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Ligand-Exchange Processes on Solvated Lithium Cations: Acetonitrile and Hydrogen Cyanide[‡]

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Solutions of $LiClO_4$ in solvent mixtures of acetonitrile and water, or acetonitrile and nitromethane, were studied by ^7Li NMR spectroscopy. Measured chemical shifts indicate that the Li^+ cation is coordinated by four acetonitrile molecules. In the binary water/acetonitrile mixture, water coordinates more strongly to Li^+ than acetonitrile such that addition of water immediately leads to the formation of $[Li(H_2O)_4]^+$. The solvent-exchange mechanism for $[Li(L)_4]^+$ (L = CH_3CN and HCN) was studied by using DFT calculations (RB3LYP/6-311+G**). This process was found to follow a limiting associative mechanism involving the formation of relatively stable five-coordinate intermediates. The suggested mechanisms are discussed with reference to available experimental and theoretical data.

Introduction

The ongoing discussion on sustainability in chemistry[1] is partly focused on the role of solvents and especially on alternatives for common organic solvents. Such alternatives could be, for example, ionic liquids[2–5] or supercritical carbon dioxide.[6–10] A detailed knowledge of the properties and structural motifs, as well as of elementary reactions such as solvent-exchange processes in different solvents, is an important prerequisite for selecting, optimizing and tailoring the ideal solvent.

Acetonitrile is a common solvent in chemical laboratories, for example it is used in reactions[11,12] or in the investigation of complexation phenomena and complex-formation constants.[13–18] Use of its hydrogen derivative HCN is mostly prevented by its high toxicity and its boiling point of 25 °C. Experimental studies dating back to the middle of the 20th century show that HCN is a water-like solvent that is well suited for dissolving organic and inorganic compounds. Salts such as LiCl, LiBr or $LiClO_4$ are highly soluble in Hydrogen cyanide, most likely because of its high dielectric constant of 123 (at 15.6 °C).[19–23] However, HCN serves as an excellent simplified model of CH_3CN and thus can be used instead in quantum chemical studies of CH_3CN.

The behaviour of pure acetonitrile and acetonitrile mixtures was studied experimentally[24,25] and computationally.[24,26] Since an ion in solution strongly disturbs the local solvent structure,[27] a detailed knowledge of the environment is an essential prerequisite for understanding reactions in the neighbourhood of the ion. Several studies investigated solvated Li^+ ions in acetonitrile both experimentally with various spectroscopic techniques[28–31] and computationally with different classical molecular dynamics (MD) methods[32–35] and Monte Carlo simulations of solvated alkali and halide ions in CH_3CN.[36] Over the past decade, DFT and ab initio calculations on $[Li(CH_3CN)_n]^+$ and related clusters were also performed by different groups.[30,37–40]

There has been a special interest in the properties of Li salts, such as conductivity,[41–44] transport abililty,[45–47] viscosity,[48] and osmotic behaviour[49], in solvents and solvent mixtures because of the use of Li^+ ions in batteries of high energy density.[50] Such studies are not restricted to liquid systems. Li^+ mobility in potential solid electrolytes was also investigated intensively both experimentally and theoretically.[51–53]

To the best of our knowledge, however, investigations of solvent-exchange reactions in acetonitrile and acetonitrile/water mixtures or in HCN and HCN/water mixtures have not been performed. Whereas experimental investigations study reactions under real conditions in a whole ensemble of molecules,[54,55] quantum chemical calculations focus on one molecule and a small number of solvent molecules, for example, the first solvent shell.[56–60] This approach enables a more detailed mechanistic insight.

In this contribution, we extend our combined quantum chemical and experimental investigations on ligand coordination and ligand exchange on Li^+ in acetonitrile and

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HCN, as well as in CH_3CN/H_2O and HCN/H_2O mixtures. The calculations mainly focus on HCN for two reasons: (1) to gain a deeper insight into this solvent, which is not used often, and (2) HCN is a good working model for CH_3–CN as its use prevents well known problems associated with rotating CH_3 groups and to facilitate studies with solvent models.

