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Citation: The Journal of Chemical Physics 109, 4258 (1998); doi: 10.1063/1.477031
View online: http://dx.doi.org/10.1063/1.477031
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Solvation of the Li\(^+\)-Cl\(^-\)-Li\(^+\) triple ion in the gas phase

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(Received 17 October 1997; accepted 12 June 1998)

Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry was employed to study solvations of the Li\(^+\)-Cl\(^-\)-Li\(^+\) triple ion with oxygen-donor Lewis bases in the gas phase. The LiClLi\(^+\) triple ions were produced in an ICR cell by laser desorption ionization of a lithium chloride/dibenzo-18-crown-6-ether matrix pasted on a Teflon substrate. O-donor Lewis bases include 1,4-dioxane, 1,3-dioxane, tetrahydrofuran (THF), acetone and diethyl ether. All O-donors associate directly with LiClLi\(^+\) with the maximum solvation numbers of 3 for 1,4-dioxane, 1,3-dioxane and diethyl ether, and 4 for THF and acetone at room temperature. The rate constants for the stepwise solvations were measured, and the solvent binding energies were determined from van’t Hoff plots. The structures and energetics of LiClLi\(^+\) and the 1:1 complexes of Li\(^+\) and LiClLi\(^+\) with the dioxanes, THF, and acetone were calculated at the Hartree-Fock (HF) level with a 6-311G(d,p) basis set, and those of more highly coordinated LiClLi\(^+\) complexes were calculated with a 6-31G(d) basis set. Solvation enthalpies and free energies were calculated, and solvent binding energies were compared with experiments. The mechanisms of stepwise solvations of the LiClLi\(^+\) triple ion with dioxanes, THF, and acetone are discussed in light of experimental kinetics and binding energies and theoretical structures and solvation energies. © 1998 American Institute of Physics. [S0021-9606(98)01635-3]

I. INTRODUCTION

Electrolyte solutions contain a wide spectrum of ionic and neutral solute species ranging from solvated free ions to higher order cluster ions.\(^1,2\) At infinite dilution, a strong electrolyte exists in the form of solvated “free” cations and anions. As the solute concentration increases, the opposite charge ions associate to form ion pairs. As ion pairs undergo Brownian motions in ionic liquids, they encounter either a free ion or an ion pair and form triple ions (+ + + or − − −) or higher order clusters.\(^3\) The formation of triple ions in low dielectric constant media was first proposed as early as 1933 by Fuoss and Kraus\(^4\) to account for the occurrence of a minimum in the conductance curve that deviates from classical Debye-Hückel laws.\(^5\) To the contrary, Grigo showed how to fit the conductance curve without the assumption of triple ion formation.\(^6\) Recently, a number of groups suggested the existence of triple ions from the studies of infrared and Raman spectra of solutions of lithium and sodium electrolytes,\(^7-11\) \(^6\)Li and \(^15\)N NMR chemical shifts in lithium electrolytes,\(^12,13\) and conductometric measurements.\(^14\) Recent developments in the theory of electrolytes\(^15-22\) also dealt with the treatment of higher order ion association beyond Bjerrum’s ion paring.\(^23\) The idea of ion pairs and triple ion formation was also introduced into the theory of cyclic voltammetry of a redox-active self-assembled monolayer.\(^24,25\) These experimental and theoretical studies firmly establish the presence of electrostatically stabilized triple ions and higher associated complexes in some electrolyte solutions. However, there was no report of the intrinsic properties of triple ions in the gas phase mainly due to the difficulty in preparing predominantly triple ions of nonvolatile salts in the gas phase. Very recently, a number of novel ionization methods have been developed for the routine production of large cluster alkali-metal halide ions in the gas phase.\(^26,27\) In this report, the matrix-assisted laser desorption ionization (MALDI) method\(^28-30\) was employed to generate the Li\(^+\)-Cl\(^-\)-Li\(^+\) triple ion with high yield in the ion cyclotron resonance (ICR) cell.

