$Cl^-(H_2O)$			-9.7	-10.9	-10.8
Cl_2^{2-}			52.4	52.2	52.2
$(H_2O)_2$			1.7	0.9	1.0
$Cl^-(H_2O)_3Cl^-$	D_{3h}	-0.4	4.5	-3.9	-3.0
$Cl^-(H_2O)$			-11.0	-12.6	-12.4
Cl_2^{2-}			60.1	59.8	59.8
$(H_2O)_2$			1.7	0.8	0.9
$Cl^-(H_2O)_4Cl^-$	D_{4h}	-13.7	-7.4	-18.5	
$Cl^-(H_2O)$			-11.3	-12.8	-12.7
Cl_2^{2-}			65.9	65.4	65.4
$(H_2O)_{2\perp}$			2.2	1.2	1.3
$(H_2O)_{2\parallel}$			1.2	0.5	0.5

^a Pair interaction energy was calculated using the geometry in the corresponding complex.

Table II. Computed Complexation Energies for $X^-(H_2O)_n$ and Dissociation Energies for $X^-(H_2O)_nX^- \rightarrow X^-(H_2O)_m + X^-(H_2O)_p$, $n = m + p$ (kcal/mol)

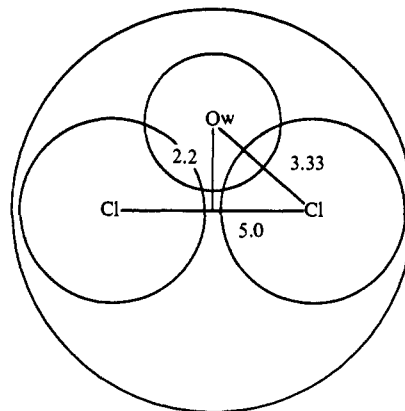
	HF/ 6-31+G(d)// 6-31+G(d)	MP3/ 6-31+G(d)	exp ^a
$F^-(H_2O)$	-24.8	-26.7	-23.3
$F^-(H_2O)_2$	-45.1	-48.6	-39.9
$F^-(H_2O)_3$	-62.7	-67.6	-53.6
$Cl^-(H_2O)$	-12.6	-14.7	-13.1
$Cl^-(H_2O)_2$	-24.1	-28.1	-25.8
$Cl^-(H_2O)_3$	-34.8	-40.4	-37.5
$F^-: n = 2, m = 1, p = 1$	-46.6	-51.1	
$F^-: n = 3, m = 1, p = 2$	-47.6	-44.5	
$F^-: n = 4, m = 1, p = 3$	-50.1	-46.2	
$F^-: n = 4, m = 2, p = 2$	-52.8	-49.1	
$Cl^-: n = 2, m = 1, p = 1$	-44.2	44.6	
$Cl^-: n = 3, m = 1, p = 2$	-43.2	-39.8	
$Cl^-: n = 4, m = 1, p = 3$	-40.0	-36.6	
$Cl^-: n = 4, m = 2, p = 2$	-40.8	-37.7	

^a Kebarle, P. *Annu. Rev. Phys. Chem.* 1977, 28, 445.

effect is smaller and the energy change is more progressive (18.2 kcal/mol for $2 \rightarrow 3$ vs. 14.6 kcal/mol for $3 \rightarrow 4$).

As noted in our early study of anion-water complexes,²³ there is a significant basis set dependence in the computed interaction energy, particularly for the smaller fluoride ion. The complexation energies for $F^-(H_2O)_nF^-$ were slenderized by 13–15 kcal/mol per water molecule with the addition of a set of diffuse functions, whereas the energy change for the chloride complexes was only ca. 1.5 kcal/mol. Correction of electron correlation was made through Moller–Plesset perturbation theory and was found to increase the stabilization energy by ca. 2.7 kcal/mol per water for all complexes except $F^-(H_2O)_2F^-$, whose interaction energy was reduced by 0.6 kcal/mol. The energy difference between MP2 and MP3 calculations was negligible in all cases.

The reaction energy for the dissociation process, $X^-(H_2O)_nX^- \rightarrow X^-(H_2O)_m + X^-(H_2O)_p$, was also computed by considering the hydration energies of multiply solvated ions and was found to be ca. 40–50 kcal/mol exothermic for all systems (Table II). Consequently, small $X^-(H_2O)_nX^-$ clusters are extremely unstable and would not exist in the gas phase. Then, what are the forces that stabilize the chloride ion pair in water? Earlier theoretical works using the reference hypernetted chain approximation (RHNC)¹⁰ and extended RISM calculations⁹ showed attractive