Results and Discussion

Coordination Number of Li^+

The structures of Li^+–acetonitrile solvates are in general less well known than the structures of Li^+–water solvates. The Li^+ ion was found to be four coordinate by NMR spectroscopic studies in which acetonitrile was gradually replaced by water when water was added to an acetonitrile solution of $LiClO_4$ (1.6 M),[61] and on the basis of IR spectroscopic intensities measured for the acetonitrile CN stretching vibrations.[62,63] Even compounds with mixed coordination of a counterion and acetonitrile were reported to be four coordinate, namely $[Li(CH_3CN)_3Br]$ formed from 0.58 M LiBr in CH_3CN.[64] Extensive concentration-dependent ion-pairing was also found for weak coordinating counterions, such as in $LiBF_4$[30] and $LiClO_4$,[62] by studying the CN vibration.[65] These findings for the coordination number are in good agreement with published X-ray structures.[66–68]

However, Sajeevkumar and Singh found the average coordination number to be 4.7,[69] whereas Megyes et al. found up to six acetonitrile molecules surrounding the Li^+ ion in the gas phase by means of mass spectrometry.[70] Therefore, we reinvestigated the maximum coordination number of $[Li(CH_3CN)_n]^+$ both experimentally and computationally, and purely quantum chemically for $[Li(NCH)_n]^+$.

In order to determine the coordination number of Li^+ by using NMR techniques, the concentration of $LiClO_4$ was kept constant and the CH_3CN concentration was varied over a wide range. To use this method, the cation must be dissolved in solvent mixtures consisting of one coordinating and one non-coordinating component. The measured chemical shifts are then plotted against the mol ratio of cation to coordinating solvent. When such a plot shows a marked discontinuity, the appropriate solvent/cation ratio can be taken as the coordination number of the cation. There are, however, a few conditions that must be obeyed. An inert non-coordinating solvent must be available that will dissolve all solution components, a measurable parameter must exist that is a function of the solvent composition, and the formation constant of the solvate must be sufficiently large so that a limiting value of the parameter can be reached. In this case, the selected parameter was the Li^+ NMR signal; its position in the NMR spectrum depends on the composition of the coordination sphere of the studied ion. Typical alkali metal salts are not appreciably soluble in truly inert solvents. Therefore, it is necessary to select a solvent that minimally interacts with CH_3CN and the alkali metal ion.[71]

Nitromethane (Gutmann donor number DN = 2.7)[72] represents a good compromise for the various requirements. It appreciably dissolves alkali metal salts and its interaction with Li^+ is much weaker than that between CH_3CN (Gutmann donor number DN = 14.1) and a metal cation. The mol ratio data obtained confirms the "inertness" of this solvent and indicates that it is in fact sufficiently unreactive for the purpose of this study.

Figure 1 and Figure 2 illustrate the results obtained from the ^7Li NMR spectroscopic study. Figure 2 shows a plot of the chemical shift as a function of the mol ratio of the $CH_3CN/LiClO_4$ system; the $LiClO_4$ concentration was kept at 0.05 M in nitromethane. A clear break can be observed at a $[CH_3CN]/[Li^+]$ ratio of 4:1, which indicates that Li^+ is coordinated by 4 acetonitrile molecules under these conditions. It appears, therefore, that NMR studies of alkali metal ion coordination can be carried out even in solvents that are not totally inert toward the reacting metal ion provided that the interaction between the metal ion and the stronger donor solvent dominates.

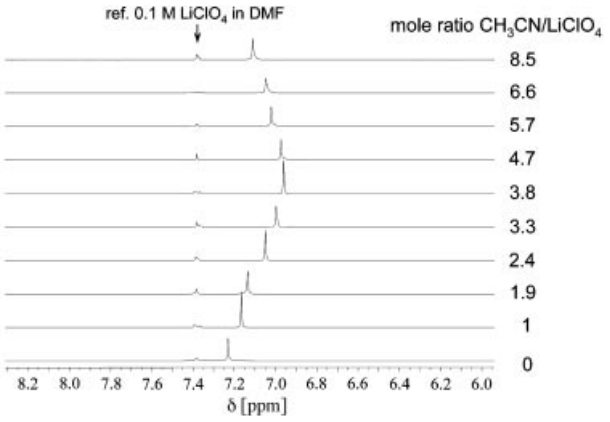

Figure 1. ^7Li NMR spectra recorded as a function of $CH_3CN/LiClO_4$ mol ratio (0.05 M $LiClO_4$ in the CH_3CN/nitromethane mixture) at 25 °C.