Interactions of lithium electrolyte triple ions with O-donor solvents have attracted considerable interest in recent studies of nonaqueous lithium battery electrolytes.\(^31\) Torell and co-workers suggested the formation of triple ions from the concentration-dependent frequency shift in Raman spectra of LiCF\(_3\)SO\(_3\).\(^31\) In nonaqueous lithium battery electrolytes, poly(ethylene glycol) and poly(ethylene oxide) are commonly used as substrates, while dioxanes, tetrahydrofuran (THF), and alkyl carbonates are additional cosolvents to balance the stability and conductivity.\(^32-34\) The conductance measurements suggested that the interactions of triple ions with O-donors in polyether complicate the temperature dependence of ion conductivity.\(^32,35\) The successful development of a rechargeable lithium battery depends upon a proper selection of the suitable electrolyte-solvent system that suppresses the ion association process which is the major cause of diminished conductivity. Thus, a better understanding of solvation of triple ions by O-donor Lewis bases is of value in optimizing the electrolyte-solvent systems.

As the first step toward the molecular level understanding of solvations of lithium electrolyte triple ions, the Li\(^+\)-Br\(^-\)-Li\(^+\) triple ion has been prepared in the gas phase, and its stepwise solvations by O-donor Lewis bases have been studied with Fourier-transform ion cyclotron resonance...
remarkable structural diversity in the solid state. The equilibrium constants.

Binding energies were determined from the temperature dependence of equilibrium constants. Rates were measured for the stepwise solvations, and solvent binding energies were determined from the temperature dependence of equilibrium constants.

Solvations of lithium halide salts by Lewis bases show remarkable structural diversity in the solid state. The triple-ion type salt-bridge structure was observed to be a common backbone linkage in the crystal structures of lithium halide complexes solvated by Lewis bases. They form various types of complexes ranging from solvent-separated ion pairs to polymers. This structural diversity is typically understood by the relative strengths of Li-donor versus Li-halide interactions, the entropy changes in complex formation, the coordination number, and the steric factors of the ligands.

The present study on the rates of association of Li⁺–Cl⁻–Li⁺ with O-donor Lewis bases and on the coordination number in the absence of bulk solvent sheds light on the fundamental factors governing the diverse structures found in lithium halide-Lewis base donor complexes. To help elucidate the mechanism of solvations, ab initio calculations were carried out on complexes of Li⁺ and LiClLi⁺ with 1,4-dioxane (1,4-2O), 1,3-dioxane (1,3-2O), THF, acetone and diethyl ether (Et₂O).

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The background pressure in the ICR chamber was typically below 6×10⁻⁸ Torr. Gaseous samples were leaked into the ICR chamber. The sample pressures were measured by calibrating the ion-gauge mounted in the ICR chamber against a capacitance manometer (MKS Baratron head 390HA-00010). The less than two orders of magnitude pressure extrapolation is estimated to have an accuracy of ±25%. For the rate constant measurements, ion signals were monitored as a function of time delay, and the results were simulated with pseudo-first order reaction kinetics by a least-squares fitting program.

The 308-nm output was from a XeCl excimer laser (Lambda-Physik, EMG-53 MSC), with a typical pulse width of ~10 ns. The laser beam was mildly focused to ~2-mm diameter to desorb lithium salt ions. Dibenzo-18-crown-6-ether absorbs at 308 nm. A typical laser power used in the desorption-ionization was ~2 mJ.

All chemicals were purchased from Aldrich Inc., and were used after several freeze–pump–thaw cycles. The purity of each sample was tested by EI mass spectra. Sample inlet lines were baked and pumped out overnight to prevent cross-contamination between samples.

III. COMPUTATIONAL DETAILS

All calculations were performed by use of the GAUSSIAN-94 suite of programs on a Silicon Graphics Power Indigo2 workstation. The geometry of the LiClLi⁺ triple ion was optimized at the MP2 level with a standard 6-311G(d,p) basis set. The basis set superposition error (BSSE) was estimated at the MP2 level by using the full counterpoise method. The basis set deficiency error was calculated at the MP2 level with a 6-311G(3df,2pd) basis set. Geometries of the 1:1 complexes of Li⁺ and LiClLi⁺ with 1,4-2O, 1,3-2O, THF and acetone were optimized at the HF level with a standard 6-31G(d) basis set. Vibrational frequencies were calculated at the HF level. Solvent binding energies were corrected for zero-point energies scaled by 0.9248 and 0.9135 for the 6-31G(d,p) and 6-31G(d) basis sets, re-
Solvation enthalpies and free energies were calculated by using statistical mechanics.