**Figure 5.**

wells on the potential of mean force, while similar results were found in molecular dynamics and Monte Carlo simulations.^{13,14} The stabilization of the chloride ion pair in aqueous solution was rationalized as the formation of solvent-bridged structures in which water molecules hydrogen bond simultaneously to both ions.^{13,14} Although computations based on a continuum representation of the solvent exhibited no minima on the pmf as the interchloride distance decreases,¹⁸ qualitative explanation in the framework of the Born model of solvation has been suggested.^{19,20} According to this idea, the total macroscopic free energy of hydration of two separate ions of radius R and charge q is $-(q^2/R)(1 - 1/\epsilon)$, where $\epsilon = 78$ for water, and would be the same as that for the contact ion pair of radius $2R$, noting that the Born energy is proportional to the square of charge on the ion.²⁸ However, the repulsion between two like-charged ions at contact distance is significant since there is no dielectric screening to the electrostatic interaction between two contact ions.¹⁹ Thus, a tremendous stabilization energy is required to offset the unfavorable Coulombic interaction. Examining the cavity within the “spherical” contact ion pair, there is sufficient space to allow water molecules to form bridged-hydrogen bonds with both chloride ions (Figure 5). Though precededented, the intrinsic stability of the solvent-bridged ion pair has never been computed.^{13,14} Our present calculations indicate that the total binding energy from 3 water-bridged hydrogen bonds is enough to neutralize the ion–ion repulsion (Table I), leading to a net stabilization as observed in the pmf studies. This result is in excellent accord with the finding of three water molecules in the solvent-bridged structure from Monte Carlo simulations.¹⁴ Not surprisingly, the ab initio results were reproduced by the simple OPLS potential functions used in these computations (see below).

For both $F^-(H_2O)_nF^-$ and $Cl^-(H_2O)_nCl^-$ systems, the change in geometrical variables clearly reflects an incremental effect in the number of bridging water molecules (Figure 1). The 6-31+G(d) F–F distances are 4.397, 3.892, and 3.554 Å for $n = 2, 3,$ and $4,$ respectively, while the Cl–Cl separations are recorded as 6.290, 5.448, and 4.943 Å. The latter value for the Cl_2^{2-} ion pair is in good agreement with the average interionic distance of 5.1 Å observed in crystal structures and of 4.8–5.0 Å corresponding to the free energy minimum computed via Monte Carlo simulations.¹⁴ The much shorter separation of 3.6 Å obtained by Pettitt and Rossky using the extended RISM⁹ and molecular dynamics methods¹³ appeared to be an underestimate and inconsistent with the ab initio results. Interionic chloride distances of less than 4 Å were mostly found between chloride ligands in metal complexes from the CSD search. Moreover, it is noticed that most of the data points in Figure 3 occurred at Cl–Cl separations greater than 4.6 Å. Since an average of three water molecules was found to form bridged structures from MC simulations and an increase of the “water bridges” would yield a much bigger total coordination number for Cl^- than that predicted by experiments and earlier simulations,^{13,25} the distance predicted by the ab initio computations for $X^-(H_2O)_4X^-$ ($X = F, Cl$) is likely to be the low limit

Table III. Calculated Stabilization Energies for $X^-(H_2O)_nX^-$ Using Different Computation Schemes (kcal/mol)

species	6-31+G(d)			MP3/6-31+G(d)			ΔE^c
	ΔE_{ai}	ΔE_p^a	$\Delta\Delta E^b$	ΔE_{ai}	ΔE_p^a	$\Delta\Delta E^b$	
$F^-(H_2O)_2F^-$	-3.0	-6.7	-3.7	-2.4	-16.0	-13.6	-4.5
$F^-(H_2O)_3F^-$	-22.3	-34.6	-12.3	-30.8	-51.0	-20.2	-36.5
$F^-(H_2O)_4F^-$	-37.4	-47.5	-10.1	-48.1	-69.6	-21.5	-55.0
$Cl^-(H_2O)_2Cl^-$	19.0	15.5	-3.5	15.2	10.2	-5.0	16.6
$Cl^-(H_2O)_3Cl^-$	4.5	-0.8	-5.3	-3.0	-12.1	-9.1	-1.6
$Cl^-(H_2O)_4Cl^-$	-7.4	-13.6	-6.2	-18.5	-31.6	-13.1	-16.5

^a Computed from ab initio pair interaction energies. ^b $\Delta\Delta E = \Delta E_p - \Delta E_{ai}$. ^c Estimated using the OPLS and TIP4P water potentials.

for these ion pairs in water. Additionally, the F–O distances in $F^-(H_2O)_nF^-$ clusters were found to be 2.844, 2.835, and 2.911 Å for $n = 2, 3,$ and $4,$ respectively, with a variation of only 0.07 Å, while the F–F distance has concomitantly changed by 0.84 Å. A similar trend exists in the chloride system; the Cl–O separation is 3.832 Å for $Cl^-(H_2O)_2Cl^-$ and 3.672 Å for the D_{3h} and D_{4h} structures with a total change of 0.16 Å, now that the distance between the two ions decreases by 1.35 Å. Interestingly, these results nicely mirror the trend in crystal structures as depicted in Figures 3 and 4. Finally, water monomer geometry was also affected by the fluoride ions. At the shortest inter-fluoride contact, the water HOH bond angle is 101.3°, about 4° smaller than that of an isolated water molecule, while it is 105.6° in $F^-(H_2O)_2F^-$ with little distortion. The change in $Cl^-(H_2O)_nCl^-$ systems is minimal due to the weaker interactions between Cl^- and water.