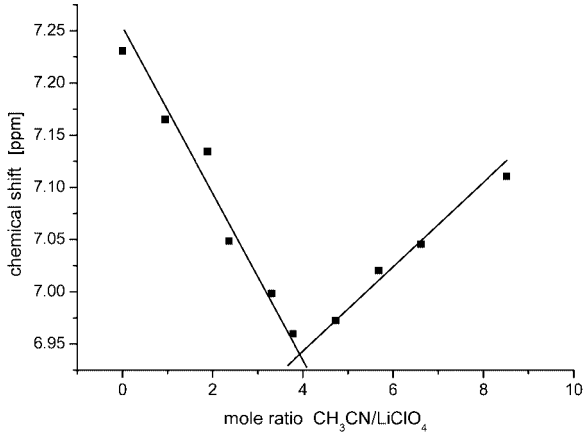

Figure 2. ^7Li NMR shift measured for 0.05 M $LiClO_4$ in CH_3CN/nitromethane solvent mixtures.

Selective Coordination of Li^+

Selective coordination occurs when the solvate prefers one of the solvent components over the other. The exchange of ions between different environments is usually rapid with respect to the NMR time scale, and this results in only one resonance signal at an average frequency determined by the magnetic shielding and lifetime of the nucleus in each of the sites. Variation of parameters such as concentration, counterions and solvent produces changes in the relative proportion and type of environment, which may be reflected by the NMR spectra in terms of chemical shift, line shape and/or line width of the observed resonance.[73]

We performed the measurements by keeping the concentration of $LiClO_4$ constant (0.1 M) and by changing the composition of the H_2O/CH_3CN mixtures. The concentration of H_2O (molar ratio) was increased from 0 to 100%. For each sample, the ^7Li NMR spectrum was recorded. The chemical shift changed as the amount of water in the sample was varied.

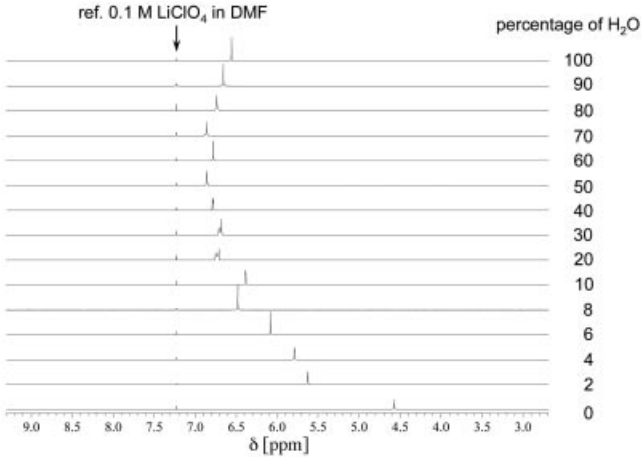

Figure 3. ^7Li NMR spectra of 0.1 M $LiClO_4$ in H_2O/CH_3CN mixtures.

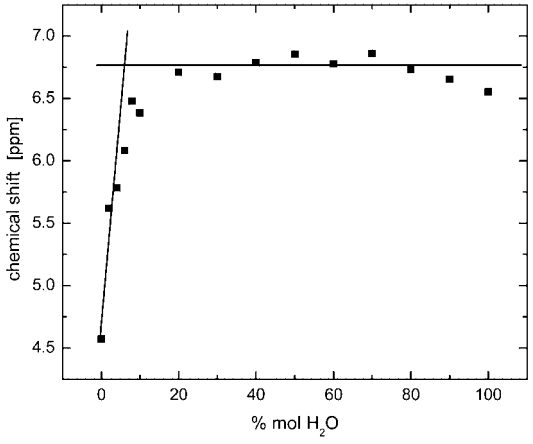

Figure 4. ^7Li NMR shift for 0.1 M $LiClO_4$ as a function of the H_2O/CH_3CN composition.