**IV. RESULTS**

**A. The solvation kinetics and the solvent binding energy**

The rate constants for the solvation of the LiClLi⁺ triple ion with five O-donor Lewis bases are reported in Table I. The general equation for the stepwise solvation process is defined in Eq. (1):

\[
\text{LiClLi}^+ (S)_{n-1} + S \rightarrow \text{LiClLi}^+ (S)_n,
\]

where \( S \) represents the solvent. The pressure of each solvent was 1.3 \( \times \) \( 10^{-6} \), 0.7 \( \times \) \( 10^{-6} \), 1.7 \( \times \) \( 10^{-6} \), 1.2 \( \times \) \( 10^{-6} \), and 1.2 \( \times \) \( 10^{-6} \) Torr for 1,4-2O, and 1,3-2O, THF, acetone, Et₂O, respectively. Dioxanes and Et₂O coordinated up to three molecules, whereas THF and acetone coordinated up to four at room temperature. The abstraction of Li⁺ was not observed with any of the Lewis bases examined herein. In reactions with 12-crown-4-ether and 15-crown-5 ether, the abstraction of Li⁺ occurred exclusively at room temperature as reported for LiBrLi⁺.\(^{36}\)

Thermal equilibria of solvation were observed where \( n = 3 \) for all solvents and \( n = 4 \) for THF and acetone. Thermal equilibria were checked by isolating multiply solvated complexes. The enthalpy of solvation was determined from the temperature dependence of the equilibrium constant at constant pressure as given in Eq. (2), van’t Hoff plots are shown in Fig. 2:

\[
\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},
\]

\[
K_{eq} = \frac{[\text{LiClLi}^+ (S)_n]}{[\text{LiClLi}^+ (S)_{n-1}] \cdot \frac{P(S)}{P(1 \text{ atm})}},
\]

where \( K_{eq} \) is the equilibrium constant, \( \Delta H \) and \( \Delta S \) are the enthalpy and the entropy of solvation, \( R \) is the gas constant, \( T \) is the temperature, and \( P(S) \) is the pressure of the solvent. Solvent binding energies were determined from the slopes of van’t Hoff plots. Results are listed in Table I. The values in parenthesis denote the 90% confidence interval of the enthalpy, some of which are quite large due to the limited temperature ranges in experiments. Entropies of solvation are not listed due to their large uncertainties, but fall within the range -22 to -32 eu.

**B. Structures and energetics of LiClLi⁺, Li⁺·(S) and LiClLi⁺·(S) complexes**

The LiClLi⁺ triple ion was linear at both HF and MP2 levels. At the MP2 level, the Li–Cl bond distance in the LiClLi⁺ triple ion was 2.14Å, which is 0.12Å longer than that in the LiCl ion pair. The calculated bond dissociation energy \( D_0(\text{LiCl–Li}^+) \) is 50.1 (HF) and 50.8 (MP2) kcal mol\(^{-1}\). The BSSE correction lowered \( D_0(\text{LiCl–Li}^+) \) by 1.1 kcal mol\(^{-1}\) at the MP2 level. The basis set extension to 6-311G(3df,2pd) decreased \( D_0(\text{LiCl–Li}^+) \) by 0.5 kcal mol\(^{-1}\). The best estimate for \( D_0(\text{LiCl–Li}^+) \) is 49.2 kcal mol\(^{-1}\), compared with \( D_0(\text{Li–Cl}) = 112 \pm 3 \) kcal mol\(^{-1}\) of the neutral ion pair.\(^{63}\)

The lowest energy structure for 1,4-2O in the 1:1 complex with Li⁺ was a twisted boat with \( C_2 \) symmetry. Note that in free 1,4-2O, the chair conformation is 6.4 kcal mol\(^{-1}\) lower in energy than the boat form. The bidentate interaction with Li⁺ favors this boat form of 1,4-2O. The lowest energy structure of 1,3-2O in the 1:1 complex with Li⁺ was a chair form with \( C_1 \) symmetry, as in free 1,3-2O. Monodentate coordination complexes lie 0.9 and 1.2 kcal mol\(^{-1}\) higher in energy than bidentate coordination complexes for 1,4-2O and 1,3-2O, respectively, at the HF/6-311G(d,p) level. THF coordinated to Li⁺ with the twisted conformation in \( C_1 \) sym-
Acetone coordinated to Li$^+$ with a linear O–Li–Cl geometry and with one of the C–H bonds in both methyl groups forming cis to the carbonyl, giving it a C2 symmetry.