Comparison with Empirical Potential Functions and Polarization Effects. Since pair-wise, effective potential functions have been commonly used in condensed-phase simulations, it would be valuable to provide a detailed analysis of the many-body polarization effect in the ion pair clusters studied here. First, the ab initio pair interaction energy was calculated using the geometry taken from each individual complex (Table I). The pair-wise, additive stabilization energy (ΔE_p) was then obtained by summing over energies of all pair interactions in the complex. The results are listed in Table III and are compared with the ab initio stabilization energy (ΔE_{ai}), which includes many-body polarization effects. The difference between the two energies ($\Delta\Delta E = \Delta E_p - \Delta E_{ai}$) would be a measure of the polarization effect due to higher-order interactions. In addition, the interaction energy was computed using the OPLS potential function and given in Table III.

Obviously, the non-additive polarization effect is substantial in all cases. At the MP3/6-31+G(d) level, the binding energy computed without including many-body interactions was overestimated by ca. 6–7 and 3 kcal/mol per water bridge in the fluoride and chloride complexes, respectively. This suggests that use of the ab initio pair potential function in condensed phase simulations should be extremely cautious. In fact, there has been little success in liquid simulations using potential functions directly derived from ab initio calculations.²⁹ It is interesting to examine the predictions from effective, empirical potential functions. As shown in Figure 1 and Table III, the agreement with the ab initio results in both geometrical and energetic parameters was excellent. The interionic distance estimated using the OPLS functions was 0.2–0.4 Å shorter than the corresponding ab initio values, except for $Cl^-(H_2O)_2Cl^-$ in which the difference was 0.7 Å (Figure 1). However, it should be mentioned that the hydrogen bond distance was actually deliberately optimized to be 0.1–0.2 Å shorter in the OPLS potentials than the ab initio value for monohydrated ions in order to obtain better solution properties.^{25,30} The OPLS binding energy was estimated to be ca. 2 kcal/mol stronger than the ab initio number for each water bridge in $F^-(H_2O)_nF^-$ complexes, while it was 0.5 kcal/mol weaker in the chloride system. The OPLS functions correctly predicted a net stabilization of 1.6 kcal/mol for $Cl^-(H_2O)_3Cl^-$, which may be compared to the MP3/6-31+G(d) value of 3.0 kcal/mol. In contrast, the stabilization energy estimated from the ab initio pair interactions is 12.1 kcal/mol, an overestimation of 9.1 kcal/mol. Considering

the simplicity of the potential functions which consist of only Coulomb and Lennard-Jones terms,^{25,30} the results are indeed remarkable. However, it is not entirely surprising to witness the success of the OPLS potential because polarization effects have been, on an average sense, implicitly included in the parametrization process. These results indicate that the observation of a Cl_2^{2-} aggregate in water from MD and Monte Carlo simulations is consistent with the electronic structures of small ion pair clusters predicted by ab initio computations and that pairwise, effective potential functions can provide meaningful predictions for the electrolyte systems considered here.

Conclusion

The present combined approach of crystallographic analyses and ab initio MO calculations provided strong support to the previous theoretical and simulation results of the possible existence of a stable solvent-bridged chloride ion pair in water. The CSD search revealed that contact chloride ions, stabilized by forming solvent-bridged hydrogen bonds in addition to interactions with counterions, are common in the crystalline state. The hydrogen bonding pattern is also apparent and mirrors the trend found in the optimized ab initio structures. The stabilization of a Cl_2^{2-} aggregate in water was rationalized as the combined result of a cancellation in the Born free energies of solvation for the contact ion pair and separated ions and the solvent-bridged hydrogen-bonding interaction that offsets Coulombic repulsion between the two ions. That 3 water molecules are needed to provide such a stabilization is in good agreement with the prediction by proximity analysis in the Monte Carlo simulations.¹⁴

Geometrical and energetic parameters computed using the OPLS potential function and TIP4P model for water were found in good agreement with the ab initio results, although these potential functions are entirely pairwise additive in nature. The remarkable performance of the effective potentials is due to the incorporation, on an average sense, of polarization effects in the parametrization process. Although the results presented here indicate that use of an effective potential function in condensed phase simulations is reasonable, comparison with simulation results using explicit polarization potentials would be desirable.³¹

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Registry No. $F^{\cdots}F^-$, 81361-72-0; $Cl^{\cdots}Cl^-$, 117458-09-0.

Supplementary Material Available: Listings of full geometrical details and total energies for the complexes in Z-matrix format along with the references and CSD refcodes for Figures 3 and 4 (4 pages). Ordering information is given on any current masthead page.

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