It was observed that the position of the NMR signal moved significantly (from 4.5 to 6.4 ppm) even when the amount of added water was very small (only 10% H_2O). The chemical shift value then increased slightly and remained almost constant when the amount of water was changed from 10 to 100% (see Figure 3 and Figure 4). This observation confirms that water coordinates much more strongly to the Li^+ ion than acetonitrile. Thus, addition of water immediately leads to the formation of the aquated cation.

Ligand Exchange on Solvated Li^+

It was not possible to follow the exchange process for CH_3CN on Li^+ experimentally. As reported before, the rate constant of water exchange on Li^+ is extremely fast (approximately 10^9 s^{-1} at 25 °C) although water is a relatively strong donor (*DN* = 33.0). As CH_3CN coordinates much more weakly (*DN* = 14.1), its exchange on Li^+ is even faster, which makes it impossible to study experimentally. Therefore, theoretical calculations are essential and may be very useful in such investigations.

Quantum Chemical Calculations

We studied the ligand exchange process in more detail and provide computational evidence for a limiting associative exchange mechanism on the HCN- and CH_3CN-solvated lithium cation. As mentioned before, HCN was employed as a simplified working model to perform quantum chemical calculations on CH_3CN. Our calculations corroborated the results of the experimental study in solution (vide supra)[29] and in the solid state,[68] which showed that the first coordination sphere around Li^+ consists of four tightly bound CH_3CN and HCN molecules. The five-coordinate intermediates are 3.7 kcal/mol and 4.6 kcal/mol [3.2 kcal/mol B3LYP(IPCM: acetonitrile)/6-311+G**//B3LYP/6-311+G**] higher in energy for acetonitrile and HCN, respectively. The computed Li–N distance for $Li(NCH)_4$ and $Li(NCCH_3)_4$ are 2.06 and 2.05 Å, respectively. Additional solvent molecules do not coordinate to Li^+, but instead form a second coordination sphere, mainly through electrostatic interactions. The gas-phase binding energy for the fifth acetonitrile molecule in $[Li(NCCH_3)_4(NCCH_3)]^+$ is 6.1 kcal/mol, with a Li–N distance of 6.65 Å. The fifth molecule is stabilized only by a weak H_{CH_3}–NC–CH_3 interaction of 2.32 Å. The fifth HCN molecule is bound through a weak hydrogen bond (2.04 Å) in the second coordination sphere. This bond stabilizes the system by 8.9 kcal/mol (see Figure 5).

The HCN exchange itself proceeds through a trigonal-bipyramidal intermediate $[Li(NCH)_5]^+$ that is reached via a late transition state. The entering HCN molecule approaches the lithium cation directly and pushes three coordinated solvent molecules away toward the equatorial positions. In line with the experimental observation of a very fast exchange process (vide supra), the computed activation