The calculated thermochemical data for the formation of the 1:1 complexes of Li$^+$ and LiCl$^+$ with the dioxanes, THF, and acetone, and their corresponding dissociation limits are summarized in Table II with selected geometrical parameters. In thermal reactions of LiCl$^+$ with O-donors, the dissociative solvation channels to the formation of 1:1 LiCl$^+$ (dioxide) complexes is identical to the $\Delta E_0$ ordering for both dioxanes. However, the $\Delta G^\circ_{298}$ ordering deviates from the enthalpy ordering in the case of 1,4-2O due to entropy changes in solvation. The formation of the monodentate end-on complex became most exoergic for 1,4-

![Image](image-url)

FIG. 3. Structures of LiCl$^+$-(1,4-2O) and LiCl$^+$-(1,3-2O) at the HF/6-311G(d,p) level. 1,4-2O: (a) side, (b) monodentate end-on, and (c) bidentate end-on coordinations; 1,3-2O: (d) side, (e) monodentate end-on, and (f) bidentate end-on coordinations.
TABLE III. Geometrical parameters and relative energies of \((S)_{n-m}\)-LiClLi\(^+\) at HF level with a 6-31G\((d)\) basis set.

<table>
<thead>
<tr>
<th>((S)_{n-m}) (isomer) (^b)</th>
<th>Li1–O1 ((\AA))</th>
<th>Li2–O2 ((\AA))</th>
<th>Li1–O3 ((\AA))</th>
<th>Li2–O4 ((\AA))</th>
<th>Li1–Cl ((\AA))</th>
<th>Li2–Cl ((\AA))</th>
<th>(\angle) Li–Cl–Li (deg)</th>
<th>(\Delta E) (^a)</th>
<th>(\Delta H_{298})</th>
<th>(\Delta G_{298})</th>
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<td>1,4-2O (s)</td>
<td>1.930</td>
<td>1.930</td>
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<td></td>
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<td>2.214</td>
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<td>−23.4</td>
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<tr>
<td>1,4-2O (m)</td>
<td>1.854</td>
<td></td>
<td></td>
<td></td>
<td>2.233</td>
<td>2.175</td>
<td>179.2</td>
<td>−31.5</td>
<td>−31.2</td>
<td>−23.9</td>
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<tr>
<td>(1,4-2O)(_2) (m,s)</td>
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<td>1.921</td>
<td>1.884</td>
<td></td>
<td>2.275</td>
<td>2.193</td>
<td>104.0</td>
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<td>−60.3</td>
<td>−40.5</td>
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<tr>
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<td>1.858</td>
<td></td>
<td></td>
<td>2.208</td>
<td>2.208</td>
<td>176.3</td>
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<td>−61.3</td>
<td>−46.2</td>
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<td>1.981</td>
<td>1.890</td>
<td>1.890</td>
<td>2.253</td>
<td>2.253</td>
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<td>−85.2</td>
<td>−84.4</td>
<td>−55.4</td>
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<tr>
<td>1,3-2O (s)</td>
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<td>1.950</td>
<td></td>
<td></td>
<td>2.216</td>
<td>2.216</td>
<td>101.2</td>
<td>−39.0</td>
<td>−39.5</td>
<td>−27.9</td>
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<tr>
<td>1,3-2O (m)</td>
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<td></td>
<td></td>
<td>2.234</td>
<td>2.173</td>
<td>175.7</td>
<td>−32.3</td>
<td>−32.2</td>
<td>−25.0</td>
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<td>1.935</td>
<td>1.907</td>
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<td>2.267</td>
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<td>2.000</td>
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<td>1.914</td>
<td>2.245</td>
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<td>2.239</td>
<td>2.171</td>
<td>179.9</td>
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<td>1.854</td>
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<td></td>
<td>2.209</td>
<td>2.209</td>
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<td>−92.5</td>
<td>−91.4</td>
<td>−66.8</td>
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<td>(THF)(_4)</td>
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<td>1.915</td>
<td>1.915</td>
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<td>180.0</td>
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<td>2.241</td>
<td>2.167</td>
<td>180.0</td>
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<td>1.810</td>
<td></td>
<td></td>
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<td>2.209</td>
<td>180.0</td>
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<td>1.818</td>
<td>1.900</td>
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<td>2.312</td>
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<td>157.4</td>
<td>−96.4</td>
<td>−95.1</td>
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<tr>
<td>(Acetone)(_4)</td>
<td>1.889</td>
<td>1.900</td>
<td>1.911</td>
<td>1.900</td>
<td>2.289</td>
<td>2.290</td>
<td>140.9</td>
<td>−116.5</td>
<td>−115.0</td>
<td>−83.5</td>
</tr>
</tbody>
</table>

\(^a\)Zero-point energies are included and scaled by 0.9135 as suggested by Scott and Radom (Ref. 62).

\(^b\)When two geometrical isomers are given the structures are designated (s) for side and/or (m) for monodentate coordination(s).

2O, whereas the formation of the side complex remained to be most exoergic for 1,3-2O.

The monodentate solvents, THF and acetone, favor end-on coordination as the lowest energy complexes compared to side coordination of two lithiums to one oxygen. The LiClLi\(^+\) moiety remained linear, and the O–Li–Cl angles were \(\sim 180^\circ\) in both LiClLi\(^+\)·(THF) and LiClLi\(^+\)·(acetone) complexes. Geometries of the 1:1 complexes of LiClLi\(^+\) with THF and acetone were similar to those of the corresponding 1:1 complexes of Li\(^+\).

C. Multiply solvated LiClLi\(^+\)·(S)\(_n\) complexes

Using the smaller 6-31G\((d)\) basis set, the structures and energetics of LiClLi\(^+\)·(S)\(_n\) complexes were calculated for \(n = 1\), up to the highest experimentally observed solvation number for each solvent. Selected geometric parameters as well as solvation energies are listed in Table III. Comparison of the first solvation energies between the 6-31G\((d)\) and the 6-311G\((d,p)\) basis sets shows that the basis set reduction causes an increase in the first solvent binding energy by 0.5–1.0 kcal mol\(^{-1}\).

1. 1,4-Dioxiane

The optimized structures of the bis and tris solvation complexes with 1,4-2O are shown in Fig. 4. The second 1,4-2O favors the monodentate end-on coordination over the bidentate end-on coordination. Among the bis coordination complexes, the lowest energy structure has two monodentate end-on coordination of 1,4-2O, whose formation is also most exoergic. The most stable structure for the tris compound comprises two monodentate end-on and one side coordination of 1,4-2O. The structural isomer with two bidentate end-on and one side coordination of 1,4-2O lies 5.3 kcal mol\(^{-1}\) higher in energy. In the condensed phase, the monodentate end-on coordination of 1,4-2O has been observed as a polymeric linkage in \([\text{(LiCl)}_2·(1,4-2O)]_\infty\) by X-ray crystallography.

2. 1,3-Dioxane

The optimized structures of the bis and tris solvations of 1,3-2O are shown in Fig. 5. The second 1,3-2O favors the...
monodentate end-on coordination. The lowest energy structure consists of one monodentate end-on and one side coordination of 1,3-2O, whereas the most exoergic structure has two monodentate end-on coordination. Meanwhile, the second solvent binding energy of the bindentate end-on coordination was less than 14 kcal mol\(^{-1}\). The most stable structure for the tris solvation complex contains two monodentate end-on and one side coordination of 1,3-2O. No condensed phase structure was reported for lithium halide complexes with 1,3-2O.

3. THF

The monodentate THF favors end-on coordination for all solvations. The second THF was coordinated to the other “free” lithium with a binding energy, 34.7 kcal mol\(^{-1}\). The Li–O bond distances in the second solvation complex were almost comparable to that in the first. The equilibrium structures of the tris and tetrakis solvation complexes of THF are shown in Fig. 6. When the third THF was attached by sharing one lithium with a preexisting THF, the binding energy dropped significantly to 21.8 kcal mol\(^{-1}\). The coordination of two THF to one lithium site extends the Li–O distance by 0.05 Å compared with the bis solvation complex. The fourth THF binding energy was 20.6 kcal mol\(^{-1}\). Both Li–O and Li–Cl bond distances in LiCILi\(^+\)-(THF)\(_4\) were ~0.06 Å longer than those in LiCILi\(^+\)-(THF)\(_2\). In the condensed phase, the same coordination pattern was found in [LiCl\(_2\)-2THF]\(_2\). Meanwhile, [LiBr-THF]\(_x\) displays an infinite “corrugated” ladder structure arising from the association of cubes of [LiBr-THF]\(_4\).