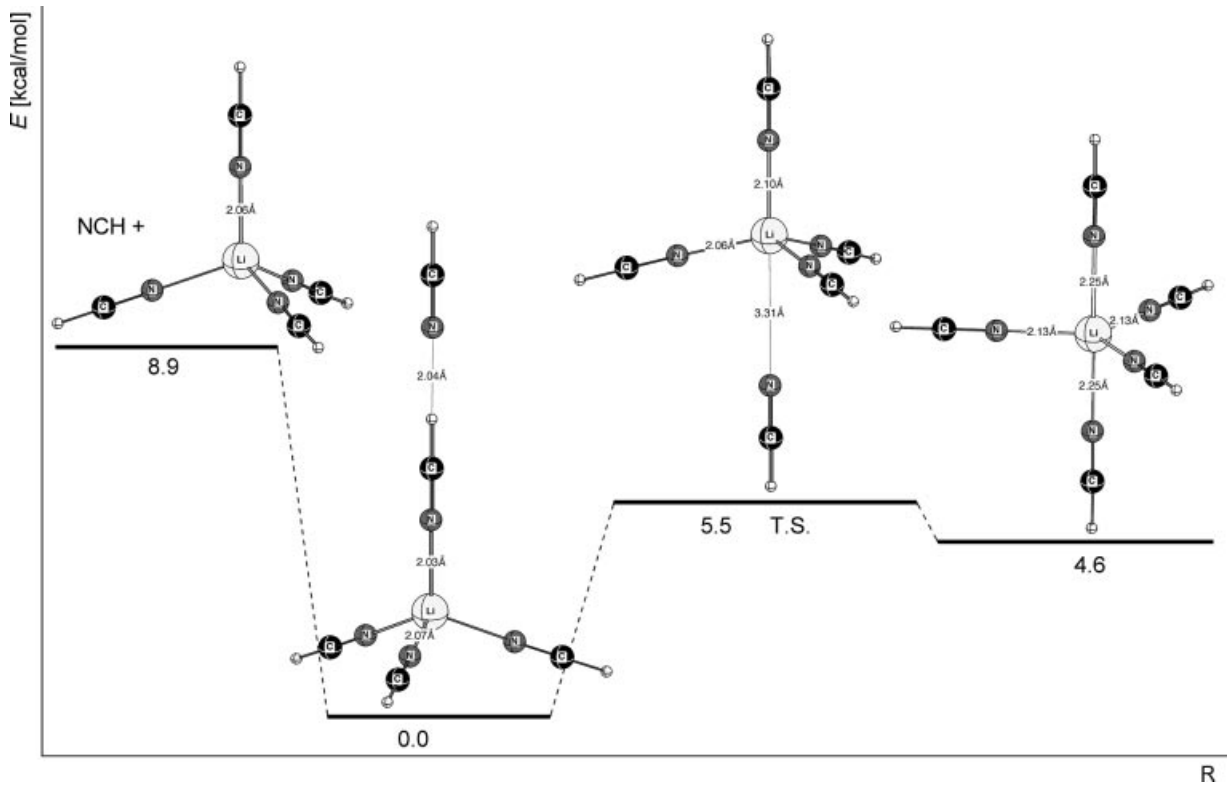

Figure 5. Energy profile (RB3LYP/6-311+G**) for the exchange of HCN on $[Li(NCH)_4]^+$.

barrier is only 5.5 kcal/mol, while the five-coordinate intermediate is 4.6 kcal/mol less stable than the precursor complex. The very low barrier toward dissociation of only 0.9 kcal/mol means that the five-coordinate intermediate is very short-lived. The evaluation of the energy at the MP2(full)/6-311+G**//B3LYP/6-311+G** and B3LYP/6-311+G**//B3LYP/6-311+G** levels shows only minor differences in the computed energies, except in those for the intermediate ($[Li(L)_4(L)]^+$) (see Table 1). We attribute this to an incorrectly balanced description of the metal–ligand and hydrogen-bond strengths by DFT methods as observed earlier by Rotzinger and others in studies on water exchange reactions.[74,75] Inclusion of solvent effects at the B3LYP(CPCM)/6-311+G**//B3LYP/6-311+G** and B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** level clearly favours a four-coordinate structure with NCH in the second coordination sphere or uncoordinated. Therefore, the transition state is also stabilized since the entering NCH molecule can best be addressed as uncoordinated (see Table 1 and Figure 5). Unfortunately, the transition state is modelled as being too stable in the B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** approximation, irrespective of whether acetonitrile or water is used in the modelling by the IPCM formalism.

In trigonal-bipyramidal $[Li(NCH)_5]^+$, the axial Li–N distances are 0.11 Å longer than the equatorial distances, which may be taken as a clear indication that one of the axial ligands will be expelled. The energy profile for the exchange of acetonitrile on $[Li(NCCH_3)_4]^+$ shows the same topology, only the energy differences are somewhat smaller.