4. Acetone

The monodentate acetone also favors end-on coordination for all solvations. Both the first and the second solvations of acetone attached the carbonyls linearly to the Li–Cl bonds. The equilibrium structures of the tris and tetrakis solvation complexes of acetone are shown in Fig. 7. In the third solvation, the Li–Cl–Li angle became 157° due to the hydrogen bonding between the methyl hydrogen and chlorine. The Li–Cl–Li bends to 141°, with the fourth solvation containing three hydrogen bonds. This bent minimum structure lies ~0.3 kcal mol\(^{-1}\) below a linear Li–Cl–Li transition state structure that resembles the coordination pattern observed in [LiBr-2acetone]\(_2\) in the condensed phase. The calculated solvent binding energies are 38.4, 36.5, 21.5, and

![FIG. 5. Structures of LiCILi\(^+\)-(1,3-2O)\(_2\) and LiCILi\(^+\)-(1,3-2O)\(_3\) at the HF/6-31G(d) level: (a) bis monodentate end-on coordinations; (b) side and monodentate end-on coordinations; (c) bis monodentate end-on and side coordinations. Atom labels are referenced in Table III.](image1)

![FIG. 6. Structures of (a) LiCILi\(^+\)-(THF)\(_3\) and (b) LiCILi\(^+\)-(THF)\(_4\) complexes at the HF/6-31G(d) level. Atom labels are referenced in Table III.](image2)

![FIG. 7. Structures of (a) LiCILi\(^+\)-(acetone)\(_3\) and (b) LiCILi\(^+\)-(acetone)\(_4\) complexes at the HF/6-31G(d) level. Atom labels are referenced in Table III.](image3)
20.1 kcal mol\(^{-1}\) for the first, second, third and fourth solvations of acetone, respectively. Similarly to THF, both Li–O and Li–Cl bond distances in LiClLi\(^{+}\)(acetone)\(_{4}\) were 0.08–0.09 Å longer than those in LiClLi\(^{+}\)(acetone)\(_{2}\). 

V. DISCUSSION

A. Solvation energetics

The present experiment differs from typical ICR equilibrium measurements in that thermal equilibria are established between solvation and thermal dissociation of solvated complexes. Thus, a van’t Hoff plot yields the enthalpy of solvation in the absolute scale. Comparison of solvation enthalpies between experiment and theory is made for dioxanes, THF, and acetone. For a direct comparison, theoretical \(\Delta E_0\) values between the most stable isomers are corrected for thermal energies by taking the heat capacities into account. Theoretical solvent binding enthalpies, \(D_{298}[\text{LiClLi}^{+}\cdot(S)_{n-1}-S]\) and \(D_{298}(\text{Li}^{+}-S)\), are summarized and compared with the experimental results in Table IV. Theoretical values for \(n=3\) and \(4\) are in good agreement with the experimental ones. In the case of \(n=4\) of acetone, a direct comparison between theory and experiment is inappropriate because of the 9 kcal mol\(^{-1}\) uncertainty in the experiment. This agreement between theory and experiment provides theoretical blessings to the present equilibrium methodology and validates the HF wave function as a reasonable approximation for the lithium ion solvation. Note, however, that thermal equilibria observed in experiments are not necessarily between the most stable structures but more likely between thermally populated conformations.

The 298 K solvent binding enthalpies for 1:1 Li\(^{+}\)·(S) complexes calculated at the HF/6–311G(d,p) level were 40.8 kcal mol\(^{-1}\) for 1,4-2O (twist-boat), 42.2 kcal mol\(^{-1}\) for 1,3-2O (chair), 45.5 kcal mol\(^{-1}\) for THF, and 49.4 kcal mol\(^{-1}\) for acetone. Monodentate coordination of acetone and THF binds more strongly to Li\(^{+}\) than bidentate coordination of dioxanes. Highly polar acetone binds more tightly than THF. The theoretical Li–O binding energy for acetone is 6 kcal mol\(^{-1}\) greater than the value of 43 kcal mol\(^{-1}\) derived from the bracketing ICR equilibrium measurements reported by Staley and Beauchamp\(^{64}\) combined with \(D_{298}(\text{Li}^{+}–\text{H}_2\text{O}) = 32.7\) kcal mol\(^{-1}\) recommended by Rodgers and Armentrout\(^{65}\).