Table 1. Calculated relative energies (in kcal/mol) for the exchange of L at $[Li(L)_4]^+$ (L = HCN, CH_3CN).[a]

L = HCN	$[Li(L)_4]^+ + L$	$[Li(L)_4\cdots(L)]^+$	TS	$[Li(L)_4(L)]^+$
B3LYP	8.9	0.0	5.5	4.6
MP2(full)	9.5	0.0	3.2	0.5
IPCM	–2.8	0.0	–2.6	3.2
CPCM	–0.4	0.0	1.8	1.4
L = H_3CCN				
B3LYP	6.1	0.0	4.1	3.7

[a] B3LYP: B3LYP/6-311+G**//B3LYP/6-311+G**; MP2(full): MP2(full)/6-311+G**//B3LYP/6-311+G**; IPCM: B3LYP/(IPCM: acetonitrile)/6-311+G**//B3LYP/6-311+G**; CPCM: B3LYP/(CPCM: water)/6-311+G**//B3LYP/6-311+G**.

We attribute this difference to stabilization effects caused by the methyl group and to the absence of hydrogen bonding. A detailed investigation was prevented since a local minimum was not reached with $[Li(NCCH_3)_4(NCCH_3)]^+$ because of the rotation of the methyl groups, and the IPCM calculations show the well-documented problems in reaching an energy convergence.[4,76]

These findings fully corroborate the results expected for small ions coordinated by small ligands. The dissociation of a molecule of HCN from $[Li(NCH)_4]^+$ results in the intermediate $[Li(NCH)_3]^+$ with a D_{3h} symmetry, which is 14.3 kcal/mol higher in energy and less favourable. In addition, there is no visible steric crowding, which is necessary for a dissociative mechanism. Interchange mechanisms are known for Li^+, e.g. in the case of ammonia exchange on

Table 2. Calculated energies for the subsequent reactions of $[Li(NCH)_4]^+$ with water.

B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** [kcal/mol]	Gas phase	IPCM: acetonitrile	IPCM: water
$[Li(NCH)_4]^+ + H_2O \rightarrow [Li(H_2O)(NCH)_3]^+ + NCH$	–0.5	+1.7	+1.6
$[Li(H_2O)(NCH)_3]^+ + H_2O \rightarrow [Li(H_2O)_2(NCH)_2]^+ + NCH$	–0.5	–1.4	–1.6
$[Li(H_2O)_2(NCH)_2]^+ + H_2O \rightarrow [Li(H_2O)_3(NCH)]^+ + NCH$	–0.3	–3.6	–3.9
$[Li(H_2O)_3(NCH)]^+ + H_2O \rightarrow [Li(H_2O)_4]^+ + NCH$	+0.1	–0.9	–1.2
Σ	–1.3	–4.2	–5.1

Li^+,[77] but requires a five-coordinate transition state that would contradict the five-coordinate intermediate in our mechanism. Analogous arguments can also be applied for the second reaction under investigation.

Under actual experimental conditions water can never be excluded. Therefore, and because of the importance of solvent mixtures in technical and laboratory applications, we modelled the HCN/H_2O exchange process exemplarily for $[Li(NCH)_4]^+$ to $[Li(NCH)_3(H_2O)]^+$ (Table 2). In this case, NCH can again be considered as a model for acetonitrile.

From experiments (vide supra) and from the Gutmann donor number for acetonitrile, which is only 50% of that for water, it is known that addition of water to solutions of lithium ions in acetonitrile leads to the formation of a water-coordinated Li^+ complex. This can be reproduced for HCN as a model by quantum chemical calculations (RB3LYP/6-311+G**).

By including solvent effects at the B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** level, the reaction energies are significantly increased, regardless of whether water or acetonitrile is selected as solvent.

We investigated the mechanism of the first reaction step in detail (see Figure 6). As shown before,[29,68] the first coordination sphere around Li^+ consists of four tightly bound acetonitrile molecules, here NCH molecules. An additional solvent molecule does not coordinate to the Li^+ ion; a second coordination sphere is formed in which water is bound by one linear hydrogen bond (1.88 Å). The gas-phase hydrogen-bond energy for the H_2O molecule in $[Li(NCH)_4\cdots(OH_2)]^+$ is 9.5 kcal/mol. Again, the entering solvent, here water, approaches the Li^+ ion directly through a face of the $[Li(NCH)_4]^+$ tetrahedron and pushes three coordinated HCN molecules away. According to the movement of the water molecule in the transition state (7.1 kcal/mol higher in energy), one would expect an intermediate with three HCN molecules in equatorial positions and the fourth together with the H_2O molecule in the axial positions. During the optimization steps, the structure rearranges to form an intermediate 3.7 kcal/mol lower in energy, with two HCN molecules in the axial positions and the H_2O molecule together with the two remaining HCN molecules in the equatorial positions. The bonds for the axial molecules are

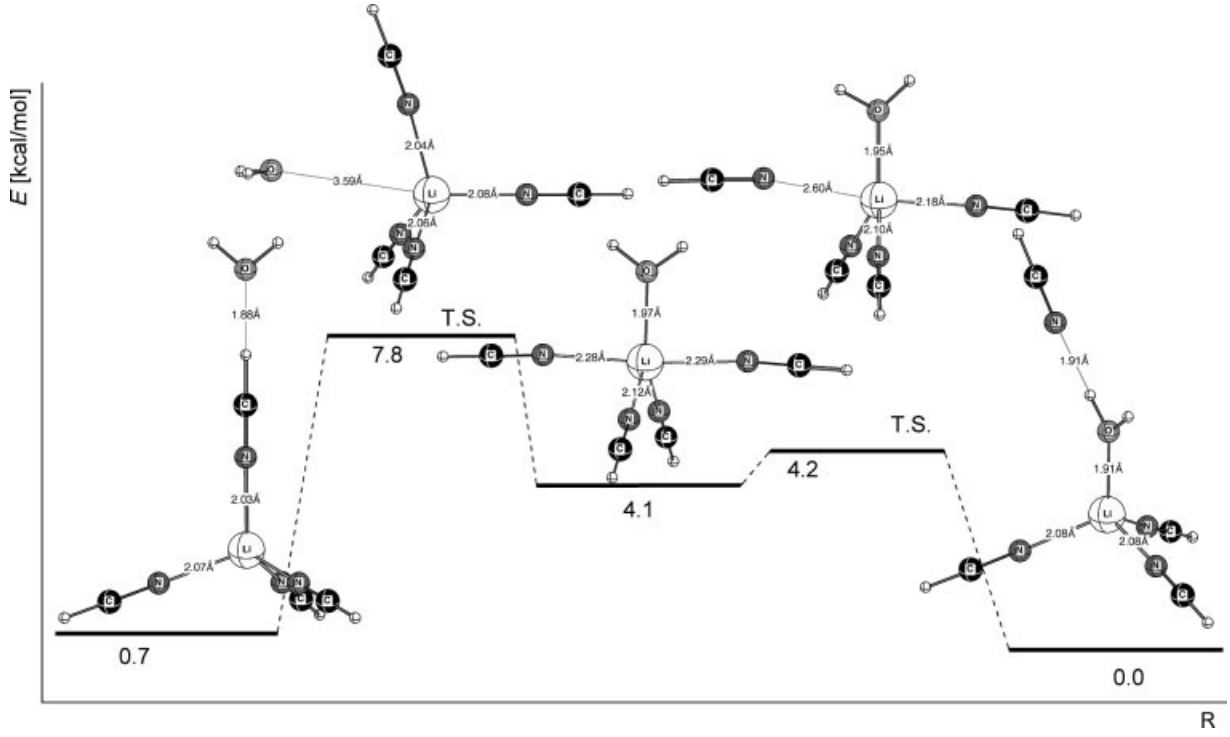

Figure 6. Energy profile (RB3LYP/6-311+G**) for the HCN/water exchange on $[Li(NCH)_4]^+$.

0.16 Å longer than those for the equatorial HCN ligands – it can be concluded that one axial ligand will be expelled to reach a four-coordinate product. The activation barrier for the release of an axial HCN molecule is rather low (0.1 kcal/mol), which means that the five-coordinate intermediate will be very short-lived. On the assumption that the expelled HCN molecule will form a hydrogen bond with the nearest hydrogen atom, one would expect the product $[Li(NCH)_3(H_2O)\cdots(NCH)]^+$ to form at an energy that is 4.2 kcal/mol lower than that of the second transition state. The energy required to destroy this hydrogen bond is 9.7 kcal/mol (Table 3).