Geometry changes involved with successive solvations of the LiClLi\(^{+}\) triple ion indicate an increase in molar volume by the triple ion solvation compared with the Li\(^{+}\) solvation. Geometrical parameters listed in Table III manifest that both the Li–O and Li–Cl bond distances increase as the number of solvent coordination increases.

B. Stepwise solvation kinetics and mechanisms

The solvation of LiClLi\(^{+}\) provides interesting association kinetics that exhibit the effects of heat capacity and steric hindrance. For ease of comparison, the rate constants for the successive solvations are plotted in Fig. 8. Those for the first solvations of dioxanes and THF are quite comparable to each other in the range 2.3×10\(^{-11}\) to 3.4×10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Those for acetone and Et\(_2\)O are 4.8×10\(^{-11}\) and 10.5×10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively. It appears that the increase in the number of internal rotors in acetone and Et\(_2\)O facilitates the first solvation, most likely due to the increase in heat-dissipating capacity. The second solvation occurs faster than the first solvation for all solvents, owing to the increase in heat capacity in going from LiClLi\(^{+}\) to LiClLi\(^{+}\)·(S). Theoretical energetics suggest that the most stable 1:1 complexes are side coordination for 1,4-2O and 1,3-2O and end-on coordination for THF and acetone. On the other hand, the most exoergic process at 298 K involves side coordination for 1,3-2O and monodentate end-on coordination for 1,4-2O, THF, and acetone. These differences in geometry of the 1:1 complexes could affect the kinetics of the second solvation as well. In 1:1 end-on LiClLi\(^{+}\)·(S) complexes one lithium site is coordinatively free, whereas in side LiClLi\(^{+}\)·(dioxane)

![FIG. 8. Logarithmic plot of the rate constants of successive solvations of LiClLi\(^{+}\) with O-donors.](image-url)
complexes both lithium sites are partially hindered by a pre-existing ligand. The descending order of rate constants for the second solvation, \( k_2(\text{acetone}) > k_2(\text{Et}_2\text{O}) > k_2(\text{THF}) > k_2(\text{1,3-2O}) > k_2(\text{1,4-2O}) \), provides evidence of steric hindrance by the side coordinated dioxanes at room temperature. The rate constants for the third solvation decrease for all solvents, some more dramatically than others, owing to the steric hindrance caused by preexisting ligands that occupy the coordination sites. It is interesting to note that the rate constant for the third solvation of 1,3-2O is about five times greater than that for 1,4-2O. Solvation energies listed in Table III show that the two monodentate end-on coordination of dioxanes is most exoergic in the formation of bis coordination complexes for both 1,4-2O and 1,3-2O. The third solvation of 1,4-2O requires conformational change of one 1,4-2O from a chair to a boat for side coordination, whereas 1,3-2O needs no such changes for side coordination. It appears that this extra step involving conformational changes makes a difference in the rate of the third solvation between the two dioxanes. The fourth coordination is absent in 1,4-2O, 1,3-2O, and Et_2O. Meanwhile, the fourth solvation of THF is four times slower than its third, and that of acetone is three times slower than its third due to steric hindrance. The absence of the fourth coordination of Et_2O is ascribed to the excessive steric hindrance of the bulky ethyl groups. The condensed phase structure of \([\text{LiBr-Et}_2\text{O}]_4\) shows a cubane diethylether-solvated LiBr lattice fragment.