Table 3. Calculated relative energies for the exchange of H_2O/NCH at $[Li(NCH)_4]^+$ (L = HCN; W = H_2O).[a]

	$[Li(L)_4\cdots W]^+$	TS	$[Li(L)_2\{W(L)_2\}]^+$	TS	$[Li(L)_3(W)\cdots L]^+$
B3LYP	0.7	7.8	4.1	4.2	0.0
MP2(full)	0.9	6.1	0.6	1.2	0.0
IPCM	0.1	2.8	1.3	1.8	0.0
CPCM	0.1	5.6	1.0	1.5	0.0

[a] B3LYP: B3LYP/6-311+G**//B3LYP/6-311+G**; MP2(full): MP2(full)/6-311+G**//B3LYP/6-311+G**; IPCM: B3LYP/(IPCM: acetonitrile)/6-311+G**//B3LYP/6-311+G**; CPCM: B3LYP/(CPCM: water)/6-311+G**//B3LYP/6-311+G**.

Whereas MP2(full)/6-311+G**//B3LYP/6-311+G** calculations show typical discrepancies, the application of the IPCM- and CPCM-solvent models dramatically lowers the energy for the intermediate and the transition states. The barriers of 2.8 and 1.8 kcal/mol corroborate the experimental findings for an efficient formation of a water-coordinated Li^+ complex.

Conclusions

It was confirmed both experimentally and theoretically that Li^+ is coordinated by four acetonitrile molecules. In the binary mixture of water and acetonitrile, water is coordinated more strongly to the Li^+ ion than acetonitrile. Thus, addition of water immediately leads to the formation of the aquated cation. Ligand exchange reactions on Li^+ most probably follow an associative mechanism as indicated by the formation of stable five-coordinate intermediates.

Experimental Section

General Procedures: All transformations were carried out under a Ar or N_2 atmosphere by using standard Schlenk techniques, under Ar atmosphere in a glove box, or under vacuum. $LiClO_4$ (Aldrich, battery grade) was vacuum dried at 120 °C for 48 h and was then stored under dry nitrogen. Acetonitrile (Acros, extra dry, water < 10 ppm) was used as received. Nitromethane (Roth) was purified and dried by a previously reported method.[78] Solutions of $LiClO_4$ were prepared under dry nitrogen. For ^{7}Li NMR spectroscopic studies, these solutions were sealed under a Ar atmosphere in 5-mm NMR tubes.

^{7}Li NMR Spectroscopy: Fourier transform ^{7}Li NMR spectra were recorded at a frequency of 155 MHz on a Bruker Avance DRX 400WB spectrometer equipped with a superconducting BC-94/89 magnet system. Spinning 5-mm tubes were used with a 1-mm o.d. melting point capillary inserted coaxially in the spinning tube and filled with an external reference solution (usually 1 M $LiClO_4$ in DMF). The experiments were conducted at room temperature and at ambient pressure. For a typical kinetic run, 0.8 mL of solution was transferred under Ar to a Wilmad screw cap NMR tube equipped with a poly(tetrafluoroethylene) septum. All samples were prepared in the same way.

Quantum Chemical Calculations: All structures were fully optimized at the B3LYP/6-311+G**[79–82] level of theory and characterized as minima or transition-state structures by computation of vibrational frequencies (for minima, all frequencies are positive, NIMAG = 0; for transition-state structures, exactly one imaginary frequency is present, NIMAG = 1). Single-point energy calculations were performed at the MP2(full)/6-311+G**//B3LYP/6-311+G** level;[83] the influence of the bulk solvent was probed by using the IPCM[84] and CPCM[85,86] formalism and water or acetonitrile as solvent, i.e. B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** and B3LYP(CPCM)/6-311+G**//B3LYP/6-311+G**.[87] The Gaussian 03 suite of programs was used throughout.[88]

Acknowledgments

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