Combining experimental kinetics and solvent-binding energies with theoretical structures and solvation energies leads to deeper insights into the mechanism of the stepwise solvation. The first solvation involves ligation of oxygen to one of the Li^+, likely forming 1:1 monodentate end-on complexes. Collision complexes then either predissociate to reactants or relax and rearrange to more stable association complexes. Thermal structures for the 1:1 complexes involve both the side coordination and the monodentate end-on coordination for dioxanes, but only the end-on coordination for the monodentate O-donors. The second solvation of the monodentate O-donors involves ligation of oxygen to an available lithium site by following the pathway similar to that of the first solvation. The second solvation of the bidentate dioxane involves significant intramolecular rearrangements to accommodate and dissipate heat released by solvation. Vibrational predissociation of collision complexes to reactants, which appears as the ligand displacement reaction, competes with relaxation and rearrangement to more thermally stable structures. The second dioxane favors the formation of two monodentate end-on coordination complexes as the most exoergic products. The successive solvation proceeds in much the same way as long as the free energy of solvation is negative. Variations in the rate constants of successive solvations represent the difference in efficiency between predissociation and relaxation.

C. Comparison of solvations of LiClLi^+ with those of LiBrLi^+

The equilibrium geometry of LiClLi^+ is linear with \( r(\text{Li–Cl}) = 2.14 \text{ Å} \), while that of LiBrLi^+ is bent with an angle of 153° and \( r(\text{Li–Br}) = 2.32 \text{ Å} \) at the MP2/6-311G(d,p) level. It appears that the valence electron repulsion is greater in LiBrLi^+ than in LiClLi^+.

The best estimate for \( D_{298}(\text{LiCl–Li}^+) \) is 49.4 kcal mol\(^{-1}\), whereas that for \( D_{298}(\text{LiBr–Li}^+) \) is 47.0 kcal mol\(^{-1}\). Solvation kinetics and energetics of LiClLi^+ with 1,4-2O, 1,3-2O, and THF are compared with those of LiBrLi^+.

Changes in rate of the successive solvations were remarkably similar to each other. Experimental enthalpies show that LiClLi^+ binds as or more strongly than LiBrLi^+: \( D_{298}(1,4\text{-2O})_{\text{LiClLi}^+} = 21 \pm 2 \text{ (X=Cl) vs 20} \pm 2 \text{ (X=Br) kcal mol}^{-1} \); \( D_{298}(1,3\text{-2O})_{\text{LiClLi}^+} = 23 \pm 5 \text{ (X=Cl) vs 23} \pm 3 \text{ (X=Br) kcal mol}^{-1} \). Vibrational predissociation of collision complexes to more ther- steric hindrance caused by preexisting ligands affords a stronger binding with dioxanes for side coordination than in LiClLi^+. Another interesting difference between LiClLi^+ and LiBrLi^+ was found in reactions with acetone. LiClLi^+ was solvated by acetonitrile acetone, but no abstraction of Li^+ was observed. On the other hand, LiBrLi^+ was solvated by acetone and also dissolved to yield Li^+ (acetone) with a loss of LiBr. This result suggests that \( D_{298}(\text{Li}^+\text{-acetone}) \) is less than \( D_{298}(\text{LiCl–Li}^+) \) but close to \( D_{298}(\text{LiBr–Li}^+) \). \( D_{298}(\text{Li}^+\text{-acetone}) \) is estimated to be \(~47 \text{ kcal mol}^{-1} \).

VI. CONCLUSION

The present results firmly establish the existence of triple ions and their solvation mechanisms in the presence of gas- eous O-donor Lewis bases. The first step of solvation involves the formation of collision complexes by charge-induced dipole interactions between the charge centers and O-donors. Vibrational predissociation of collision complexes compete with radiative relaxation, collisional quenching, and structural rearrangements to more stable association products. Thermal equilibria between solvation and thermal des-
olvation are established in the ICR cell. The temperature dependence of equilibrium constants provides the solvent binding energies in the absolute scale from van’t Hoff plots, which contrasts with the relative solvent binding energy measurement that utilizes thermal ion-transfer equilibria between two neutrals. The present FT-ICR/MALDI methodology is generally applicable to other inorganic solid salt ions for the isolation and thermochemical characterization of transient ionic intermediates present in the condensed phase.

ACKNOWLEDGMENTS

S.K.S. acknowledges the support from the National Science Foundation Young Investigator Award CHE-9457668 and the Arnold and Mabel Beckman Foundation Young Investigator Award. This work was also made possible by the Santa Barbara Laser Pool under NSF Grant No. CHE-9413030. We thank Mike Bowers for the loan of the ICR setup.